Mid-Infrared Supercontinuum Generation in Chalcogenides

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Declaration

The contents of this thesis are the results of original research undertaken at the Laser Physics Centre within the Research School of Physics and Engineering at the Australian National University between October 2012 and August 2016 while I was enrolled for the Doctor of Philosophy degree. The research has been conducted under the supervision of panel chair Prof. Barry Luther-Davies, supervisors A/Prof. Stephen Madden, A/Prof. Duk-Yong Choi and advisor Dr. Xin Gai. However, unless explicitly stated otherwise, materials presented within this thesis are my own original work. None of the work presented here has ever been submitted for any degree at this or any other institution or university.

Yi Yu
August, 2016
Publications

Those published journal papers which have been included or partly included in this thesis are typed in bold.

Refereed journal articles


**Refereed conference papers**


a suspended core chalcogenide fiber”, annual meeting for the Optical Society of Denmark 2014.


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Abstract

Bright, broadband, mid-infrared (MIR) sources are useful for microscopy and spectroscopy as well as many other areas of science and technology. Among the available sources, supercontinuum (SC) sources stand out because of their high brightness and continuous spectral coverage. SC generation involve a range of nonlinear optical effects including self-phase modulation, four-wave mixing, stimulated Raman scattering, etc. Anomalous dispersion plays a major role and interacts with nonlinearity leading to the creation of optical solitons that are essential to create a broad spectrum.

The goal of this PhD was to generate practical, octave-spanning MIR SC sources spanning at least 2-10 µm using optical waveguides. To achieve this, firstly, it was necessary to identify the best nonlinear materials for SC generation. Chalcogenide glasses were chosen due to their high third-order optical nonlinearity, low nonlinear absorption and good transparency in the MIR. The potential of chalcogenides for SC generation was first demonstrated using bulk samples leading to a SC spectrum covering more than one octave.

A challenge with chalcogenides is that they typically have long zero dispersion wavelengths (ZDWs) (beyond 5 µm) and this makes it difficult to pump them directly in the anomalous dispersion region. Two approaches were used to overcome this: 1) the dispersion was engineered via waveguide design to shift the anomalous region to shorter wavelengths; and 2) long-wavelength femtosecond pump sources were developed with appropriate powers to pump them.

Both optical fibers and planar waveguides were explored and the measured SC spectra were compared with simulations based on the split-step Fourier method. Dispersion-engineered, step-index fibers were drawn by collaborators in China whilst dispersion-engineered rib waveguides were fabricated in house. Both allowed the first ZDWs to be shifted to wavelengths around 3 µm, however, ZDW below 3 µm was incompatible with the need for the waveguide to operate to beyond 10 µm.

Simulations showed that MIR SC generation required a pump pulses in the 3-5 µm band with duration of a few hundred fs. We developed laser-seeded optical parametric amplifiers (OPA) pumped with femtosecond pulses from
mode-locked Yb lasers, to create either 330 fs or 200 fs pulses tunable around 4 µm. In addition, we demonstrated a method for chirping and compressing the OPA pulses down to <60 fs which is needed to create a coherent SC spectrum.

Combining the dispersion design and the femtosecond MIR OPA system, SC spectra more than two octaves wide with moderate average output powers (10s mW) were obtained from both fibers and waveguides. For the step-index chalcogenide fibers, typical experimental SC spectra covered the ranges of 2-10 µm or 2.2-12 µm depending on the fiber composition, however, due to their circular symmetry, the output was generally unpolarised. The fibers were also multimode over some of the SC spectrum. Both these deficiencies could be overcome by moving to a planar waveguide design. A tri-layer rib waveguide allowed the production of a linearly-polarized SC spanning from 2.0 µm to 10.8 µm. This source was used successfully for demonstrations of MIR spectroscopy.
Common Abbreviations

MIR: mid-infrared
SC: supercontinuum
ZDW: zero dispersion wavelength
OPA: optical parametric amplifier
NIR: near-infrared
QCL: quantum cascade laser
SNR: signal-to-noise ratio
SPM: self-phase modulation
GNLSE: generalized nonlinear Schrödinger equation
SSFM: split-step Fourier method
PPLN: periodically poled lithium niobate
SHG: second-harmonic generation
FROG: frequency-resolved optical gating
MCT: mercury cadmium telluride
FTIR: Fourier transform infrared spectroscopy
XPM: cross-phase modulation
FWM: four-wave mixing
MI: modulational instability
SRS: stimulated Raman scattering
SBS: stimulated Brillouin scattering
GVD: group velocity dispersion
PCF: photonic crystal fiber
OPO: optical parametric oscillator
MPA: multi-photon absorption
FCA: free carrier absorption
NA: numerical aperture
GeAsSe: Ge_{11.5}As_{24}Se_{64.5}
GeAsS: Ge_{11.5}As_{24}S_{64.5}
TE: transverse electric
TM: transverse magnetic
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Chapter 1: Introduction

Visible light (from ≈ 380 nm to 770 nm) by which we see the world occupies only a small portion of the electromagnetic spectrum [1] and there are many other “invisible” components that are of great importance. For example, X-rays with wavelengths from 0.01 nm to 10 nm are useful for medical applications such as computed tomography (CT) [2-4], fluoroscopy [5,6], and radiotherapy [7,8] whilst radio waves from 1 mm to 1000 mm are widely used for communication [9], broadcasting [10] etc.

At the long wavelength end of the visible spectrum we find near-infrared (NIR) and mid-infrared (MIR, 2.5-25 µm) light. The latter is particularly important because it interacts strongly with all molecules since the corresponding photon energy is resonant with their fundamental vibrational modes [11]. As a result, MIR sources can be used for efficient detection of almost any biological, toxic or dangerous material via absorption spectroscopy because almost every molecule exhibits unique absorption features in the MIR. For example, carbon dioxide has its typical absorption dips around 4.2 µm and beyond 13 µm whilst water vapour absorption can be detected around 2.7 µm and 6-7 µm [12].

There are two sub-bands which are used to divide the MIR: one is known as the functional group band and spans from 2.5 µm to approximately 6.6 µm (1500-4000 cm⁻¹ in wavenumbers) where the absorption peaks identify the functional group that exists in the molecule (such as alkyl, alkenyl, amine etc.). The other is the fingerprint band that lies between about 6.6 µm and 25 µm (400-1500 cm⁻¹) where every organic compound produces a unique absorption signature and, therefore, its identity can often be confirmed by comparison with a known spectrum [13]. MIR light is used in many other important applications, for instance, metrology [14-17], microscopy [18-21] and tomography [22-24] and, thus, the development of high quality MIR light sources is of considerable interest.

When it is necessary to measure absorption features over a wide spectral range, broadband or widely tuneable sources are required. Currently broadband
MIR light sources include globars; infrared beam lines of synchrotrons; and arrays of quantum cascade lasers (QCLs). However, each has their respective advantages and disadvantages. Conventional globar sources are simple, inexpensive and have been around for many years but they do not have sufficient spectral brightness (defined as the radiance per unit optical bandwidth) for applications when high spatial resolution (of the order of the wavelength, \( \lambda \)) is required because they emit incoherent light. As a result rapid, high signal-to-noise ratio (SNR) measurements can only be performed using sources with significantly higher brightness. Synchrotron sources have brightness that exceeds a globar by around 2 or 3 orders of magnitude [25], however, they do not allow widespread use of MIR micro-spectroscopy in ordinary laboratory environments [21]. The development of QCLs has provided the opportunity to vastly increase the source brightness in some wavelength bands [26]. Typically a QCL produces a diffraction-limited beam with a brightness \( (4 \times 10^{23} \text{ ph/s/sr/mm}^2/\text{cm}^{-1}) \) which is more than 5 orders of magnitude greater than any synchrotron. However, the tuning range of an individual QCL is quite limited. Consequently very many individual lasers need to be combined to cover both the functional group and fingerprint bands, which leads to the sources being costly and complex. Moreover, currently QCLs operating at the short wavelength end of the functional group region are unavailable and this region covers many important absorption features like the amine (N-H stretch) and the hydroxyl (alcohol O-H stretch) [13]. MIR supercontinuum (SC) sources, however, could overcome many of these shortcomings and could provide moderate brightness with continuous broadband coverage and ideally comparable average power to the alternative MIR sources. The comparison of these MIR sources is summarized in Fig. 1.1.

![MIR source comparison](image)

Figure 1.1: Comparison of various MIR broadband sources.
SC generation involves the creation of new light frequencies via nonlinear effects in a medium irradiated by a high power laser source. This phenomenon was first described in the 1970s [27,28] and has received a lot of attention ever since. Before the turn of the century, the physics underlying SC generation had been well explored and many experimental demonstrations had been reported using a wide range of pump conditions and media. There are two factors that most influence SC generation: one is the optical nonlinearity and the other is the dispersion.

In terms of nonlinearity as, in general, isotropic materials are employed for SC generation, the second order susceptibility is zero and hence the third-order susceptibility $\chi^{(3)}$ becomes the dominant nonlinear term. This can be characterized by a nonlinear refractive index, $n_2$. The value of $n_2$ quantifies the change in refractive index that occurs as a function of the light intensity and results in a nonlinear shift of the phase of the propagating light, a phenomenon known as self-phase modulation (SPM). Due to SPM, the leading edge of a pulse will red-shift whilst the trailing edge will blue-shift, causing the pulse to broaden in the spectral domain. There are a number of other nonlinear effects that rely on either the real or imaginary parts of $\chi^{(3)}$ which also broaden the spectrum of the pulse, they include cross-phase modulation (XPM), four-wave mixing (FWM), the modulational instability (MI), and stimulated Raman scattering (SRS).

In terms of dispersion, two regimes exist. One is the normal dispersion regime where red-shifted components travel faster than the blue-shifted components; the other is the anomalous regime where the reverse occurs. A pulse undergoing SPM propagating in a nonlinear material with normal dispersion will broaden rapidly in time whilst if the dispersion is anomalous it will be compressed in most cases. Such compression increases the pulse power enhancing SPM and further broadening the pulse spectrum. Therefore, to obtain a broadband SC, anomalous dispersion is more ideal. When pumping in the anomalous dispersion region, SPM and group velocity dispersion can balance each other resulting in the formation of stable (or periodic) pulses known as solitons. Once solitons form, their frequency can red-shift as a result of preferential amplification of their red frequency components by SRS, a phenomenon known as the Raman-induced soliton self-frequency shift. As
solitons propagate in the anomalous region, they can also lose energy to phase-matched dispersive waves that propagate in regions where the dispersion is normal. This can extend the spectrum to both short and long wavelengths around the pump. A complete description of these and other phenomena involved in SC generation is contained in the comprehensive review article by Dudley et al. [29].

One of the landmark experimental demonstrations of SC generation was by Ranka et al. in 2000 where an air-silica micro-structured optical fiber was pumped in the anomalous dispersion regime at 790 nm using a femtosecond Ti:sapphire laser which led to the production of a SC spectrum spanning from 400 nm to 1600 nm [30]. This marked the start of research into the production of visible and NIR SC from dispersion engineered micro-structured fibers that can also be endlessly single mode, leading to bright broadband sources.

At the beginning of this century, most experimental demonstrations of SC generation focussed on the visible and NIR with considerable emphasis on extending the emission to short wavelengths in the ultraviolet (UV) [31-36]. To generate SC in the MIR, however, creates new challenges. For one thing, most of the materials used for UV, visible or NIR SC generation can no longer be used as they are not transparent in the MIR. The other problem is that as the nonlinear refractive index $n_2$ decreases with increasing wavelength, the nonlinear effects become much weaker in the MIR compared to NIR or the visible [37]. Therefore, suitable materials with good transparency and high nonlinearity in the MIR are required for MIR SC generation. There are several candidates including tellurite, fluoride, and chalcogenide glasses as well as semiconductors such as silicon, germanium and gallium arsenide. Among the glasses, chalcogenides stand out because of their broad transparency in the MIR with sulphides transmitting until about 10 μm; selenides to 16 μm; and tellurides to 20 μm [38]. This contrasts with the transmission limits for tellurites and fluorides at ~6 μm and ~8 μm respectively [39]. Silicon, which can transmit to about 10 μm and is a popular optical material for optical signal processing, suffers from nonlinear absorption including multi-photon absorption (MPA) and free-carrier absorption (FCA) [40]. The same is observed in narrow band semiconductors such as Si-Ge [41, 42]. In terms of the third-order nonlinearity, chalcogenides possess a Kerr nonlinearity $n_2$ which can be two to three orders of magnitude larger than silica but possess
negligible nonlinear absorption in both the NIR and MIR because they can have a larger bandgap energy (1.5-2.5 eV) compared to materials like crystalline silicon (1.1 eV). Of concern with chalcogenides, however, is that their zero material dispersion wavelengths (ZDWs) are much longer than other materials like silica (1.3 μm), tellurites (~2 μm), or fluorides (~2 μm) [43]. For example, the zero dispersion wavelength (ZDW) for the sulphides is close to 5 μm while for the selenides that transmit to longer wavelengths, the zero dispersion point is typically beyond 6 μm. Hence it becomes difficult to access the anomalous dispersion region using commercially available high power ultrashort pulse lasers.

Waveguide dispersion can be used to shift the zero dispersion points to shorter wavelengths through appropriately engineering the structure of planar waveguides or optical fibers. However, as will be shown later there are limits to what can be achieved in waveguides that retain broad MIR transparency. In the best scenario, the dispersion of chalcogenide waveguides is generally only anomalous at wavelengths longer than ~3 μm where commercially available pump sources with high peak powers are still rare. As a result a suitable MIR pump needed to be developed for this work.

The generalized nonlinear Schrödinger equation (GNLSE) describes the process of SC generation and was solved by the adaptive size split-step Fourier method (SSFM). Using this it was determined that relatively short pulses in the MIR are preferred for the pump. In the framework of this thesis, we have developed a femtosecond optical parametric amplifier (OPA) system for the MIR which provides pump pulses in the 3-5 μm band that allow the SC spectrum to spread as far into the long wavelength end of the MIR regime as practical. The design of the OPA system was undertaken using the SNLO software which calculates the nonlinear mixing processes in bulk crystals. The final femtosecond OPA system uses an ytterbium pump laser and a tunable continuous wave (CW) semiconductor laser which are combined in a 10 mm long MgO doped periodically poled lithium niobate (MgO:PPLN) crystal. The typical output from the OPA was 330 fs pulses at a repetition rate of 21 MHz and 200 mW of average power at 4 μm.

Thus, this thesis focuses on the choice of suitable chalcogenides; the engineering of waveguide dispersion and nonlinearity for chalcogenide-based
planar waveguides or optical fibers; and the configuration of a femtosecond MIR pump source, as the main methods for extending the coverage of SC to the MIR. The final goal of this thesis was to demonstrate 2 μm to 10 μm SC generation and beyond in chalcogenides with practical input and output parameters which can deliver real-life applications like high sensitivity MIR spectroscopy. This was achieved using several fiber and waveguide devices.

**Thesis Outline**

This thesis focuses on MIR SC generation in various platforms based on chalcogenide glasses. In Chapter 2, a detailed account of the underlying physics of SC generation under various pumping conditions is given with emphasis on soliton fission in the anomalous dispersion regime together with the numerical methods used for modelling work presented in the thesis. They include the full-vector finite difference method for calculation of eigenvalues of waveguide modes and the adaptive-size SSFM for the solution of the GNLSE to predict and analyse SC results. Chapter 3 mainly discusses the challenges of SC generation in the MIR and how they can be overcome, in principle, by the use of a dispersion-engineered chalcogenide planar waveguide by using a suitable MIR pump. Firstly, the need for bright MIR sources is emphasized by describing some applications. Next, the superiority of chalcogenides over other materials, in particular silicon, as a medium for MIR SC generation is presented. An example of SC generation in bulk chalcogenide glasses is described which demonstrates their potential as the platform for octave-spanning MIR SC from the perspective of transparency and nonlinearity. In the third part, the design of chalcogenide platforms is illustrated using the example of a tri-layer buried rib chalcogenide waveguide. This waveguide shows good property of high birefringence, quasi-single mode and distinct dispersion between the transverse electric (TE) and transverse magnetic (TM) mode. For this device, the best pump configuration in terms of wavelength and pulse duration was investigated using numerical simulations. According to these numerical results, femtosecond long wavelength MIR pulses are required for effective SC generation. This led to the development of the simple MIR OPA
system which was designed and built in house. The pulses from the OPA were characterized via the second-harmonic generation (SHG) frequency-resolved optical gating (FROG) technique. Typically at 4 µm, the pulses deliver an average power of 200 mW and have a width of about 330 fs with negligible chirp. Description of the SC measurement system follows. It contains an InSb camera, two coupling lenses, one monochromator filters, various MIR detectors and a lock-in amplifier under LabVIEW control.

The dispersion design can also be applied to fiber geometries which generally have longer interaction length and lower loss. Chapter 4 describes SC generation in chalcogenide optical fibers. At first two commercial chalcogenide fibers from IRflex and PERFOS are discussed briefly. Next and more importantly, specifically dispersion engineered step-index chalcogenide fibers designed in our group and provided by the Jiangsu Normal University (JNU) in China are used. Depending on the compositions of the core and the cladding materials, they are divided into all-arsenic fibers and all-selenide fibers. Various multi-milliwatt, multi-octave-spanning SC spectra were obtained by pumping these fibers in the anomalous dispersion regime using the femtosecond MIR OPA pump described in Chapter 3 and validated by numerical analyses. Further, to improve the stability of the generated SC spectra, an asymmetric fiber structure was designed and used to enhance the birefringence of the step-index chalcogenide fibers. However, the fiber was multimode at short wavelengths due to the relatively large index contrast between the core and cladding materials. Also, as multiple solitons were formed which interfered with each other, fluctuations in the generated SC spectra were still inevitable. Brief summary of this Chapter is followed.

Chapter 5 moves on to SC generation in planar waveguides made from chalcogenides. Two types of chalcogenide waveguides are discussed, one is a two-layer “air-clad” rib waveguide and the other is a tri-layer buried rib chalcogenide waveguide designed in Chapter 3. The fabrication processes of chalcogenide waveguides are presented in detail with difficulties in the glancing angle deposition of the over cladding being resolved. Waveguide characterization is discussed including the dispersion calculation and the loss measurement via the cut-back method. In the optimum scenario, the SC extended from 1.8 µm to beyond 9 µm for the two-layer waveguide whilst the best achieved for the tri-layer waveguide was from 2 µm to 10.8 µm. These sources possess high
brightness exceeding the infrared beam lines of the synchrotrons by a factor of 100-1000. Additional advantage of the tri-layer rib waveguide is that its birefringence is high; the dispersions of the fundamental TE and TM mode are quite different; and the waveguide is quasi-single mode over its full transmission range. These properties significantly reduce polarization mode coupling and mode coupling effects in general. Even though multiple solitons were still present, the linearly polarized SC generated by the tri-layer waveguide allows us to perform dual beam spectroscopy with high resolution and good dynamic range.

Chapter 6 discusses SC coherence and how coherence can be improved to stabilize the generated SC creating a frequency comb. Reduction of the pulse duration is the natural approach and a simple scheme that can be implemented with the MIR OPA that chirps and compresses its output pulses is described. Simulations of the scheme are presented and in experiments the pulses were compressed down to several cycles (4-5) with duration of ~ 55 fs. The compressed pulse could be used as the pumping source for coherent SC generation.

Conclusions, suggestions for future work and epilogue are given in the final Chapter 7 followed by the bibliography.
Chapter 2: Supercontinuum (SC) Generation: Background & Numerical Tools

The first demonstration of SC generation dates back to the 1970s [27,28]. Over the years since then, researchers have studied in detail the underlying physics of SC generation and developed numerical methods for simulating, predicting and explaining the SC processes. As a result of these fundamental studies, this century has witnessed the development of mature, commercial SC sources particular for the visible and NIR. Nowadays, therefore, the physics of SC generation is completely understood and numerical tools have been developed to guide physical designs and explain experimental phenomena. As a result in this Chapter, I summarise the fundamental background for SC generation extracted from existing literature as well as the basic numerical tools that are used in the prediction of SC spectra.

2.1 Fundamentals of SC Generation

SC generation is a process where relatively narrow bandwidth light experiences extreme nonlinear spectral broadening thereby generating a broadband continuous spectrum. The two most important parameters involved in SC generation are dispersion and nonlinearity.

Dispersion (as will be discussed in detail later) is categorized as either normal or anomalous. In the normal dispersion regime, long wavelengths of light travel faster than short wavelengths whilst in the anomalous regime the reverse is true. In terms of nonlinearity, the significant nonlinear effects underlying SC generation include self-phase modulation (SPM); cross-phase modulation (XPM); four-wave mixing (FWM); the modulational instability (MI); stimulated Raman scattering (SRS); soliton formation and fission; and dispersive wave generation.
The way in which these processes are involved in SC generation can be summarised as follows. Due to the interplay of dispersion and nonlinearity, pulses can either broaden in time or be compressed; they can fission into multiple pulses; or can even maintain a stable temporal shape. Which of these occurs depends on the type of dispersion, nonlinearity, the pump power and the pulse duration. For broad SC generation, the dispersion should be anomalous at the pump wavelength. In this regime the input pulses compress and solitons can form. If the solitons are of high order they evolve periodically, but as a result of perturbations, such as high-order dispersion, they are unstable and undergo fission into multiple lower order solitons that evolve independently. These soliton pulses interact with the material to produce Raman gain on the long wavelength side of the pump. Because of their wide bandwidth, the red end of the soliton spectrum overlaps with the region where Raman gain exists and therefore the red side of the spectrum is amplified preferentially. This causes the central frequency of the solitons to shift progressively to the red, a process known as the Raman-induced soliton self-frequency shift.

The dispersion of a material or a waveguide will depend on wavelength and as a result any system will contain wavelength ranges where the dispersion is normal and ranges where it is anomalous. Once solitons have formed they can transfer some of their energy to a narrow-band resonance in the normal dispersion regime. This emission is normally termed dispersive wave generation [29]. The interaction of solitons and dispersive waves will lead to further spectral broadening in both the normal and anomalous dispersion regimes, i.e. the bandwidth of the SC is further extended on both the long and the short wavelength edges [29].

The phenomena discussed above occur in both bulk material and optical waveguides; however, there are several disadvantages of SC generation in bulk materials. In particular, the intensities required are often close to the damage limit of the material because the propagation length is limited to the Rayleigh length of the focussed beam. The brightness and spatial coherence of the generated SC can also be poor due to self-focussing and filamentation of the pump beam as it propagates through the material. Finally, due to self-focussing,
the long wavelengths can be highly divergent and therefore difficult to collimate particularly when short pump wavelengths are employed.

Most of these disadvantages can be overcome by employing a waveguide geometry either in the form of an optical fiber or a planar waveguide where propagation is controlled, path lengths can be increased, dispersion can be tailored and the required peak laser powers to create a SC reduced. To design the optimum optical waveguide for SC generation, a key factor is the total dispersion that takes into account both the material dispersion and the dispersion of the waveguide mode. The latter is related to the effective refractive index $n_{\text{eff}}$ of the waveguide mode which can be calculated accurately using the full vector finite difference method. Once the waveguide parameters have been determined, to predict the bandwidth of SC and better understand the SC spectrum generated in experiments, the GNLSE can be solved via the adaptive size SSFM which significantly speeds up calculations. These numerical tools will be discussed in detail in later sections.

### 2.1.1 Dispersion

Dispersion describes the broadening of light pulses as they propagate in a medium and originates from the fact that light with different wavelengths, mode, or polarization state propagates at different velocities because the medium response is dependent on such characteristics. Dispersion can be generally separated into material dispersion, waveguide dispersion, modal dispersion and polarization mode dispersion. Modal dispersion results from multi-mode transmission and polarization mode dispersion results from transmission of different polarization states in the medium. Here material dispersion and waveguide dispersion are initially the main concerns and will be discussed in detail next.

Material dispersion originates from the wavelength dependence of the intrinsic refractive index of the material. For most of the glasses, the relation between the refractive index $n$ and the wavelength $\lambda$ can be expressed approximately by an empirical Sellmeier equation as [44]:
where $B_i$ and $\lambda_i$ are values that are obtained from the fitting of the measured wavelength-dependent material refractive indexes by ellipsometry or other methods. The variable $m$ normally takes the value of 2 or 3. If Eq. 2.1 is written as a function of the optical frequency $\omega$, it becomes [44]:

$$n^2(\omega) = 1 + \sum_{j=1}^{m} \frac{C_j \omega_j^2}{\omega^2 - \omega_j^2},$$

(2.2)

where $C_j$ and $\omega_j$ possess physical meanings, meaning the strength of the $j$th resonance and the corresponding resonance frequency.

Waveguide dispersion, on the other hand, originates from the change of light distribution in a confined medium like an optical fiber or planar waveguide. It is relatively smaller than material dispersion in magnitude, but can still be large enough to significantly modify the total dispersion in some instances.

Mathematically, the effects of dispersion can be characterized by expanding the propagation constant $\beta(\omega)$ as a Taylor series around a central angular frequency $\omega_0$ as below [44]:

$$\beta(\omega) = \beta_0 + \beta_1 (\omega - \omega_0) + \frac{1}{2} \beta_2 (\omega - \omega_0)^2 + \frac{1}{6} \beta_3 (\omega - \omega_0)^3 + \ldots,$$

$$\beta_k = \left( \frac{d^k \beta(\omega)}{d\omega^k} \right)_{\omega=\omega_0} \quad (k = 1, 2, 3, \ldots).$$

(2.3)

The first two terms of $\beta_k$ are the most important and possess particular physical meanings. The group velocity $v_g$ describes the velocity of the pulse envelope and the relation between $\beta_1$ and $v_g$ is as [44]:

$$n^2(\lambda) = 1 + \sum_{i=1}^{m} \frac{B_i \lambda_i^2}{\lambda^2 - \lambda_i^2},$$

(2.1)
where \( n_g \) is the group refractive index.

\( \beta_2 \) describes group velocity dispersion (GVD) and can be deduced as [44]:

\[
\beta_2 = \left( \frac{d^2 \beta}{d \omega^2} \right)_{\omega=\omega_0} = \frac{d \beta_1}{d \lambda} = \frac{1}{c} \left( 2 \frac{dn}{d\omega} + \omega \frac{d^2 n}{d\omega^2} \right) \approx \frac{\omega}{c} \frac{d^2 n}{d\omega^2} \approx \frac{\lambda^3}{2 \pi c^2} \frac{d^2 n}{d\lambda^2},
\]

where \( n \) hereafter denotes the effective index of refraction. GVD results from the fact that the group velocity of light in a transparent medium is dependent on the optical wavelength or frequency. The basic unit of \( \beta_2 \) is \( s^2/m \).

\( \beta_2 > 0 \) corresponds to normal dispersion regime whereas when \( \beta_2 < 0 \) the dispersion is anomalous. The wavelength where \( \beta_2 = 0 \) is called the zero-dispersion wavelength (ZDW). Near the ZDW higher order terms of \( \beta_2 \) play a more important role in pulse propagation and must be considered.

One important characteristic length when considering dispersion is the dispersion length which satisfies the following relation for an input pulse of width \( T_0 \) [44]:

\[
L_D = \frac{T_0^2}{|\beta_2|}.
\]

In many instances the so-called dispersion parameter, \( D \), is used instead to characterize dispersion and the relationship between \( D \) and \( \beta_2 \) is [44]:

\[
D = \frac{2 \pi c}{\lambda^2} \beta_2 \approx -\frac{\lambda}{c} \frac{d^2 n}{d\lambda^2}.
\]

The typical unit for \( D \) is ps/nm/km. It is obvious from Eq. 2.7 that \( D \) and \( \beta_2 \) take opposite signs. For example, \( D \) is positive while \( \beta_2 \) is negative in the anomalous dispersion regime. Both the material dispersion and the waveguide dispersion contribute to the magnitude and the sign of the dispersion parameter \( D \). The contribution of the waveguide dispersion to \( D \) depends on the waveguide
dimensions and the relative core-cladding index difference for a simple rib waveguide or a step-index fiber. These offer the freedom to shift the ZDW of the waveguide and vary the dispersion regime in which available pump can reside. The dispersion can also be modified due to the microstructure of a suspended-core or photonic crystal fiber (PCF).

Not only does dispersion cause pulse distortion but more importantly, it interacts with the optical nonlinearity and influences nonlinear spectral broadening and frequency conversion such as phase matched FWM, soliton formation, high-order soliton fission and dispersive wave generation etc. These will be discussed in detail in the following sections.

2.1.2 Optical Nonlinearity

Optical nonlinearity comes into play when the electromagnetic field \( E \) is intense enough for the response of a dielectric to be no longer linear and higher order terms of induced polarization \( P \) from the electric dipoles can no longer be neglected. Here \( P \) takes the general form [45]:

\[
P = \varepsilon_0 (\chi^{(1)} \cdot E + \chi^{(2)} : EE + \chi^{(3)} : EEE + ...),
\]

where \( \varepsilon_0 \) is the vacuum permittivity and \( \chi^{(j)} (j = 1, 2, 3, \ldots) \) is the \( j \)-th order susceptibility. The symbol \( : \) and \( \cdot \) denote the multiplication of tensors.

\( \chi^{(1)} \) represents the dominant linear contribution to \( P \) and is normally described in terms of the linear refractive index \( n \) and the attenuation coefficient \( \alpha \). For materials with inversion symmetry \( \chi^{(2)} \) is zero, so normally the lowest order nonlinear effects are associated with the third-order susceptibility \( \chi^{(3)} \). This parameter is responsible for many phenomena such as SPM, XPM and FWM etc. which will be discussed in the following sections. These nonlinear effects are classed as elastic interactions (no energy is exchanged with the medium) but there is another class of nonlinear effects in which energy is exchanged between the electromagnetic field and the medium which are fundamentally related to the imaginary part of the third order susceptibility \( \chi^{(3)} \) [44]. These originate from the stimulated inelastic scattering and are related to vibrational excitation modes of
the medium. Depending on the type of phonons participating in the process, stimulated inelastic scattering can be divided into two types. One is called stimulated Raman scattering (SRS) in which optical phonons are involved and the other is called stimulated Brillouin scattering (SBS) which involves acoustic phonons [44]. A simple quantum-mechanical description of both processes is that a photon of the incident pump field is annihilated to create a photon with a different energy and a phonon such that energy and momentum are conserved. In the process of broadband SC generation by short pulses, SRS process is mainly discussed as SBS nearly ceases to contribute for pulses with a width of shorter than 10 ns even though SBS process has lower power thresholds [44].

2.1.2.1 Self- and Cross-Phase Modulation

SPM and XPM result from the light intensity \( I \) dependent refractive index \( n \) which can be written as [46]:

\[
    n = n_L + n_2 I,
\]

(2.9)

where \( n_L \) is the linear refractive index and \( n_2 \) is the nonlinear refractive index related to the third order susceptibility \( \chi^{(3)} \) as in the following equation under the assumption that the electric field is linearly polarized and the only component that contributes to the refractive index is \( \chi^{(3)}_{zzzz} \) of the fourth-rank tensor [44]:

\[
    n_2 = \frac{3}{8n} \text{Re}(\chi^{(3)}_{zzzz}).
\]

(2.10)

One important and universally used term to characterize nonlinearity of a waveguide is the nonlinear coefficient (also called the nonlinear parameter) \( \gamma \) which is defined by [44]:

\[
    \gamma = \frac{2\pi n_2}{A_{\text{eff}} \lambda},
\]

(2.11)

where \( A_{\text{eff}} \) is the effective mode area which is given by [44]:

\[
    A_{\text{eff}} = \left( \int \int_{-\infty}^{\infty} |F(x, y)|^2 \, dx \, dy \right) \frac{1}{\int \int_{-\infty}^{\infty} |F(x, y)|^4 \, dx \, dy},
\]

(2.12)
in which $F(x,y)$ is the modal distribution. A large value of $\gamma$ signifies higher nonlinear response. From Eq. 2.11 it is clear that the value of $\gamma$ typically decreases as the wavelength increases and can be enhanced by using a more nonlinear material or by reducing the effective mode area of the waveguide.

Related to the nonlinearity, there is a characteristic length called the nonlinear length [44]:

$$L_{NL} = 1/(\gamma P), \quad (2.13)$$

where $P$ is the coupled peak power.

SPM is a phenomenon where the self-induced nonlinear phase shift is present due to the light intensity modulated refractive index when pulses are transmitted in an optical waveguide. If the medium loss is considered to limit the propagation distance, the effective length of the media can be defined as [44]:

$$L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha, \quad (2.14)$$

where $L$ is the actual length of the optical waveguide. In this case, the maximum nonlinear phase shift due to SPM can be shown as [44]:

$$\phi_{NL} = \frac{2\pi}{\lambda} n_2 L_{\text{eff}} I = \gamma PL_{\text{eff}}. \quad (2.15)$$

From the above equation, the intuitive way to enhance the nonlinear phase shift is either to enhance the nonlinearity coefficient, couple more power into the waveguide or to increase the effective sample length.

The nonlinear phase shift causes the light frequency to shift from the central frequency, meaning, across the pulse the instantaneous (transient) frequency is varying as implied by the instantly changing phase. The frequency change from the central frequency can be written as [44]:

$$\delta \omega(T) = -\frac{\partial \phi_{NL}}{\partial T} = -n_2 k_0 L_{\text{eff}} \frac{dI}{dT}. \quad (2.16)$$

where $k_0 = 2\pi / \lambda$ if the electric field takes the form of $\exp(\beta z - \omega t)$.

The time dependence of $\delta \omega$ is called the frequency chirp. From Eq. 2.16 we know that the SPM induced frequency chirp increases with the effective
transmission distance, which means that the spectrum is broadened and the broadening rate is dependent on the temporal distribution of the light intensity. Also, for \( n > 0 \) which is normally the case, the frequency chirp is negative (positive) near the leading (trailing) edge of the pulse.

When ultrashort pulses are considered, for example on a scale of 100 fs, higher order nonlinear effects need to be included. One important higher-order nonlinear effect is self-steepening which results from the intensity dependence of the group velocity \([47]\). This results in an asymmetry in the SPM broadened spectra with the trailing edge becoming steeper and steeper during propagation \([48,49]\). A steeper trailing edge on the pulse means there will be larger spectral broadening on the blue side as SPM generates blue components near the trailing edge \([44]\). Eventually, an optical shock will form \([50]\).

When two or more light beams with different wavelengths are transmitted simultaneously in the medium, the refractive index will also be influenced by the intensity of the other co-propagating beams as well as the intensity of the light beam itself. This is the origin of XPM whose complete description can be complicated.

Suppose two linearly polarized pulses are co-propagating in a single mode waveguide with their respective electric field intensities being \( E_1 \) and \( E_2 \) and their frequencies being \( \omega_1 \) and \( \omega_2 \). Under the approximation of a quasi-monochromatic field, the total electric field can be written as \([44]\):

\[
E(r, t) = \frac{1}{2} \hat{x} [E_1 \exp(-i\omega_1 t) + E_2 \exp(-i\omega_2 t)] + c.c.,
\]  

(2.17)

where \( \hat{x} \) is the unit polarization vector of the light polarized along the \( x \) direction and c.c. signifies the complex conjugate.

If the phase matching condition is satisfied, the intensity dependent nonlinear phase shift can be obtained as follows \([44]\):

\[
\phi_{j}^{NL} = \frac{2\pi}{\lambda_j} n_2 I_{\text{eff}} \left( |E_j|^2 + 2|E_{3-j}|^2 \right),
\]  

(2.18)
where \( j = 1 \) or 2. The first term of the above equation is induced by SPM, and the second term results from XPM effects. It can be inferred that with the same light intensity, the influence of XPM effect is twice that of SPM. By taking the derivative of the Eq. 2.18, a \( dl / dt \) term appears, from which we know that both SPM and XPM are more effective in pulses with steeper leading and trailing edges.

During the process of SC generation, the conditions required for XPM are generally difficult to satisfy. This is because co-propagating pulses will generally have different group velocities and thus will propagate with different speeds and this will result in walk-off between them which limits the influence of XPM. The walk-off distance can be defined as [44]:

\[
L_w = \frac{T_0}{|\beta_1(\omega_1) - \beta_1(\omega_2)|} = \frac{T_0}{|1/v_g(\omega_1) - 1/v_g(\omega_2)|}. \tag{2.19}
\]

Actually there is another more subtle case of XPM in which it is the two orthogonal polarization states of the same wave that influence each other. In this case, both the intrinsic mode birefringence and the optically induced nonlinear birefringence need to be considered [44].

The above discussion ignores dispersion, but in reality the effects of dispersion cannot simply be neglected. The relative relation between the dispersion length \( L_D \), the nonlinear length \( L_{NL} \) and the medium length \( L \) determines whether the dispersive or nonlinear effects become more important for pulse evolution. When the medium length is much smaller than both the characteristic dispersive length \( L_D \) and the nonlinear length \( L_{NL} \), neither dispersion nor nonlinearity plays an important role during pulse propagation. When the propagation length is much smaller than the one of the characteristic lengths but comparable with the other, the pulse evolution will be dominated by just one of the processes. When the waveguide length is comparable to both of the two lengths, the interplay between two effects will lead to a qualitatively different behaviour compared to that expected from the dispersion or the nonlinearity alone. For example, as SPM and normal group velocity dispersion both result in negative frequency chirp near the leading edge of pulses and positive chirp near the trailing edge, pulses get broadened even more under the
influences of both effects. However, when SPM interacts with anomalous GVD, pulses will have the potential to maintain their shapes in certain conditions, which is the stable soliton state. Practically in the anomalous dispersion regime, pulses can be compressed in time or break up into multiple pulses. These soliton-related phenomena are important and will be discussed in detail in Section 2.1.3.

2.1.2.2 Four-Wave Mixing and the Modulation Instability

FWM is another third-order nonlinear effect related to the third-order susceptibility. The main features of FWM can be understood by the third order polarization term [44]:

\[ P_{NL} = \varepsilon_0 \chi^{(3)}; \quad EEE. \quad (2.20) \]

Suppose all four optical fields considered are propagating in the same direction and their linear polarization states are maintained along the medium distance, then the total electric field can be noted as [44]:

\[ E = \frac{1}{2} \hat{x} \sum_{j=1}^{4} E_j \exp[i(\beta_j z - \omega_j t)] + c.c., \quad (2.21) \]

where \( \beta_j = n_j \omega_j / c \) (\( n_j \) is the effective mode refractive index of the corresponding wave), by integrating the two equations above, we can obtain:

\[ P_{NL} = \frac{1}{2} \hat{x} \sum_{j=1}^{4} P_j \exp[i(\beta_j z - \omega_j t)] + c.c.. \quad (2.22) \]

And we can find that \( P_j (j = 1 - 4) \) is consisted of several terms containing the product of three electric fields. For instance, \( P_4 \) can be written as [44]:

\[ P_4 = \frac{3\varepsilon_0}{4} \chi^{(3)}_{xxx} \left( |E_1|^2 + 2(|E_1|^2 + |E_2|^2 + |E_3|^2)E_4 
+ 2E_1E_2E_3 \exp(i\theta_1) + 2E_1E_2E_3 \exp(i\theta_2) + \ldots \right), \quad (2.23) \]
where $\theta_+ \,$ and $\theta_- \,$ are defined as [44]:

$$\theta_+ = (\beta_1 + \beta_2 + \beta_3 - \beta_4)z - (\omega_1 + \omega_2 + \omega_3 - \omega_4)t, \quad (2.24)$$

$$\theta_- = (\beta_1 + \beta_2 - \beta_3 - \beta_4)z - (\omega_1 + \omega_2 - \omega_3 - \omega_4)t. \quad (2.25)$$

In Eq. 2.23, those terms containing $E_t$ correspond to SPM and XPM effects and the remaining terms correspond to FWM effects. Whether the effects of FWM is significant or not depends on the phase matching condition which is determined by phase mismatch quantities $\theta_+$ and $\theta_-$. To facilitate effective FWM processes, frequency and wave vector matching are necessary; the latter is normally known as phase matching. From the perspective of quantum mechanics, FWM can be explained in terms of one or more photons being annihilated and one or several new photons with different frequencies being created. During the process, the total energy and momentum are conserved.

Terms containing $\theta_+$ in Eq. 2.23 correspond to the process when three photons annihilate to form a single photon $\omega_4$. When $\omega_1 = \omega_2 = \omega_3$, it is the case of third harmonic generation (THG). Generally, the phase matching conditions which allow effective FWM are difficult to satisfy. On the other hand, terms containing $\theta_-$ represent the most effective FWM process where two photons are annihilated and another two photons are created and the energy conservation and the phase matching condition can be written as $\omega_3 + \omega_4 = \omega_1 + \omega_2$ and $\Delta k = \beta_3 + \beta_4 - \beta_1 - \beta_2 = (n_3 \omega_3 + n_4 \omega_4 - n_1 \omega_1 - n_2 \omega_2)/c = 0$ respectively [44]. It is comparatively easier to satisfy the condition $\Delta k = 0$ if $\omega_1 = \omega_2$. Most of the FWM processes belong to this kind of partially degenerate FWM.

The modulational instability (MI) is closely related to FWM and was initially studied by introducing an amplitude perturbation onto a CW wave in a nonlinear medium where it was found that in certain conditions the perturbation would grow. This instability originates from the fact that when the carrier frequency $\omega_0$ is in the anomalous dispersion regime, a disturbance with frequency $\Omega$ can increase exponentially with transmission distance. In the time domain, the beat
frequency among $\omega_0$, $\omega_0 - \Omega$ and $\omega_0 + \Omega$ will appear and the beat will modulate the intensity of the continuous wave with a frequency $\Omega$ and transform the CW light into a train of short pulses. In a frequency domain description, there will be two sidebands generated at $\omega_0 - \Omega$ and $\omega_0 + \Omega$, which is equivalent to degenerate FWM. Actually, FWM and MI are simply frequency-domain and time-domain descriptions of the same physics with different emphasis to explain different aspects of field evolution [29]. The need for anomalous dispersion is due to the prerequisite of phase matching. MI is significant in the process of SC generation in the long pulse or CW pumping regime as it is MI which transforms long pulses or CW light into short pulses. For short pulses to generated FWM effectively, not only phase matching is required, group velocity matching between the pump, the red-shifted and the blue-shifted light is also required.

2.1.2.3 Stimulated Raman Scattering

SPM, XPM and FWM (MI) discussed above belong to the elastic nonlinear effects during which there is no energy transfer between the light fields and the medium. Stimulated Raman scattering (SRS), however, results from stimulated non-elastic scattering and during the process part of the energy of the light field is transferred to the nonlinear medium.

In any molecular medium, spontaneous Raman scattering will transfer part of the input light power from one beam to another beam with a down-shifted frequency in which the frequency shift is determined by characteristic resonances of the medium: the process is known as the Raman effect. Quantum mechanically, a photon injected with an energy of $\hbar \omega_p$ is scattered to be another low energy photon with energy $\hbar \omega_s$ which is called the Stokes light and the molecule simultaneously transitions to a higher oscillation state. For a pump that exceeds a certain threshold level, significant conversion of pump energy to Stokes energy occurs and this scenario is called SRS. Note that SRS only occurs over distances characterized by walk-off between the pump and Stokes pulses.

Under continuous or quasi-continuous pumping condition, the initial increase of Stokes light can be described as [44]:

$$0 \omega \quad 0 \omega - \Omega \quad 0 \omega + \Omega$$
where $I_s$ is the light intensity of the Stokes light and $I_p$ is the pump intensity. The Raman gain factor $g_R(\Omega) \ (\Omega = \omega_p - \omega_s)$ is the most significant parameter to describe SRS and is related to the cross section of spontaneous Raman scattering. It is mostly determined by the composition of the medium and can be greatly influenced by doping [51,52]. Also, $g_R$ is affected by the polarization state relation between the pump and the Stokes light. $g_R$ can be expressed as [53]:

$$g_R(\Omega) = \frac{\alpha_0}{cn} f_R \xi_{ZERZ} \text{Im}[\tilde{h}_R(\Omega)],$$

(2.27)

where $f_R$ is the Raman fractional factor and $h_R$ is the Raman response function which is responsible for the Raman gain width. $\text{Im}[\tilde{h}_R(\Omega)]$ can be obtained from the measured Raman gain spectrum and by solving the Kramers-Kronig relation, $\text{Re}[\tilde{h}_R(\Omega)]$ can be deduced. The interplay of Raman scattering and other effects will be discussed later.

### 2.1.3 Solitons & Dispersive Waves

A soliton is a special kind of self-reinforcing solitary wave (wave packet or pulses) which can remain unchanged after propagating over long distances. It is formed due to a balance of dispersive and nonlinear effects. This kind of phenomenon was first discovered in water waves [54] and was named “wave of translation” by John Scott Russell in 1834. It was observed in optical systems more than 100 years later [55].

In the context of nonlinear optics, as SPM will red-shift the leading edge of the pulse and blue-shift the trailing edge, in the normal GVD regime, the red-shifted components travel faster than the blue-shifted ones, so the pulse will be broadened under the mutual influence of normal GVD and SPM. However, in the anomalous GVD regime, the red-shifted components travel more slowly than the blue-shifted ones, i.e. SPM actually counteracts pulse broadening. If the influences of SPM and GVD are balanced, the pulse shape can remain constant during propagation. From the perspective of chirp, the sign of frequency chirp
induced by SPM is counter to that induced by anomalous GVD. When the contributions from these two chirps cancel each other, a stable pulse with no chirp propagates through the medium and this is the origin of soliton formation.

Mathematically, if the waveguide loss is neglected and only SPM and anomalous GVD are considered, the simplified GNLSE would have an analytical solution [44]:

\[ A(z, T) = \sqrt{P_0} \text{sech}\left(\frac{T}{T_0}\right) \exp\left(-\frac{i\gamma P_0 z}{2}\right). \] (2.28)

Defining \( N \) as the order of solitons [44]:

\[ N = \sqrt{\frac{L_{\text{NL}}}{\beta_2}} = \sqrt{\frac{\gamma P_0 T_0^2}{|\beta_2|}}, (\beta_2 < 0). \] (2.29)

If the peak power \( P_0 \) and pulse duration \( T_0 \) satisfy the condition that \( P_0 = |\beta_2|/\gamma T_0^2 \), i.e. \( N=1 \), the solution is called the fundamental soliton. Fundamental solitons maintain their power distribution \( |A(T)|^2 \) during propagation.

Solitons with soliton number \( N \geq 2 \) are called high-order solitons. Unlike the fundamental soliton, their pulse shape and spectrum will evolve periodically during propagation with a period:

\[ z_0 = \frac{\pi}{2} L_{\text{D}}. \] (2.30)

The above discussions have neglected all effects except group velocity dispersion and SPM. However, the presence of perturbation will make solitons unstable. Especially for femtosecond pulses, high-order dispersion and Raman scattering will disturb the ideal periodical evolution of high-order solitons and cause them to split. Defining \( \bar{N} \) as the integral number closest to \( N \), a high-order soliton will split into \( \bar{N} \) fundamental solitons with various pulse durations and peak powers. Their pulse durations and peak powers are related to \( N \) by the following equations [56]:

\[ z_0 = \frac{\pi}{2} L_{\text{D}}. \] (2.30)
where \( k = 1 \sim \bar{N} \). We learn from the equations above that compared to the input pulse, the fundamental solitons that are generated will have shorter pulse durations and almost half of them will possess higher peak powers. The distance in which the high-order soliton propagates from formation to fission is called the soliton fission length and can be simply written as

\[
L_{\text{fiss}} = L_D / N = \sqrt{L_D \cdot L_{\text{NL}}} \propto T_0.
\]

For soliton fission to occur, the sample length should be longer than the soliton fission length.

Under the influence of the Raman scattering, pulse components with higher frequencies will act as a pump and transfer the energy to the lower frequency counterparts continuously, which is called intra-pulse Raman scattering. Intra-pulse Raman scattering will red-shift the central frequency of the soliton, and this process is also known as the soliton self-frequency shift (SSFS). It should be noted that this process only happens when the soliton bandwidth overlaps with the Raman gain region.

Solitons will also be perturbed by high-order dispersion as they red-shift, and this makes them unstable so that they radiate dispersive waves via Cherenkov radiation in which the energy of the soliton is partly transferred to a narrow-band resonance in the normal dispersion regime. This process is also called the dispersive wave generation [44]. The phase of the dispersive wave and the corresponding soliton is equal thus the position of the dispersive wave is determined by the following equation [29]:

\[
\beta(\omega_d) - \omega_d / v_s + (1 - f_R)\gamma P_s = \beta(\omega_s) - \omega_s / v_s,
\]

where \( \omega_d \) and \( \omega_s \) is the optical frequency of the dispersive wave and the soliton respectively, while \( v_s \) and \( P_s \) is the group velocity and the peak power of the soliton respectively. For a waveguide with several ZDWs, more than one position of the SC spectrum can cause the formation of dispersive waves with matching
frequencies and group velocities.

Once the dispersive wave and the Raman frequency-shifted soliton approach each other, they will interact via XPM, which will change the spectrum of the dispersive wave and forces them to propagate with the same speed as the soliton. In other words, the Raman frequency-shifted soliton will trap the dispersive wave and drag it along. This process is called soliton trapping. Since the soliton and the dispersive wave overlap in time domain and propagate together, they can also interact by FWM, which will smooth and broaden the SC even further.

2.1.4 Brief Summary

From the above discussions we know it is important when analysing the effects influencing SC generation that the interplay of various dispersive and nonlinear effects are considered simultaneously. In this section a brief summary of the physics underlying SC generation in various conditions will be given on the basis of the respective explanation of multiple nonlinear and dispersive effects above.

In terms of the dispersion regime, the scenario can be divided into the normal and the anomalous dispersion regime with distinctly different mechanisms dominating. In the normal dispersion regime, generally SPM and normal dispersion will interact to result in simultaneous temporal and spectral broadening with the appearance of a linear chirp across the central region of the pulse [57]. For the purpose of generating a coherent SC source, the normal dispersion regime is beneficial. In the anomalous dispersion regime, however, the nonlinear chirp induced by the SPM processes and the linear chirp from GVD (only considering $\beta_2$ for simplicity) combines to yield either stable or periodically evolving solitons. For fundamental solitons that have a soliton number of 1, both the spectral and the temporal profiles remain unchanged during propagation. Higher-order solitons undergo periodic spectral and temporal evolution but they will break up into a series of sub-pulses under the influence of perturbations. The perturbations include higher-order dispersion and Raman scattering. A soliton propagating close to the ZDW will transfer a part of its energy to the normal GVD regime and this is normally referred as the dispersive wave generation. Meanwhile the soliton itself can be red-shifted due to the soliton self-frequency shift when the individual soliton bandwidth
overlaps with the Raman gain. Moreover, the effects of group velocity matching and XPM between the solitons and the dispersive wave radiation will induce soliton trapping and results in further increase in the bandwidth both at the short and the long wavelength edges of the SC spectrum. These processes all increase the SC bandwidth and this is why pumping in the anomalous dispersion regime is preferred when large bandwidth is required.

2.2 Numerical Methods

To provide guidelines to predict waveguide performance for SC generation, numerical tools are needed that will allow optimization of the waveguide and pulse parameters. Among various factors, the nonlinear parameter or the nonlinear coefficient $\gamma$ of the waveguide and the group velocity dispersion are the two most important parameters. There are many methods to calculate these two parameters numerically, including mode-matching methods [58,59], finite element methods [60,61], finite difference methods [62,63] etc. In this thesis, finite difference methods were mainly used as they provide easy access to visualization, manipulation and post-processing without the need to interpolate the mesh. The MATLAB codes used were mostly written by my advisor Dr. Xin Gai and modified by the author of this thesis on the basis of the open source code developed by Murphy et al. [64].

As for the prediction of how SC can be generated in conditions of the experiments, the generalized nonlinear Schrödinger equation (GNLSE) needs to be solved. Here one of the most common approaches, the split-step Fourier method (SSFM) was adopted. It was implemented under the assumption that the dispersive and nonlinear effects act independently over a short propagation length, $h$. The method was implemented using a MATLAB code provided by advisor Dr. Xin Gai and modified by this author. The simulations show good agreement with experimental results as will be shown in later Chapters.
2.2.1 Full-Vector Finite Difference Method

To obtain the nonlinearity and the dispersion features of an optical waveguide, the mode distribution needs to be calculated by solving the eigenvalue equation for transverse magnetic fields which is shown below [64]:

\[ \nabla \times (\varepsilon^{-1} \nabla \times H) - \omega^2 \mu_0 H = 0, \]  

(2.34)

where the material is assumed to be nonmagnetic (\( \mu = \mu_0 \)) and all fields have a time dependent quantity of \( e^{j\omega t} \). \( \varepsilon \) here denotes the permittivity tensor and it takes the form [64]:

\[
\varepsilon = \varepsilon_0 \begin{bmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & 0 \\
\varepsilon_{yx} & \varepsilon_{yy} & 0 \\
0 & 0 & \varepsilon_{zz}
\end{bmatrix}.
\]  

(2.35)

For an isotropic material, Eq. 2.34 can be further simplified into the Helmholtz equation for the transverse magnetic field components [64]:

\[ \frac{\partial^2 H_{x(y)}}{\partial x^2} + \frac{\partial^2 H_{y(x)}}{\partial y^2} + (\varepsilon k^2 - \beta^2)H_{x(y)} = 0, \]  

(2.36)

where \( k \) is the wave vector. Assuming a \( z \)-dependence for all fields, the longitudinal component of the magnetic field \( H_z \) can be calculated by applying the divergence relation \( \nabla \cdot H = 0 \) [64]:

\[ H_z = \frac{1}{j\beta} \left( \frac{\partial H_x}{\partial x} + \frac{\partial H_y}{\partial y} \right). \]  

(2.37)

After integrating Eq. 2.35 and Eq. 2.36 the coupled eigenvalue equations can be written as [64]:

\[
\begin{bmatrix}
\frac{\partial^2}{\partial x^2} + \frac{\varepsilon_{xx}}{\varepsilon_{zz}} \frac{\partial^2}{\partial y^2} + \frac{\varepsilon_{xx}}{\varepsilon_{yy}} \frac{\partial^2}{\partial x \partial y} + (1 - \frac{\varepsilon_{xx}}{\varepsilon_{yy}}) \frac{\partial^2}{\partial x \partial y} - \frac{\varepsilon_{zz}}{\varepsilon_{yy}} \frac{\partial^2}{\partial x^2} + k^2 (\varepsilon_{zz} H_x - \varepsilon_{yy} H_y) = \beta^2 H_x, \\
\frac{\partial^2}{\partial y^2} + \frac{\varepsilon_{yy}}{\varepsilon_{zz}} \frac{\partial^2}{\partial x^2} + \frac{\varepsilon_{yy}}{\varepsilon_{xx}} \frac{\partial^2}{\partial x \partial y} + (1 - \frac{\varepsilon_{yy}}{\varepsilon_{xx}}) \frac{\partial^2}{\partial x \partial y} - \frac{\varepsilon_{zz}}{\varepsilon_{xx}} \frac{\partial^2}{\partial y^2} + k^2 (\varepsilon_{xx} H_y - \varepsilon_{yy} H_x) = \beta^2 H_y
\end{bmatrix}.
\]  

(2.38)
where \( k^2 = \omega^2 \mu \varepsilon_0 \).

The essence of the full vector finite difference method is that it solves differential equations by approximating them with difference equations with finite differences substituting for the derivatives and it is performed by defining and applying mesh points of the permittivity in one calculation sub-cells as shown in Fig. 2.1. It shows that the magnetic fields are defined at the nodes signified by the dots at the line crossing and the permittivity is defined in the empty regions bound by the nodes. Inside a certain rectangular region, the permittivity is taken to be constant. The normally used grid size was 20 nm with stretched grid spacing at the edge of the computation window in this thesis. A typical calculation window had a dimension of 15 μm by 15 μm.

![Diagram illustrating mesh points used in the full vector finite difference methods.](image)

Fig. 2.1: Diagram illustrating mesh points used in the full vector finite difference methods. N, S, W, E is short for north, south, west and east respectively.

In this way, all of the magnetic components can be solved in a MATLAB program [64] and the electric fields can then be obtained in the post-processing codes via the following Maxwell’s equations:

\[
\begin{align*}
\nabla \times H &= j \omega D \\
E &= \varepsilon^{-1} D
\end{align*}
\]

From this the effective refractive index as a function of wavelength can be obtained and the dispersion parameters can be inferred. It should be noted that the material dispersion represented by the Sellmeier equations was included in the calculations. Also the nonlinear parameter was calculated using
\[ \gamma = \frac{2\pi n_2}{A_{\text{eff}} / \lambda} \] by feeding in the effective mode area calculated from the above procedures.

### 2.2.2 Nonlinear Schrödinger Equation & Split-Step Fourier Method

After solving the parameters characteristic of dispersion and nonlinearity using the full vector finite difference method, these parameters can be fed into the GNLSE which takes into account both the dispersive and nonlinear effects. It generally takes the form [29]:

\[
\frac{\partial A}{\partial z} + \frac{\alpha}{2} A - \sum_{k} i^{k+1} \frac{\beta_k}{k!} \frac{\partial^k A}{\partial T^k} = i\gamma \left( 1 + i\tau_{\text{shock}} \frac{\partial}{\partial T} \right) \left( A(z,t) \int_{-\infty}^{\infty} R(T') \left| A(z,T'-T') \right|^2 dT' \right). \tag{2.40}
\]

where \( A \) is the electric field amplitude, \( \alpha \) is the linear loss, \( \beta_k \) is the \( k \)-th order dispersion that can be obtained by the full vector finite difference mode solver described in the last section, \( T = t - \beta_1/z \) is the shifted time frame that moves at the envelope group velocity, \( \gamma \) is the nonlinearity coefficient and \( \tau_{\text{shock}} = 1/\omega_0 \) is the term associated with effects such as self-steepening and optical shock formation. \( R(T) \) introduces the Raman effect and takes the form [44]:

\[ R(T) = (1 - f_R) \sigma(T) + f_R h_R(T), \tag{2.41} \]

where \( f_R \) is the Raman fractional factor which represents the fractional contribution of the delayed Raman response to the nonlinear polarization and \( h_R(T) \) is the Raman response function that is responsible for the Raman gain width and is determined by the vibrations of the medium material [44]. \( h_R(T) \) can be obtained by Fourier transforming \( \tilde{h}_R(\Omega) \) which can be deduced by the method described in Section 2.1.2.3. The Raman response function was obtained by measuring the Raman response by my colleagues [65].

Typically, a Gaussian shaped or Sech pulse was fed into the GNLSE as the input. The temporal calculation window was of the order of 100 ps and the resolution was on the fs level. White noise or Gaussian noise could be added in
the input together with waveguide losses. Up to 20th orders of parameters in the Taylor expanded propagation constant were generally used to enhance accuracy.

One of the most prevalent methods to solve the GNLSE is the SSFM which assumes that nonlinearity and dispersion act independently over a tiny step length $h$ as shown in Fig. 2.2.

![Fig. 2.2: Illustrating sketch for the split-step Fourier method. $h$ is the step size.](image)

Here the two operators $\hat{N}$ and $\hat{D}$ denote the effects of nonlinearity and dispersion respectively thus the GNLSE can be simplified as [44]:

$$\frac{\partial A}{\partial z} = \left( \hat{D} + \hat{N} \right) A$$  \hspace{1cm} (2.42)

$$\hat{D} = \sum_{k=2}^{k+1} \frac{i^{k+1}}{k!} \beta_k \frac{\partial^k}{\partial T^k} - \frac{\alpha}{2},$$  \hspace{1cm} (2.43)

$$\hat{N} = \frac{i}{A(z,T)} \left( 1 + i \tau_{\text{shock}} \frac{\partial}{\partial T} A(z,T) \right) \left[ e^{\int_{-\infty}^{\infty} R(T') \times |A(z,T-T')|^2 \, dT'} \right].$$  \hspace{1cm} (2.44)

Specifically, propagation over a certain distance from $z$ to $z+h$ is carried out in two steps in the SSFM. In the first step, the nonlinear effects act alone thus $\hat{D}$ is taken to be zero and in the next step the nonlinearity operator is fixed to be zero. Mathematically [44],

$$A(z+h,T) = \exp(h\hat{D}) \exp(h\hat{N}) A(z,T).$$  \hspace{1cm} (2.45)
Operator $\exp(h\hat{D})$ is executed in the Fourier domain using the prescription [44]:

$$\exp(h\hat{D}) A(z,T) = \left\{ F^{-1} \exp\left[ h\hat{D}(i\omega) \right] F \right\} A(z,T). \quad (2.46)$$

where $F$ here means the Fourier transform operation, $\hat{D}(i\omega)$ is obtained by replacing $\partial/\partial T$ by $i\omega$ in Eq. 2.43 and $\omega$ is the frequency in the Fourier domain. Also, an adaptive step size can be used to enhance the calculation speed and stabilize the output results. Using the separation approximation and the fast Fourier transform (FFT) algorithm, the GNLSE can be solved with good accuracy and moderate speed.

### 2.3 Summary

In this Chapter, the fundamental background and the numerical tools used in the whole thesis have been discussed in detail, and these lay the foundation of the following designs and simulations.

Two of the most important factors in SC generation were introduced, i.e., dispersion and nonlinearity. These never act alone, and it is the complex interplay between them that facilitates efficient SC generation. In terms of dispersion, two dispersive regimes exist. One is the normal dispersion regime and the other is the anomalous regime where group velocity dispersion and self-phase modulation cancel each other and solitons can form. It is soliton formation, soliton fission and its associated dispersive wave generation under the influence of higher-order dispersion and Raman scattering that significantly expand the spectrum of the SC.

Following the fundamentals of SC generation, it is necessary to calculate the parameters that are characteristic of nonlinear and dispersive effects. In this thesis, a full-vector finite difference method was adopted to calculate the nonlinear coefficient $\gamma$ and the dispersion parameter $D$. In addition, to predict the spectral width a certain pump condition can reach, it is essential to solve the GNLSE. In this thesis one of the most effective methods, the adaptive-size SSFM was adopted which separates the influences of nonlinearity and dispersion within a small adaptive step size. As will be shown in the following Chapters, these two approaches serve as effective and accurate design and prediction tools.
Chapter 3: Extending SC into the Mid-Infrared (MIR): Challenges & Opportunities

In 1970 Alfano and Shapiro reported the first series of measurements on frequency broadening in crystals and glasses using a frequency doubled Nd:Glass mode-locked pump laser [27,28]. They are regarded as the discoverers and inventors of supercontinuum (SC) generation although at that time the phenomenon was known as white light generation. The spectral coverage of the filaments formed at that time was 400-700 nm and the phenomenon was attributed to SPM and FWM. Since then there have been various demonstrations of SC generation in bulk materials, conventional silica fibers, photonic crystal fibers (PCFs) using CW, picosecond or fs pulses at various pumping wavelengths [30-36, 66-73]. Most of the media used were oxides glasses such as fused silica which have limited transmission in the MIR and thus most of the spectral broadening was restricted to the visible and NIR.

To extend SC into the MIR, MIR transparent materials are required. Furthermore, as the third order nonlinearity is predicted to decrease as the wavelength increases [37], materials with a higher nonlinearity than silica are preferred. Moreover, in a waveguide, waveguide dispersion and the nonlinear parameter need to be engineered together with the configuration of a suitable pump.

This Chapter introduces the rational for extending SC into the MIR and how this can be readily achieved using chalcogenide glass waveguides rather than other material platforms such as those based on silicon. For effective generation in the MIR from simple chalcogenide waveguides it is shown that a femtosecond MIR pump is required. The design of an optical parametric amplifier (OPA) system that achieves this is described.
3.1 Why the MIR?

The definition of the MIR varies significantly depending on the context in which it is used. For example, a sub-division scheme well received by chemists defines MIR infrared light wavelengths to be 2.5-50 μm while the most common definition of the MIR region is from 2.5 μm to 15 μm [74]. However, from an astronomer’s perspective, 5 μm to (25-40) μm belongs to the MIR [75]. Another division method proposed in [76] defines mid-wavelength infrared (MWIR) to be 3-8 μm while 1.4-3 μm is considered to be the short-wavelength infrared (SWIR) and 8-15 μm is considered to be the long-wavelength infrared (LWIR) region. In this thesis, we consider that infrared light with wavelengths between 2.5 and 25 μm comprises the MIR.

3.1.1 Applications of Broadband MIR Sources

The importance of MIR light lies in the fact that MIR photon energies are resonant with fundamental vibrational modes of molecules via a change in the dipole moment and, thus, can be absorbed. The absorption spectrum is unique to every molecule and, hence, can be used to identify that molecule leading to molecular “fingerprint” spectroscopy [77].

Typically, two regions of the MIR are used to identify a molecule: one is called the functional group band which spans from 4000 cm⁻¹ to 1500 cm⁻¹ (2.5-~6.6 μm) where there are peaks characteristic of the functional groups that reveal the basic molecular structure. The second band is called the fingerprint region and spans from 1500 cm⁻¹ to 400 cm⁻¹ (~6.6-25 μm) where almost every organic compound produces a unique pattern (i.e. its fingerprint) from which its exact identity can be determined by comparison with a known spectrum [13].

In organic chemistry, functional groups are specific groups of atoms or bonds within molecules which are responsible for the characteristic chemical reactions of those molecules. Typically the same functional group will produce similar absorption features. For example, N-H bonds appear around 3400 cm⁻¹ while carbon-hydrogen stretch appears at around 2800-3100 cm⁻¹ [13]. Identifying the functional groups alone doesn’t necessarily identify the molecule itself as different bonds may have overlapping absorption lines so more delicate study in the fingerprint region is needed. Peaks in this fingerprint region
originate from complex deformations of the molecules. They may be characteristic of molecular symmetry or simultaneous effects of deformations from multiple bonds. For example, isomers propan-1-ol and propan-2-ol contain exactly the same functional groups thus they show similar absorption spectrum around 3000 cm\(^{-1}\) but in the fingerprint region between 1500 and 500 cm\(^{-1}\), they have distinct differences in their absorption spectra and thus can be distinguished easily [78].

From the above explanations we can know that MIR light sources can be used effectively in spectroscopy [79-81] as an unequivocal way to identify and quantify the molecular species and even isotopologues under certain conditions. MIR spectroscopy can also be applied to composite physical, chemical or biological systems for non-intrusive diagnostics [82-85].

Other than this, the MIR region also contains two important atmospheric windows (3–5 μm and 8–13 μm) which can be exploited to detect small traces of environmental and toxic vapours etc. with high sensitivity [86-88]. The relatively low Rayleigh scattering losses in the MIR region also benefit tomography and imaging applications offering deeper penetration [22, 24,89,90].

### 3.1.2 Comparison of Broadband MIR Sources

Typically, to identify a molecule from an absorption spectrum, broadband or widely tunable MIR light sources are needed. Currently common available MIR sources include globars, synchrotrons, quantum cascade lasers (QCLs) and tunable optical parametric oscillators (OPOs) or optical parametric amplifiers (OPAs) and these all have their respective advantages and disadvantages.

A conventional globar is made of a silicon carbide rod which is electrically heated to between 1,000 and 1,650 °C [91]. When combined with a downstream variable interference filter, it emits infrared energies from around 4 μm to 15 μm with similar spectral behaviour to a black body. The main disadvantage of globars is that they do not have sufficient brightness for applications when high spatial resolution (~λ) is required. Thus, conventionally, high SNR measurements at high spatial resolution (as is desirable for analysing small scale biological tissue, for example) can only be performed using bright MIR broadband sources such as those based on synchrotrons whose brightness exceeds that of a globar
by 2–3 orders of magnitude [25]. Typically the infrared beam line of a synchrotron system provides a few milli-watts of average power. However, the shortcomings of this setup are also obvious. Synchrotron sources would in no way be a user-friendly laboratory tool nor can it be used in applications in the field.

The development of the QCLs has provided the opportunity to vastly increase the source brightness in some wavelength bands in a compact and portable form. Typically a QCL produces a diffraction-limited beam with brightness \(4 \times 10^{23} \text{ph/s/sr/mm}^2/\text{cm}^{-1}\) which is more than 5 orders of magnitude greater than any synchrotron. However, the tuning range of an individual QCL is quite small. Consequently many individual lasers need to be combined to cover the complete MIR spectrum. This makes QCL sources quite costly and complex. Moreover, currently QCLs are still limited in their capability to operate at wavelengths shorter than 2.6 μm though some theoretical designs have been presented [92, 93].

OPOs and OPAs make it possible to access MIR wavelengths with wavelength tunability and thus can be used for MIR spectroscopy [94,95]. They provide coherent and bright beams. However, the tuning of wavelength is mostly achieved by varying the phase-matching conditions, e.g. by changing crystal temperature, the angular orientation of a crystal or the poling period thus the tuning speed is limited, which is not ideal for rapid collection of spectroscopic data. The design for OPOs is also relatively complex, particularly if the emission needs to be narrowband, and the crystal is often operated close to the laser damage threshold particular for crystals used in the MIR. Moreover, the transparency region of the nonlinear material is critical for the tuning range of both OPOs and OPAs [96-98].

In this context SC generation could provide a cost effective approach for generating a bright broadband MIR source. As SC is normally generated in a single mode waveguide, the spatial coherence of SC can be comparable with that of a laser. If similar average power levels can be achieved to the infrared beamlines of synchrotrons, the SC generated in a waveguide will have significantly higher brightness compared to the synchrotron whose beam is not emitted in a single spatial mode. Thus it is quite interesting to explore MIR SC as a bright MIR source. However, there are many challenges that need to be
overcome to achieve this. Firstly, a suitable material should be chosen that possess high nonlinearity, low nonlinear absorption and good transparency in the MIR. A proper waveguide structure should then be designed with optimum dispersive and nonlinear properties. Finally, a pump source should be developed that allows the SC spectrum to extend into the MIR using only moderate pulse powers. We can anticipate that this implies that a high repetition rate (10s MHz) pump emitting ultrashort pulses with 100s mW of average power in the MIR will be required.

3.2 Material Choice

When this project started, there had already been various MIR SC demonstrations using different nonlinear optical materials such as silicon [99]; bismuthides [100,101]; single crystal sapphire [102]; lithium niobate [103]; materials with rare-earth dopants [104-107]; tellurites [108-113] and fluorides [114-119]. These previous results are briefly listed below.

Kulkarni et al. reported a SC spectrum covering from around 1.9 µm to 4.5 µm in ZBLAN (ZrF4-BaF2-LaF3-AIF3-NaF) fibers with high average output power beyond 3.8 µm [115]. The ZBLAN fiber was pumped with a thulium-doped fiber amplifier. Qin et al. reported SC generation from 350 nm to 6.28 µm in centimeter-long fluoride fibers by pumping with an fs laser at 1.48 µm and this was claimed to be the broadest MIR SC reported in fluoride fibers at that time [114]. At the long wavelength end, no further broadening was expected due to the relatively high fiber loss. Furthermore, the nonlinearity of the fluoride material is rather low and this meant that high peak powers were required to couple into the ZBLAN fiber [114] and this is ultimately a significant disadvantage for SC generation in fluorides.

Domachuk et al. reported a SC spectrum with a bandwidth of over 4000 nm which extended to 4870 nm at the long wavelength end in a 8 mm long highly nonlinear tellurite PCF pumped by 100 fs pulses at 1.55 µm [109]. Nevertheless, it will be difficult for tellurites to support emission further into the MIR again because of the glass transmission is limited to < 6 µm especially when longer samples are to be used.
Buczynski et al. generated a SC spectrum covering the 750-3000 nm range (two octaves) using a new type of lead-bismuth-galate (PBG08) photonic crystal fiber with tailored rheological and transmission properties [101]. The PCF was only 2 cm long and was pumped with fs pulses with 10 nJ of pulse energy at 1550 nm. In spite of the delicacy in fabricating this kind of PBG08 PCF, the glass itself hardly transmits beyond 5 μm, which is inadequate for MIR SC sources except in the short wave region of the MIR.

In addition, there have been some unique approaches to SC generation. In [102], a 5 cm long single crystal sapphire fiber was pumped with femtosecond laser pulses at 2 μm, and the generated SC spectrum covered from 1.2 μm to 2.8 μm. Doped media have also been used which combine the nonlinear effects of the host material with the active super-radiative processes of the dopants to generate SC. The long wavelength limits for this approach have been 2.45 μm, 2.6 μm and 2.7 μm in [104], [105] and [106] respectively. It has been proposed that this is a promising approach for SC generation at longer wavelengths if the host materials possesses better MIR transmission and the dopants are carefully chosen [107].

The examples given above all used optical fibers. In the case of planar waveguides, MIR SC was reported from a silicon nanowire by Kuyken et al. who produced wavelengths from the telecom-bands to the short wave MIR using 2 cm long silicon-on-insulator (SOI) waveguides pumped with picosecond pulses in the anomalous dispersion regime [99]. However, these SOI waveguides will not transmit further than about 4.2 μm due to absorption in the silica cladding layer of the SOI waveguide. In addition, in [103], Phillips et al. reported SC generation from a periodically poled lithium niobate (PPLN) waveguide using a Tm-doped fiber laser as the pump, with the output spreading from 1.3 μm to 2.8 μm.

The phenomenon of SC generation is not limited to optical waveguides; bulk materials can also be used. In this case, however, self-focusing due to the Kerr nonlinearity of an intense pump pulse is generally required to produce the extreme intensities that generate a SC via SPM. In the meantime, as the threshold is close to the threshold of filamentation, multiple filaments can form, which degrades the spatial coherence of the generated spectrum. This technique is commonly used, for example, to produce NIR seed pulses in commercial femtosecond tunable optical parametric amplifiers pumped by Ti:sapphire lasers.
and has been extended into the MIR by using bulk samples of tellurite or fluoride glasses as well as an yttrium aluminium garnet (YAG) crystal [120]. As SC generation examples in bulk materials, there was a demonstration by Liao et al. which reported the generation of SC up to the transmission boundary of the tellurite at about 6 µm using femtosecond pulses with a low repetition rate of 1 kHz through filamentation [113]. The same group also generated SC in bulk fluoride glasses up to their transmission limit of 8 µm, thereby covering the whole functional group region [118]. Similarly, by irradiating a YAG crystal with 85 fs pulses at 3100 nm, Silva et al. generated a SC spanning over 3 octaves from 450 to 4500 nm [120].

These cited demonstrations of MIR SC generation may not be exhaustive but it can be easily learned that none of these materials allow the production of SC at wavelengths beyond about 8 µm mostly because of their limited transmission in the MIR. In comparison, the so-called chalcogenide glasses are much more promising as they typically provide much better MIR transparency. For example, sulphides generally transmit well to approximately 10 µm, selenides to around 16 µm and tellurides to around 20 µm [38]. Chalcogenides also possess amongst the highest nonlinearities of all glasses [38], making them good candidates to generate SC in the MIR. Compared to silicon which also possesses high nonlinearity, chalcogenides have negligible nonlinear absorption (multi-photon absorption, free-carrier absorption) which makes them even more advantageous [121-123].

At the beginning of this PhD project, several SC demonstrations using chalcogenides had been performed and these are listed as follows. Marandi et al. reported SC generation from 2.2 µm to 5 µm in a tapered As$_2$S$_3$ fiber pumped with femtosecond pulses from a mode-locked Er-doped fiber laser [124]. Shaw et al. reported a SC spectrum covering from 1.5 µm to 5 µm from a single-mode step-index As$_2$S$_3$ fiber pumped at 2.5 µm, the limitation at long wavelength end being H-S absorption [125]. In previous work in our laboratory, we generated a SC spectrum from about 2.9 µm to 4.2 µm in a dispersion-engineered As$_2$S$_3$ glass rib waveguide with fluro-polymer coating and thermally oxidized (TOX) silicon substrate [126] and the pump used was around 3.25 µm. These demonstrations
did not manage to exploit the full potential of chalcogenides mainly due to loss issues and the use of a relatively short pump wavelength.

Even though at that beginning of my research the reported results for chalcogenides seemed not as good as tellurites or fluorides, the prospects of chalcogenides were much better particularly when emission covering both the functional group (2.5-6.6 µm) and fingerprint (6.6-20 µm) bands is required. The generation of a reliable and practical MIR SC source that covers as much of these two bands as much as possible using chalcogenides was the goal of my study.

### 3.2.1 Why Not Silicon?

As an alternative to the use of chalcogenides for SC generation, silicon had been suggested as an alternative material because it possesses high nonlinearity and relatively good transparency to beyond 8 µm. In addition, silicon offers the advantage of compatibility with mature electronic integrated circuit manufacturing (CMOS) and is increasingly becoming the dominant photonic material for signal processing, optical sensing and lab-on-a-chip [127-129].

However, it is well-known that silicon displays significant two-photon absorption (2PA) in the telecommunications band which is centred at 1550 nm [130,131] and this places a limit on the utility of silicon waveguides for ultrafast signal processing in telecommunications as well as SC generation in the NIR using third order nonlinear optics. Furthermore, free carriers generated by 2PA add to the total nonlinear absorption. In theory, 2PA should become negligible once the photon energy becomes less than half of the optical gap corresponding to wavelengths beyond approximately 2.2 µm. It had been widely assumed, therefore, that in the MIR nonlinear absorption in silicon would be negligible. However, whilst measurements showed a large reduction in 2PA by 2.2 µm they did not demonstrate that the nonlinear absorption disappeared completely. Pearl et al. [132] in fact measured three-photon absorption (3PA) in silicon between 2.3 µm and 3.3 µm and showed it was significant with a maximum 3PA coefficient \( \beta_{3PA} \) of around 0.035 cm³/GW² at ~2.8 µm. 3PA would be expected to become negligible beyond about 3.3 µm (1/3 of the bandgap), however, the experimental data did not unequivocally confirm this either. Beyond these wavelengths, there were no reports of the nonlinear absorption coefficients for silicon.
To determine how useful silicon was for SC generation in the MIR, at the beginning of my research, we undertook measurements of the nonlinear properties of crystalline silicon from 2.75 µm to 5.5 µm, measuring both the refractive and absorptive nonlinearities using a 500 µm thick double side polished (100) intrinsic silicon wafer. Even though the main focus was the MIR, a set of measurements at 1.55 µm was also made, which was used to obtain as accurate a value as possible for the free carrier absorption coefficient. These experiments and following fitting work were led by my advisor Dr. Xin Gai from our team and I was heavily involved in most of the work.

Our experiments used pulses generated by a Quantronix Palitra OPA pumped by a Clark MXR CPA2001 Ti:sapphire laser operating at a repetition rate of 1 kHz. In the NIR the signal output was used for z-scan measurements [133]. The MIR beams were obtained by difference frequency mixing between the signal and idler outputs and this generated 2 to 5 mW of average power at wavelengths between ~2.75 µm and 5.5 µm. After appropriate filtering to remove either the idler for the NIR measurements or both the signal and idler for the MIR measurements, the beam was truncated with an aperture to improve its spatial coherence and focused using a 10 cm focal length CaF$_2$ lens onto the sample. Because of residual aberrations and the aperturing process, images of the beam using an InSb camera showed that about 80% of the power was contained in the central spot. The pulse durations in the MIR were found to be 190 ± 20 fs from autocorrelation measurements using 2PA in an InGaAs detector with an extended IR response to 2.6 µm.

Two slightly different methods of recording data were employed in the NIR and MIR experiments respectively.

In the NIR the beam that transmitted through the sample was imaged using a Xenics InGaAs camera and a series of frames were captured as the sample was translated through the focus. This data was then post processed to extract open and closed aperture z-scans. To determine the nonlinearity as well as the two-photon and the free carrier absorption coefficients requires careful analysis of both open and closed aperture z-scans using models that accurately extract the relevant coefficients from the experimental data. In addition it is normally necessary to know with accuracy the pulse and beam parameters of the source.
used in the measurements to obtain absolute values for nonlinearity and absorption coefficients. To check that if we had correct values for the experimental parameters at 1.55 μm, our z-scan measurements were “calibrated” using a material whose nonlinearity is known accurately and where there is no nonlinear absorption to contend with. An As$_2$S$_3$ sample was used as this reference material since its nonlinearity had been measured accurately by SPM in waveguides and found consistently to have a value of $(2.9 \pm 0.3) \times 10^{-14}$ cm$^2$/W [134].

We operated in the “thin sample” regime where we could neglect diffraction and self-focussing but included the effects of 2PA and absorption due to the free carriers created by 2PA at a rate given by:

$$\frac{\partial N(z,r,t)}{\partial t} = \frac{2\pi \beta_{2PA} I(z,r,t)^2}{2\hbar \omega} - \frac{N(z,r,t)}{\tau},$$

where $N(z,r,t)$ is the radial and time dependent carrier density at a particular distance, $z$ along the z-scan direction corresponding to a beam intensity $I(z,r,t)$.

Open aperture data was recorded over a range of intensities up to $\approx 30$ GW/cm$^2$ and the scans fitted with numerical models including only 2PA or both 2PA and free carrier absorption (FCA). Examples of the fitted curves are show in Fig. 3.1(a,b) for two different intensities. As is evident, whilst at low intensity the open aperture curves are well-fitted by 2PA alone as the intensity increases past about 10 GW/cm$^2$ FCA has to be added to fit the experimental data. Fig. 3.1(c) plots the measured variation of $1/T$ as a function of intensity compared with the calculated variation for 2PA alone (red curve) and including 2PA and FCA (blue dashed curve). This shows it is essential that FCA is included to obtain a satisfactory fit over the full intensity range. From these data we obtain that $\beta_{2PA} = 1.03 \times 10^{-11}$ m/W and $\sigma_{FCA} = 1.45 \times 10^{-17}$ cm$^2$. 

\[2
\]
Figure 3.1: (a,b) Open aperture z-scans recorded at 1.55 μm at the two intensities circled in green are shown in 3.1(c). The black dots are the experimental data; the red line is a curve fit using 2PA alone and the blue dashed lines are curve fits including both 2PA and FCA. (c) Inverse transmission is plotted as a function of maximum intensity with fits to 2PA alone and 2PA plus FCA. (d,e) Closed aperture z-scans recorded at 1.55 μm at the two intensities circled in green in (f). The black dots are the experimental data; the red line is a curve fit using 2PA alone and the blue dashed lines are curve fits including both 2PA and FCA. (f) ΔT/T is plotted as a function of maximum intensity with fits to 2PA alone (red line) and 2PA plus FCA (blue dashed line).

From Fig. 3.1(c) we found that FCA is insignificant at intensities <10 GW/cm² and, hence, we could analyse the closed aperture traces using the full z-scan model described by Sheik-Bahae [135] in this range. Figure 3.1(d,e) shows fits to the experimental data based on the Kerr nonlinearity combined with 2PA (blue dashed line) and without 2PA (red line). Figure 3.1(f) demonstrates an
excellent fit is obtained using the value of $\beta_{PA}$ deduced from the open aperture trace and with $n_2 = (6.7 \pm 0.6) \times 10^{-14}$ cm$^2$/W.

In the MIR the beam transmitted through the sample was imaged using a 50 mm focal length CaF$_2$ lens onto a PbSe detector. A similar detector monitored the input signal to the sample using the surface reflection from a CaF$_2$ beam splitter. An aperture at the imaging lens could be closed to convert the detected signal from open to closed aperture configuration. The closed aperture signal was also used to determine the peak-to-valley distance, $Z_{p-v}$, and the relation $Z_{p-v} = 1.7 \pi \omega^2/\lambda$ where $\omega$ is the Gaussian electric field radius, to determine the beam size. We found that the beam area was essentially independent of wavelength and had the value $\pi \omega^2 = 6.6 \times 10^{-5}$ cm$^2$.

By closing the aperture at the imaging lens and translating the sample along the beam axis, we obtained closed aperture $z$-scans which could be used to determine the nonlinear refractive index, $n_2$. This was carried out at 500 nm intervals between 3 $\mu$m and 5.5 $\mu$m. At each wavelength several traces were obtained for different intensities allowing the normalized peak-to-valley transmittance difference $\Delta T_{p-v}$ to be determined as a function of intensity after normalization to the relevant open aperture trace. The slope of the curve at zero intensity was used to determine the nonlinear refractive index $n_2$.

The values we found for $n_2$ versus wavelength in the MIR are shown in Fig. 3.2 where we have also added the data from [130] for the NIR and our measurement at 1.55 $\mu$m [136]. We found that between 3 and 5.5 $\mu$m the nonlinearity dropped only slightly with wavelength and had an average value around $(2.7 \pm 0.5) \times 10^{-14}$ cm$^2$/W. This is qualitatively consistent with the results of Dinu [37] who predicted that for $h \nu / E_{ig} \sim 0.2-0.3$ the nonlinearity changes quite slowly with wavelength, here $E_{ig}$ is the indirect band gap of silicon and $\nu$ the frequency. Our value for $n_2$ at 1.55 $\mu$m lies within the range reported by Bristow et al. [130], so combining their results and ours suggests that the nonlinearity peaks at $1.2 \times 10^{-13}$ cm$^2$/W at 1.8 $\mu$m before then dropping progressively to approximately $3 \times 10^{-14}$ cm$^2$/W at 3 $\mu$m.
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Fig. 3.2: Measured third order nonlinearity, $n_2$, at infrared wavelengths combining our results (in blue) with those of Bristow et al. [130] (in red). The dotted line is a Lorentzian fit used simply as a guide for the eye.

We then proceeded to make the intensity dependent transmission measurements. Two sets of measurements were made at each wavelength: one with the sample in the focus and one with it well away from the focus to check the linearity of the detectors. To record a data set, the intensity incident on the sample was varied by slowly rotating the first of a pair of wire grid polarizers positioned in the input beam. Data was logged automatically as the intensity was varied under computer control. Examples of the raw data are shown in Fig. 3.3(a). The results of measurements of the transmission as a function of input intensity and wavelength are shown in Fig. 3.3(b). To obtain these curves a large number of data points representing the output versus input were first fitted using high order polynomials. The transmission was then determined using the fitted curves rather than the raw data. This proved to be the best way to reduce noise from the transmission measurements which otherwise relied on division of two small signals contaminated by noise near zero intensity to define unity transmission. An example of the raw data and fitting curves is shown in Fig. 3.3(a) corresponding to the curve for 4.0 μm in 3.3(b) shown as the dashed curve.
Fig. 3.3: (a) Illustration of the procedure used to obtain the transmission data (Fig. 3.3(b)). Two sets of data were taken at 4.0 μm the first with the sample in focus (blue) and the second out of focus (red). The data was then fitted with sixth order polynomials (yellow and orange dashed lines) constrained to have the same slope at zero intensity. The resulting curves were then divided to obtain the transmission shown as the green line. (b) Measured transmission for wavelengths between 3 μm and 5.5 μm at 0.5 μm intervals.

It is worth noting that the beam was polarised along the (110) axis of the silicon for these measurements. We did observe slight anisotropy in the absorption similar to that reported in [132] if the sample was rotated around its (001) axis, however, the change in absorption was only a few tens of percent and would not change the values of the absorption coefficients to within the accuracy of the experiments.

Several authors have discussed the analysis of transmission measurements to determine high order nonlinear absorption demonstrating that this is a far from trivial task once spatial and temporal averaging over the pulse and beam profiles have been taken into account [135,137]. The main difficulty arises from the fact that after such averaging the transmission curves for different orders of nonlinear absorption become similar. The main approach has been to plot the inverse transmission \(1/T\)^{n-1} against intensity \(I^{n-1}\) since this should produce a linear relationship only for a specific value of \(n\): the order of the multi-photon absorption. Unfortunately, spatial and temporal averaging also means that the linear region only exists for small deviations of the transmission from unity \((1/T<1.1)\) [137] and in our experiments even using hundreds of data points and averaging, noise contaminated the data in this range. Thus, the best approach appeared to compare the overall shape of the complete curves to calculations. There are, however, some additional complications: firstly, free carrier absorption needs to be taken into account and, secondly, at some
wavelengths contributions to the absorption can occur from n-photon and (n+1)-photon processes simultaneously. Wherrett [138] provided simplified scaling curves for direct-gap semiconductors which demonstrated this, however, to our knowledge similar results are not available for indirect gap materials like silicon except for 2PA [139]. Nevertheless, based on Wherrett’s results, around 3 μm one might expect both 3PA and 4PA; around 4 μm both 4PA and 5PA; and around 5 μm both 5PA and 6PA. As a result we could only fit our data to models of 3-, 4-, 5- and 6-photon absorption assuming that only the single most likely multiphoton process occurred at each wavelength and from this estimate the multi-photon absorption coefficients.

To model the transmission behaviour we used the same computer code used to calculate 2PA at 1.55 μm modified for n-photon absorption and including FCA [136]. To quantify the absorption due to free carriers we used the value of \( \sigma_{\text{FCA}}(1.55 \ \mu m) = 1.45 \times 10^{-17} \text{cm}^2 \) extracted from the z-scan at 1.55 μm and scaled this to longer wavelength using the relation \( \sigma_{\text{FCA}}(\lambda) = \sigma_{\text{FCA}}(1.55 \ \mu m) \times (\lambda(\mu m)/1.55)^2 \).

In Figs. 3.4(a-c) we show examples of measured and calculated transmissions corresponding to different orders of nonlinear absorption and for several different wavelengths. The values of the nonlinear absorption coefficients obtained from the fitted curves are tabulated in Table 3.1 and include uncertainties from two sources. Table 3.1 estimates the uncertainty due to the standard errors from least squares fitting of theoretical curves to our data. In addition there is an uncertainty of about ± 15% in the absolute values of the intensity. In this latter case the uncertainty in the absorption coefficient depends on the order of the multi photon process. For 3PA the uncertainty is (−28%, +32%); for 4PA it becomes (−40%, +60%); and for 5PA it is (−50%, +75%). With these uncertainties in mind, we found that at 4.5 μm, a convincing fit to 5-photon absorption was obtained with an estimated absorption coefficient of \( (1.4\pm 0.4)\times 10^{-6} \text{ cm}^7/\text{GW}^4 \). At 3.75 μm a good fit was obtained to 4-photon absorption with a coefficient of \( (3.6\pm 0.9)\times 10^{-4} \text{ cm}^5/\text{GW}^3 \). By 2.75 μm the fit is reasonable to 3-photon absorption with a value of \( (2 \pm 0.5)\times 10^{-2} \text{ cm}^3/\text{GW}^2 \). In the regions around 4 μm and 5 μm the fits were somewhat poorer whilst at 5.5 μm no satisfactory fit could be obtained to the anticipated 6-photon absorption.
In Figs. 3.4(d-f) we have plotted the calculated nonlinear transmission using the values for the n-photon absorption coefficient from Table 3.1 at 3 μm, 4 μm and 5 μm with and without FCA. These demonstrate that FCA is significant in all conditions of these experiments. Depending on the wavelength, FCA increases the absorption by a factor of ~1.25 at 3.0 μm and ~2 at 5 μm: that is FCA gets bigger at the longer wavelengths.

Fig. 3.4: (a) Experimental data (red) and fitted curve (blue dotted) for 3PA at 2.75 μm; (b) Experimental data (red) and fitted curve (blue dotted) for 4PA at 3.75 μm; (c) Experimental data (red) and fitted curve (blue dotted) for 5PA at 4.5 μm; (d) A comparison the predicted absorption with both FCA and 3PA (red) and 3PA alone (orange) at 3.0 μm; (e) A comparison the predicted absorption with both FCA and 3PA (red) and 4PA alone (orange) at 4.0 μm; (f) A comparison the predicted absorption with both FCA and 3PA (red) and 5PA alone (orange) at 5.0 μm.

Table 3.1 Nonlinear absorption coefficients. The values in red correspond to the expected dominant n-th order nonlinear absorption at a particular wavelength, whilst those in black represent the value assuming the (n-1)th order absorption occurred.
The numbers in Table 3.1 might, on initial inspection, seem rather small. However, take the value at 3.75 μm as an example. In a waveguide the absorption coefficient due to nonlinear absorption will be roughly 10 dB/cm at 14 GW/cm². For a typical waveguide with a mode area at 3.75 μm of ~0.83 μm² and hence this corresponds to 116 W in the waveguide. Using this power, the nonlinear phase shift can be calculated to be < 3 radians. Within the wavelength range where each n-photon process is expected to operate, the data indicates that there are maxima in the values of the coefficients at ~3 μm for 3PA; ~3.75 μm for 4PA and ~4.25 μm for 5PA. These are qualitatively consistent with the scaling predicted by Wherrett [138] for direct gap semiconductors. This suggests there may be “sweet spots” for experiments. This is illustrated in Fig. 3.5 where we plot the relative absorption due to 3PA, 4PA and 5PA versus wavelength for an intensity of 20 GW/cm². As is evident the loss is smallest around 3.25 μm and 4 μm and beyond about 4.75 μm. Since the nonlinearity \( n_2 \) is not changing much across this wavelength range, significantly larger nonlinear phase change can be expected by operating near these minima.

![Fig. 3.5: Calculated loss using the values from Table 3.1 for three (blue), four (red) and five (green) photon absorption for an intensity of 20 GW/cm² as a function of wavelength.](image)

To illustrate the detrimental role nonlinear absorption had in waveguide experiments, we measured the intensity-dependent transmission of 400nm x 1700nm silicon-on-insulator (SOI) waveguide fabricated by colleague at Ghent University [136] for wavelengths between 3.25 and 3.75 μm using 7.5 ps duration pulses. The results are shown in Fig. 3.6 where it is apparent that the
optical transmission of the cm-long sample dropped rapidly with increasing intensity due to the influence of the nonlinear absorption.

![Graph](image)

**Fig. 3.6:** Nonlinear transmission vs intensity at the input facet for a 1.7 μm wide SOI waveguide at 3.25 μm, 3.5 μm and 3.75 μm by 7.5 ps pulses. The lines are Gaussian fits which, whilst they fit the data well, are only included only as guides for the eye.

Similar results with a silicon-on-sapphire (SOS) waveguide were obtained using femtosecond pump pulses and are reported in [140]. The measurements were made in our labs at Laser Physics Centre, however the work was part of the PhD research from a colleague at Sydney University and details are therefore not used significantly in this thesis. The normalized output as a function of the coupled peak intensity in the waveguide is shown in Fig. 3.7(a).

We also measured similar phenomenon in other narrow band semiconductors namely Si-Ge [41,42] using waveguide made at LEI in France and provided to us through a collaboration with researchers from the University of Lyon. The transmission data are shown in Fig. 3.7(b). We investigated waveguides made by all these materials for MIR SC generation, but in each case the output signal saturated with increasing input power which meant that the transmission decreased as the input power increased due to nonlinear absorption. The resulting spectral broadening was thus quite limited and the output power was strongly attenuated by the nonlinear absorption [41,42, 140].
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Fig. 3.7: Input peak intensity versus normalized output for (a) SOS and (b) SiGe waveguides. The duration of the pulses was 330 fs and the wavelength was close to 4 μm. WG: waveguide.

To emphasise that no nonlinear absorption occurs in chalcogenides, we made transmission measurements of both commercial As₂S₃ (and As₂Se₃) step index fibers from IRflex in the USA, as well as some of the chalcogenide planar optical waveguides fabricated in house. The results are reported in later sections, but they showed that the power transmitted through few-cm long samples of these chalcogenide waveguides increased linearly with the input power in conditions when significant spectral broadening by SPM or SC generation occurred. Thus, nonlinear absorption was not affecting the ability of nonlinear refraction to create a broad MIR SC for chalcogenides.

In summary, in this section measurements of the third order optical nonlinearity of silicon are reported as well as the multi-photon absorption coefficients in the MIR. It is shown that the third order nonlinear refractive index averages \((2.7 \pm 0.5) \times 10^{-14} \text{ cm}^2/\text{W}\) between 3 μm and 5 μm changing little with wavelength. Most importantly it is found that 3-, 4- and 5-photon absorption together with free-carrier absorption are all present at levels that can affect
devices that require a strong nonlinear response, such as those used for SC generation. Though femtosecond pulses are less affected by free carriers and, hence, offer the possibility of larger nonlinear response due to lower total absorption and it has been realized in these demonstrations [140,141], the effects of nonlinear absorption cannot be simply neglected. This feature of silicon is a significant shortcoming compared to chalcogenides. We therefore concluded that silicon was not a good material for MIR SC generation and focused our efforts on the chalcogenide platform.

### 3.2.2 Optical Properties of Chalcogenides

Chalcogenide glasses are amorphous materials with one or more of the chalcogen elements (sulphur, selenium, and tellurium) as the dominant constituent usually bonded to III-V elements such as germanium, arsenic, gallium and antimony. Because their inter-atomic bonds are weaker than those in oxides, the bandgap of chalcogenides is red-shifted to the visible or near-infrared. The vibrational energies of the bonds are low because the constituent atoms are particularly heavy [38]. This means these glasses can transmit well into the MIR compared to silica, tellurites or fluorides [39]. For example, sulphides transmit well to ≈10 μm, selenides to ≈16 μm and tellurides to ≈20 μm [38]. Because the glass densities are high and the bonds are highly polarizable, chalcogenides possess relatively high refractive indices, for example As$_2$Se$_3$ glass has a refractive index around 2.7 at 3 μm [38]. According to Miller’s empirical rule [46], this also means that chalcogenides will also have large third-order nonlinearity. Indeed, measurements have shown that chalcogenides typically have an $n_2$ which is 2 to 3 orders of magnitude higher than that of silica. The typical value of $n_2$ for silica in the telecommunications band at 1550 nm is ≈0.03×10$^{-14}$ cm$^2$/W while values of 3×10$^{-14}$ cm$^2$/W have been measured for As$_2$S$_3$ and 10×10$^{-14}$ cm$^2$/W for As$_2$Se$_3$ [142] respectively. Moreover, the effects of multi-photon absorption are negligible in most chalcogenides due to the fact that chalcogenides have wider bandgap compared to silicon and N-photon absorption coefficient is predicted to scale with $E_g^{-\left(4N-5\right)}$ [138]. We note that all these characteristics make chalcogenides ideal candidates for extending SC generation well into the MIR.
However, one concern is that the ZDW of chalcogenides is much longer than for most other materials basically because their good MIR transparency. For example, for silica, the ZDW is around 1.3 μm and for tellurites or fluorides, it is typically around 2 μm while the ZDW is well beyond 4 μm for chalcogenides, and this is considerably longer than most currently available femtosecond pump sources. Specifically, for As₂S₃ the ZDW is approximately 5 μm and for selenides it is typically beyond 6 μm or even 8 μm for As₂Se₃ [43]. To solve this problem, one can engineer the waveguide dispersion to compensate for the material dispersion, thus shifting the zero dispersion point to shorter wavelengths, and use a pump source that can emit in the MIR near the zero dispersion point. As will be shown later these approaches are both necessary to generate sufficient extension to long wavelengths.

Two of the mostly widely used structures that permit engineering of waveguide dispersion are planar waveguides and step-index fibers. In terms of planar waveguides, we are restricted to using chalcogenides that can be successfully evaporated to form thin films since many chalcogenides decompose upon heating and the films can have a quite different stoichiometry and chemical bonds compared with the starting material. In spite of this, a reasonably wide range of chalcogenide compositions can still be employed in the fabrication of planar waveguides, in this work we focused on glass compositions that had been identified by researchers within our team as good materials for nonlinear photonics and which could be deposited with the same composition and bond structure as the bulk glass. Two compositions, Ge₁₁.₅As₂₄Se₆₄.₅ (GeAsSe) and Ge₁₁.₅As₂₄S₆₄.₅ (GeAsS) had been found to be outstanding among various chalcogenide materials in these respects and have also been shown to be amongst the strongest glasses formers in these chalcogenide systems [143, 144]. Our materials research had also shown that these glasses have high thermal and optical stability under intense illumination [145-146]. Based on these considerations, we identified them as good materials for nonlinear photonics. As shown in Section 3.4, the selenide has a linear refractive index ~0.4 higher than the sulphide allowing a waveguide with moderate index contrast between the core and the cladding material to be fabricated with the selenide as the core. In terms of dispersion, according to our ellipsometry measurements based on films,
the sulphide becomes anomalous around 5 µm and the selenide around ~7 µm. An example of tri-layer buried rib waveguide made by these two chalcogenides will be given later this Chapter while detailed discussion on waveguide fabrication and testing will be presented in Chapter 5.

We also aimed to draw chalcogenide step-index fibers from these same glasses although the compositions had to be adjusted slightly to achieve compatible glass transition temperatures for the core and the cladding. However, the compositions quite close to those used for planar waveguide fabrication proved suitable for fiber fabrication and shared the favourable glass properties [143-146]. However, in both fibers and waveguides, it is expected that the loss from the sulphide cladding would limit the overall transmission of the fiber at the long wavelength end. The intuitive solution would be to use two selenides that have moderate index contrast. In addition, the introduction of microstructured optical fibers offers another possibility to engineer the dispersion of the fibers. These fiber demonstrations will all be discussed in detail in Chapter 4.

### 3.2.3 SC Generation in Bulk Chalcogenides

The early demonstrations of SC in 1970s were made in bulk samples [27,28]. The main disadvantages of SC involving self-focusing in bulk materials are that the intensities required are often close to the damage threshold of the material; multiple filaments can be generated when the power is significantly above the self-focusing threshold and this reduces the brightness and coherence of the source; and long wavelength beams can be highly divergent and difficult to collimate particularly when short pump wavelengths are employed. However, this kind of demonstration can still show the potential of the bulk sample as a promising platform for SC generation in terms of the MIR transparency and nonlinearity.

To test this potential for chalcogenides, we irradiated a ~5 mm thick bulk sample of Ge$_{11.5}$As$_{24}$S$_{64.5}$ glass with up to 20 MW of peak power in ~190 fs duration pulses at ~5.3 µm – just beyond the estimated ZDW wavelength of this glass. The pulses themselves were generated by a Quantronix Palitra OPA fitted with a difference frequency generator and pumped by a Clark CPA2001 Ti:sapphire laser. The output beam from the Palitra OPA was filtered with a 2.5
µm long-pass filter to isolate the MIR pump beam and block the signal and idler. A beam-shaping aperture was used to select the most uniform region of the beam creating an Airy diffraction pattern at a 100 mm focal length CaF$_2$ lens that focused the beam into the glass sample. The output beam was imaged using a Thorlabs numerical aperture (NA) =0.56 molded chalcogenide lens onto the input slit of a Newport Cornerstone 1/4m monochromator fitted with a 150 line/mm grating. The output was then dispersed onto a Vigo PVI-2TE-6 mercury cadmium telluride (MCT) detector. Order blocking filters allowed the monochromator to cover the spectral range from ~2.5 µm to 7.5 µm (approximately the maximum spectral coverage of the detector) and the input signal could be attenuated by the monochromator slits to achieve high dynamic range.

The nonlinearity of the Ge$_{11.5}$As$_{24}$S$_{64.5}$ glass at 1.55 µm was determined by z-scan measurements to be (2±0.3)×10^{-14} cm$^2$/W but will be significantly smaller at longer wavelengths. In the case of As$_2$S$_3$, for example, our waveguide results [126] suggested that the nonlinearity at 3.28 µm was about half that at 1.55 µm. Based on this and using dispersive models such as those provided by Sheik-Bahae et al. [135] and Dinu et al. [37], we estimated the nonlinearity to be respectively 2 or 3 times smaller at 3 µm and 5 µm than that at 1550 nm in the absence of specific measurements. The maximum power used was ~20 MW and is about 8 times the self-focusing critical power at 5.3 µm based on a nonlinearity of ~7×10^{-15} cm$^2$/W. The focal spot diameter was determined by imaging the output onto a Xenics Onca InSb camera from which we found the FWHM beam diameter to be ~90 µm. Using this value the self-focusing distance is predicted to be ~2 mm – about half the sample length. Thus, self-focusing could contribute to SC generation. However, in our experiments the spectra were stable and evolved smoothly as the power was increased, and there was no indication of any sudden increase in nonlinear response as would be expected were self-focusing to occur.

Sample experimental data for different input powers are shown in Fig. 3.8. In Fig. 3.8(a) the black dotted line is the detector responsivity supplied by the manufacturer. With increasing power the spectrum broadens steadily. At about 3 MW it shows evidence of two weak side peaks at 4.1 µm and 7.1 µm that lie symmetrically about the pump at 5.3 µm, which we attribute to four-wave mixing
gain suggesting the dispersion is indeed small and anomalous. With increasing power the spectrum broadens and flattens. In fact, correcting the shape of the spectrum at 20 MW with the detector response produced a spectrum flat to ±5 dB from 2.5-7.5 µm as shown in Fig. 3.8(b). Moving the pump wavelength to 3.425 µm, a region where the dispersion is normal produced a different result. As shown in Fig. 3.8(c) for a pulse power of 20 MW the spectrum did not show the large spectral broadening observed for the 5.3 µm pump and had a width at -10 dB of peak of only ~ 1000 nm. This is because in the normal dispersion regime spectral broadening is the result of self-phase modulation along with self-steepening of the pulse.

![Fig. 3.8](image)

Fig. 3.8: (a). Spectra recorded at ~ 20 MW (red), ~ 6 MW (blue) and ~ 3 MW (green) peak power. The detector response is shown as a black dotted line. (b) the spectrum at ~ 20 MW has been corrected for the spectral response of the detector. (c) comparison of spectra at ~ 20 MW produced using 5.3 µm and 3.425 µm pumps.

In summary, this bulk SC demonstration confirms the high nonlinearity and good transparency of a chalcogenide in the MIR and its ability to generate broadband SC. Similar results were obtained using other glass compositions including As$_2$S$_3$ although we did not test the Ge$_{11.5}$As$_{24}$Se$_{64.5}$ material that will be used as the core in our waveguide devices because it could not be pumped in the anomalous regime with the available hardware.

### 3.3 Chalcogenide Waveguide Design Example

Ge$_{11.5}$As$_{24}$Se$_{64.5}$ (GeAsSe) and Ge$_{11.5}$As$_{24}$S$_{64.5}$ (GeAsS) have been chosen to be the core and the cladding materials respectively for the chalcogenide planar waveguide (and fiber) designs. The sulphide bulk glass was successfully used to generate a broadband MIR SC as described in the last section. This section uses
the example of a rib waveguide to elaborate our design process. With the aim of extending the SC to cover as far into the MIR as possible we designed a tri-layer buried all-chalcogenide rib waveguide with GeAsSe as the core and GeAsS being both the lower and upper claddings. The choice of the rib structures was made because it reduces the interaction between the mode and the etched sidewall thus lowering the propagation losses [147]. In addition as will be elaborated later, rib structures allow the use of a quasi-single mode design that allows single mode operation over the full transmission range of the waveguide rather like an endlessly single mode microstructured fiber.

The wavelength dependent refractive indices of these two materials were measured using an infrared spectroscopic ellipsometer (IR-VASE) and the corresponding Sellmeier equations were fitted to be [148]:

\[
\begin{align*}
n_{\text{GeAsSe}}^2(\lambda) &= 1 + \frac{5.78525\lambda^2}{\lambda^2 - 0.28795^2} + \frac{0.39705\lambda^2}{\lambda^2 - 30.39338^2}, \\
n_{\text{GeAsS}}^2(\lambda) &= 1 + \frac{4.18011\lambda^2}{\lambda^2 - 0.31679^2} + \frac{0.35895\lambda^2}{\lambda^2 - 22.77018^2}. 
\end{align*}
\]

These two equations were fed into the full vector finite difference method code to calculate the waveguide dispersion. In this kind of rib waveguide we can modify the properties such as the nonlinear parameter $\gamma$ and dispersion $D$ by varying the core film thickness $T$, and the etch depth, $E$. The geometry considered is shown in Fig. 3.9.

![Fig. 3.9: A schematic of the structure of the tri-layer all-chalcogenide buried rib waveguide.](image)

We, thereby, obtained contour plots parameterizing $D$ and $\gamma$ for various core film thicknesses and etch depths. Figure 3.10 shows a typical example for the fundamental TM mode when the core width was set to be 4 $\mu$m limited by our mask size and the core thickness was varied whilst the etch depth was maintained at 40% of the core film thickness. We chose this specific etch depth and the TM mode after comparison of simulation results for various different configurations and after consideration of practical limitations. Specifically, if the
etch depth is too small, coupling to slab modes can occur and this can make the waveguides lossy. In addition, reducing the etch depth $E$ will cause the effective mode area to increase, in general, which will reduce the nonlinear parameter $\gamma$. Alternatively, if the etch depth is large, sidewall roughness on the etched surfaces of the rib will also cause the waveguide losses to increase. Moreover, the waveguide will become multimode if the etch depth is too large based on the theories in [149,150]. For example, for the 4 $\mu$m thick case, an etching depth of less than 55% should be maintained to ensure quasi-single mode (both polarization states) operation. This has also been confirmed by numerical simulations. Thus an intermediate value of 40% is thus chosen as the initial design.

Fig. 3.10: The (a) dispersion parameter $D$ and (b) nonlinear parameter $\gamma$ for the fundamental TM mode as a function of wavelength and core film thickness for a rib waveguide with 40% etched depth. The locus of the zero dispersion and the contour for $\gamma = 0.5$ W$^{-1}$m$^{-1}$ are shown by the white lines.

It is clear from Fig. 3.10(a) that in this tri-layer all-chalcogenide waveguide with moderate refractive index contrast, the net dispersion is normal over a wide range of parameters. Only by using relatively thick films (>3.5 $\mu$m) can the anomalous dispersion regime be reached and only at long pump wavelengths (>4 $\mu$m). Even thicker films would be required for TE mode operation to obtain anomalous dispersion as shown in Fig. 3.11 and this is the main reason why TM mode was chosen. The dispersion parameter, $D$, also remains comparatively small (< 5 ps/nm/km) within the anomalous region. What is also evident is that in the region of anomalous dispersion, the nonlinear parameter will be quite low (<0.4 W$^{-1}$m$^{-1}$), and this means the power required to generate a SC will be high.
relative to that required for SC generation in the NIR (1.55 µm) where nonlinear parameters are > 10 W⁻¹m⁻¹.

![Graph showing dispersion parameter D for the fundamental TE mode as a function of wavelength and core film thickness for the tri-layer fully buried rib chalcogenide waveguide with 40% etched depth.]

Fig. 3.11: The dispersion parameter $D$ for the fundamental TE mode as a function of wavelength and core film thickness for the tri-layer fully buried rib chalcogenide waveguide with 40% etched depth.

The choice of film thickness becomes a trade-off between dispersion and nonlinearity as well as losses to leaky modes particularly for the long wavelengths contained within the SC. Based on such considerations, we chose the core film thickness to be 4 µm at this initial design stage. It is worth emphasizing that the waveguide is quasi-single mode which supports only the lowest order mode at all wavelengths longer than 1 µm and in this relatively symmetrical structure, it does not show cut-off at beyond 15 µm although losses to leaky modes start to rise beyond ~12 µm. However, this is well beyond the limit expected due to cladding absorption in this particular waveguide (~10 µm) which is ultimately the limitation of the SC coverage at the long wavelength end.

From the initial design of the buried tri-layer all chalcogenide waveguide above we can deduce what is required of the pump to generate SC from this waveguide. This is discussed next. Similar mode calculations and parameter design procedures can be applied to planar waveguides with different designs or optical fibers and will be discussed in later sections.
3.4 Pump Configuration

As shown from the dispersion calculations in Fig. 3.10 (a), even with moderately high index contrast between the core and cladding, the ZDW point cannot be pushed below about 4 µm. This means that none of the commercially available femtosecond pump sources based on Tm that operate around 2 µm could be used and even the latest pulsed fiber lasers based on Er or Ho operating around 3 µm would not allow direct pumping in the anomalous dispersion regime. Some of the options for longer-wavelength short-pulse MIR pumps include the synchronously-pumped OPOs [151, 152], OPAs [153, 154], and optical parametric chirped-pulse amplifiers (OPCPAs) [155]. OPCPAs basically replace the laser amplifier with an OPA in chirped pulse amplification (CPA) scheme and still require a two-stage setup involving a stretcher and a compressor [156], thus are more complicated than the former two approaches. OPOs require careful design of the optical resonator structure, especially to obtain ultrashort pulses, synchronously pumping is needed to make sure the resonator round-trip frequency matches the repetition rate of the pulsed pump, which adds complexity. Whilst several commercially available systems that tune to cover the 4 µm region are available these are complex and extremely costly. Furthermore, a Coherent Chameleon OPO system installed by our colleagues at the University of Sydney proved to produce poor MIR beam quality such that its power could not be effectively coupled in to a single mode waveguide.

In comparison with OPOs, OPAs with travelling wave geometry are much simpler in terms of configuration and design. Several OPAs are commercially available such as the Light Conversion Topas systems, (and our own Quantronix Palitra OPA), however, these are designed to work with high peak power (100 MW) Ti:sapphire pumps operating at repetition rates around 1 kHz. Devices like Topas produce far too much power for waveguide pumping and at an impractically low repetition rate. What is desirable, therefore, is a simple OPA design that can operate with much lower pulse power, ideally using a relatively low cost industrial style femtosecond Yb laser as its pump that operate at repetition rates of several 10s MHz.

This section deals with the configuration of such an OPA. Firstly the pump wavelength and pulse duration are further refined by comparison of simulation
results then a practical OPA system and its characterization are discussed. Since the detailed design of this OPA was undertaken by one of my supervisors and is the subject of a pending patent, I do not include full details of its operating principle in this thesis.

### 3.4.1 Choosing the Pump Wavelength & Pulse Duration

By using the adaptive step-size SSFM we solved the GNLSE to model SC generation in a 7 cm long tri-layer buried chalcogenide rib waveguide including a linear loss of 1 dB/cm at all wavelengths. The waveguide has a core width of 4 μm, core thickness of 4 μm and an etch depth of 40% as proposed in Section 3.3. We fitted the dispersion data with a Taylor series including up to 20th order dispersion since this can accurately reproduce the dispersion map over the whole wavelength range of the calculations. A sufficiently small time window was chosen to ensure the spectral coverage greatly exceeded the spectral width of the generated SC. We varied the pump wavelength, the gamma-power-length product (γPL, where P is the peak pump power and L the device length) and the pump pulse duration.

We chose two sets of pulse durations: 7.5 ps being the pulses produced from an existing picosecond MIR OPA source [157] and 250 fs, which we expect to generate from a new femtosecond OPA system by replacing the current Nd:YVO₄ pump laser used in the picosecond system, with a femtosecond mode-locked Yb laser. In addition 250 fs is typical of the value achievable from commercial synchronously pumped OPOs. In the calculations we chose to model performance at four pump wavelengths: 2, 3, 4 & 5μm. 2 μm and 3 μm can be produced by fiber lasers and these could emerge as viable pumps in some circumstances in spite of the fact they lie in the normal dispersion regime for this particular tri-layer waveguide. We assumed the longer wavelengths were produced by OPAs most likely based on PPLN with the 4 μm and 5 μm emission falling in the anomalous dispersion regime for our particular rib waveguide.

The maximum γPL values are ultimately limited by optical damage of the materials or waveguide facets. From the early work in our laboratory reported in [126], damage of the waveguide facet was already identified as a limitation to the power that could be coupled into chalcogenide waveguides. For our tri-layer...
structure, the mode area ranged from \( \sim 12 \, \mu m^2 \) at 2 \( \mu m \) to \( \sim 20 \, \mu m^2 \) at 5 \( \mu m \) and \( \gamma \) values ranges from 1.47 \( W^{-1}m^{-1} \) to 0.13 \( W^{-1}m^{-1} \) respectively. If we assume that the maximum fluence at the facet should not exceed 0.2 \( J/cm^2 \) at 7.5 ps, then the maximum \( \gamma_{PL} \) drops with increasing pump wavelength from around 550 at 2 \( \mu m \) to 50 at 5 \( \mu m \). By reducing the pulse duration the damage fluence would be expected to drop approximately in proportion to \( t_p^{-1/2} \) or the maximum intensity increase by \( t_p^{-1/2} \) raising the maximum \( \gamma_{PL} \) by a factor of \( \sim 5.5 \) at each wavelength. We calculated spectra for a range of \( \gamma_{PL} \) values at each pump wavelengths and pulse durations from as small as 7 up to \( \sim 100 \). Whilst higher \( \gamma_{PL} \) values could have been used with the 250 fs pulses this proved to be unnecessary. The trends are shown in Figs. 3.12 and 3.13 for 7.5 ps and 250 fs pump pulses respectively.

Fig. 3.12: Simulated SC spectra for different wavelengths and increasing values of \( \gamma_{PL} \) for 7.5 ps pulses. Blue 2 \( \mu m \); green 3 \( \mu m \); red 4 \( \mu m \); turquoise 5 \( \mu m \). (a) \( \gamma_{PL}=49 \); (b) \( \gamma_{PL}=77 \); (c) \( \gamma_{PL}=91 \); (d) \( \gamma_{PL}=105 \).
Chapter 3: Extending SC into the Mid-Infrared (MIR): Challenges & Opportunities

Fig. 3.13: Simulated SC spectra for different wavelengths and increasing values of γPL for 250 fs pulses. Blue 2 µm; green 3 µm; red 4 µm; turquoise 5 µm. (a) γPL=7; (b) γPL=21; (c) γPL=49; (d) γPL=77.

Figure 3.12 shows the predicted spectra for different pump wavelengths and γPL values for 7.5 ps duration pulses. It is quite apparent that pumping with the anomalous dispersion region at 5 µm produces the broadest spectrum at the lowest threshold power. At 2 µm where the dispersion is large and normal, the broadening is small. The case of 4 µm is interesting since in spite of lying in the anomalous dispersion regime, the threshold power for SC is high and more broadening is in fact predicted when using a 3 µm pump with normal dispersion.

In the case of the 250 fs pulses, shown in Fig. 3.13, the spectral broadening actually occurs at much lower values of γPL than at 7.5 ps and γPL from 10-20 is all that is needed to create SC using the 4 µm or 5 µm pumps. This corresponds to peak powers of <2200 W at 5 µm. At higher γPL, significant broadening is also observed at 3 µm for normal dispersion. In this case self-steepening of the pulse occurs which enhances the SPM creating the relatively flat-topped steep sided spectrum observed in Fig. 3.13(d). In addition the spectrum can extend past the ZDW leading to the onset of similar dynamics as produced by direct pumping in the anomalous regime. At 2 µm the broadening remained small in all conditions.
It is particularly interesting to understand why a relatively low threshold is observed for 250 fs pumping at 5 µm. The clue can be found by calculating dispersion lengths and soliton fission lengths for the various conditions. The dispersion at both 4 µm and 5 µm is small: $4.9 \times 10^{-4} \text{ps}^2/\text{m}$ at 4 µm and $6.87 \times 10^{-2} \text{ps}^2/\text{m}$ at 5 µm. Hence the dispersion lengths ($L_D$) are large indeed $\sim 10^5$ m and $10^4$ m respectively when using 7.5 ps pulses and correspondingly 820 m and 0.91 m for the case of 250 fs pulses. The soliton numbers ($N_S$) are then also large ranging from 30 for a 5 µm pump at 250 fs pulse to 11000 for a 4 µm pump and 7.5 ps pulses. As a result, only in one condition is the soliton fission length ($L_D/N_S$) less than the device length: namely in the case of the 5 µm 250 fs pump. In all other cases, the soliton fission length is in the 1-10 m range, requiring higher $\gamma PL$ values to create a broadband SC. These large soliton numbers also would normally suggest that the modulational instability causes breakup of the pump pulses into multiple low order solitons. Whilst the pulse envelope breaks up into multiple solitons in simulations using 7.5 ps pulses, in the case of the 250 fs pump it is clear that the dominant mechanism is soliton pulse compression and this results in a relatively coherent spectrum in spite of the rather large soliton number of 30. In Figs. 3.14(a) and 3.14(b) we demonstrate this by plotting the input and output pulse profiles in the case of 7.5 ps and 250 fs pulses, respectively. It is easy to see, however, that soliton numbers calculated above are overestimates. A single cycle of the carrier at 5.3 µm lasts 18 fs and hence it would be impossible for breakup of the pulse envelope into pulses shorter than a few cycles, as implied by large soliton numbers. The simulation in Fig. 3.14(a) demonstrates that the 250 fs pulses are instead compressed down to $\sim 40$ fs, two to three optical cycles.
Chapter 3: Extending SC into the Mid-Infrared (MIR): Challenges & Opportunities

Fig. 3.14: The time dependence of the power at the waveguide output from simulations. (a) 250 fs pulses for $\gamma PL = 7$ at 5 µm demonstrating soliton pulse compression. (b) 7.5 ps pulses for $\gamma PL = 64$ at 5 µm demonstrating break-up of the pulse envelope into multiple solitons.

The important point to note is that SC can be generated at low $\gamma PL$ values with a 250 fs pump corresponding to fluences far below the expected damage limit. For the longer pulses, however, the required fluence is close to or above the damage limit encountered in our experiments and generally the spectrum is narrower. We conclude, therefore, that it should be possible to generate a SC well beyond 10 µm by pumping in the anomalous regime with $\sim 250$ fs pulses, but this requires a source operating at 4 µm or longer. This proposal has been realized in a femtosecond OPA system and will be described in Section 3.4.2. This femtosecond OPA system turns out to be quite effective to deliver broadband MIR SC sources as will be shown in the following Chapters.

3.4.2 Pump Construction & Characterization

Based on the SC calculations above, it was concluded that a 250 fs source with relatively long pump wavelengths was good for broadband and low-threshold SC generation. This section discusses the realization and characterization of an OPA that produces such pulses pumped by a mode-locked Yb laser.

3.4.2.1 Pump Setup

The OPA setup is shown schematically in Fig. 3.15. It consisted of a Newport Femtotrain-Yb laser producing $\approx 2.5$ W of 500 fs pulses at 1041 nm at a repetition rate of 21 MHz. In an alternative configuration a Newport HighQ2 Yb laser
producing 1.5 W of 180 fs pulses at 63 MHz was also employed. The output from
the laser was passed through a two-lens telescope to reduce the beam to 120 μm
1/e² diameter and focussed into a MgO:PPLN crystal. PPLN was chosen as the
domain-engineered crystal and contained a fan grating with periods from 25.5
μm to 31.5 μm to allow quasi-phase matching over a wide range of signal and
idler wavelengths by translating the crystal across the pump beam. The
MgO:PPLN crystal was 10 mm long with anti-reflection (AR) coatings for the
pump, signal and idler wavelengths on both input and output faces. The OPA was
seeded with a low power CW beam from a tunable semiconductor diode laser at
the signal wavelength. The seed beam itself was produced by Santec tunable
semiconductor lasers which deliver about 20 mW of continuous power to the
crystal far exceeding the power from parametric fluorescence. Thus the
configuration can be described as a laser seeded OPA. The seed beam was
focussed through a dichroic mirror to a waist whose diameter was about 50%
larger than the pump beam in the crystal. The principle of this OPA is simply that
the CW seed beam is strongly amplified by the pump pulses (the single pass gain
is ≈10⁶) leading to the simultaneous generation of an idler at the difference
frequency between pump and signal. The typical conversion efficiency of such an
OPA is between 30% and 50% depending on the pump pulse duration.

At the output of the MgO:PPLN crystal the emission was collimated using a
25 cm focal length gold mirror and the difference frequency idler beam isolated
using a CaF₂ dichroic mirror that reflects most of the pump and amplified seed
beams followed by a long pass filter on a Germanium or Silicon substrate. With
about 2.5 W of average pump power, the power generated at idler wavelengths
was up to 250 mW before the beam quality started to deteriorate due to back
conversion. The calculated pulse duration was approximately 330 fs from the 2D-
mix-SP module of the SNLO software [158] as shown in Fig. 3.16 for the 500 fs
pump pulses. The typical tuning range of this OPA system is from 3 μm to 4.6 μm
with slightly varying average power output. The beam quality factor $M²$ is less
than 1.5 with a near Gaussian shape which varies little with wavelength. A photo
of the OPA system is shown in Fig. 3.17.
Fig. 3.15: Schematic of the optical parametric amplifier used to generate 4 µm MIR femtosecond pulses. By tuning the wavelength of the Santec semiconductor laser, the MIR output can be correspondingly tuned from 3 to 4.6 µm.

Fig. 3.16: Typical time domain output calculated from the SNLO software.

Fig. 3.17: Photo of the MIR femtosecond OPA system.
3.4.2.2 Pump Characterization Using SHG-FROG

To experimentally characterize the amplitude and phase properties of the pump pulse, the SHG-based FROG method was employed. This second order method requires lower pulse intensities as the signal strength is enhanced compared to other FROG approaches based on third order nonlinearities. An integrated platform containing the optics was constructed as shown in Fig. 3.18.

![Fig. 3.18: Schematic of the SHG FROG experimental setup. OPA: optical parametric amplifier, M: gold mirror, R: retro-reflector, BS: pellicle beam splitter, L: CaF₂ focusing lens, AGS: AgGaS₂ crystal with rotating stage, MONO: monochromator, DET: detector.](image)

A pellicle beam splitter was used to maintain negligible dispersion and avoid ghosting. A retro-reflector linked with a Thorlabs Z825B motorized actuator was used to adjust the path difference between the two arms. The translation stage travelled over 2 mm with a resolution of 0.005 mm, corresponding to a time resolution of 33.4 fs in the data acquisition run. Beams passing the two different arms were both focussed using a single 10 cm focal length CaF₂ lens into either a 1 mm or 0.4 mm thick AR coated silver gallium sulphide (AgGaS₂, AGS) crystal from Eksma Optics which was used to frequency double the beams. The choice of this specific crystal and its thickness is based on considerations of transparency angle, effective nonlinear coefficient and the acceptance bandwidth [159]. It was mounted on a xyz-stage with additional freedom on adjustment of the rotational angle and the pitch angle. An InGaAs camera was used to overlap the two beams in the crystal by monitoring the second harmonic output from the two arms of the delay line. An amplified InGaAs detector was used to detect the second harmonic signal after the wavelength discrimination using a monochromator. A LabVIEW code was programmed to control the scanning step of the translation stage and collect the spectrally and
temporally distributed data automatically. The typical data acquired using this setup and the code is shown in Fig. 3.19.

![Fig. 3.19: Contour picture of typical FROG data as a function of the wavelength and time delay.](image)

The data were then fed into the Femtosoft Technologies software to calculate the actual pulse information. The retrieval algorithm is based on general projections as described in [160] that search for a solution of the electric field which satisfies these two constraints: the experimentally acquired trace and the physical feasibility. From the above retrieval process, the pulse duration of the OPA system at 4000 nm was found to be 330 ±15 fs and the pulse has nearly flat phase as shown in Fig. 3.20, which agrees well with the values calculated using SNLO software[158].

![Fig. 3.20: Retrieved amplitude and phase information from the SHG FROG data of the MIR OPA system. The inset shows the raw data acquired from the LabVIEW code.](image)

This SHG FROG setup and the corresponding data retrieval process has also been applied to a prototype MIROPA™-fs system (pumped by Spectra-Physics
HighQ2 laser and commercialized by Hotlight Systems) \cite{161, 162} and the pulse duration of that system is measured to be 200±10 fs with negligible chirp at a wavelength of around 3.9 μm as shown in Fig. 3.21. This pump with an upgraded design of tunable wavelength will be used as one of the pump sources to produce sub-100 fs pulse using a compression method which will be described in Chapter 6.

![Fig. 3.21: Retrieved amplitude and phase information from the SHG FROG data of the prototype MIROPA™-fs. The inset shows the raw data acquired from the LabVIEW code.](image)

### 3.4.2.3 Experimental Setup for SC Spectrum Collection

Once we have the dispersion-engineered fiber or planar waveguide and the suitable OPA pump ready, the general experimental setup for SC spectrum collection is relatively simple and the schematic is shown in Fig. 3.22.

A pair of wire grid polarizers is used to adjust input power. The OPA pump was coupled into the fiber or waveguide using a moulded chalcogenide lens with NA typically 0.56 or 0.85 or in some cases a diamond-turned ZnSe lens with NA of 0.57. An InSb camera was used to identify optimal coupling in the MIR. The SC output from the fiber or waveguide was imaged using the reflective objective to eliminate chromatic aberration at a magnification of \(\sim \times 36\) onto the input slit of a Newport Cornerstone 1/4m monochromator. The slits were typically 0.3–0.5 mm wide (spectral resolution \(\sim 7.5-12.5\) nm) but could be reduced to as small as 10 μm to reduce the power entering the monochromator to counter detector saturation. Filters were used to block the higher order grating reflections from reaching the detectors. The available MIR detectors include a PbSe, a thermoelectric cooler (TEC) MCT detector and a liquid nitrogen cooled MCT
detector. The PbSe detector had a working range of 1500–4500 nm, the TEC MCT detector worked from 4000 to 7000 nm while the N₂(l) cooled MCT detector which was acquired at later stage of my study could be used from 1000 nm to 14000 nm. To facilitate measurements the input beam was chopped at about 500 Hz and the output signal processed using a Stanford Research 830 digital lock-in amplifier before being recorded automatically using a custom LabVIEW code. Typically, relatively short integration times (100–300 ms) were employed.

![Diagram](image)

Fig. 3.22: Experimental set-up for the MIR SC generation measurement of chalcogenide waveguides or fibers. A similar setup is used for chalcogenide fibers in later Chapters. WG: waveguide.

### 3.5 Summary

This Chapter discussed why we want to extend SC generation into the MIR and how we can, in principle, achieve this. The point of MIR broadband sources is that they provide a useful tool for spectroscopy in particular for identifying different molecules that exhibit unique absorption fingerprints in the MIR associated with their fundamental vibrational modes. Currently available MIR broadband sources serve this purpose to a degree but they all have their respective advantages and disadvantages. The opportunity for MIR SC sources is that they can deliver high brightness with continuous broadband coverage together with average power comparable with more conventional sources such as globars or synchrotrons.
This can facilitate spectroscopic applications with high-resolution, convenience and fidelity.

However, this all comes at a price. The challenges of achieving practical MIR SC source have also become obvious. Firstly, an ideal medium should be chosen to have high nonlinearity, low nonlinear absorption and good transparency in the MIR. In this context, chalcogenides stand out but dispersion engineering is necessary to be able to pump them in the anomalous dispersion regime. In this Chapter, a sample of a tri-layer buried chalcogenide planar waveguide design has been presented which can also be applied to fiber formats. Also, a suitable MIR fs pump should also be adopted to guarantee broadband extension of SC generation in the MIR as evidenced in simulations. Experimentally, a home-made MIR 330-fs OPA system has been developed to serve this purpose, which will prove to be an effective tool in later Chapters.
Chapter 4 MIR SC Generation in Chalcogenide Optical Fibers

Even though the design example in the previous Chapter was a chalcogenide planar waveguide, the approach can easily be applied to optical fibers. Optical fibers allow longer interaction lengths because generally they have lower losses than planar waveguides because the sidewalls between core and cladding can be much smoother. This Chapter discusses SC measurements obtained using various commercially-available and custom chalcogenide optical fibers.

Recently there have been several new companies that offer low-loss chalcogenide optical fibers as a commercial product, among them being the IRflex Corporation in the USA and PERFOS in France. However, because only a few choices of fiber geometry and chalcogenide materials are available from these manufacturers, the freedom to choose properties most suitable for SC generation is limited. This Chapter begins by discussing how samples of these commercial fibers perform with our femtosecond MIR OPA pump source.

Later in the Chapter, as a result of collaboration with Jiangsu Normal University in China, we show that we have been able to fabricate step-index chalcogenide fibers with specific core and cladding materials with optimized dispersion designs for SC generation. We were able to study several different types of chalcogenide fibers which typically generated SC of about 2-10 μm or 3-12 μm depending on the fiber composition.

4.1 IRflex Step-Index Fiber

The As-S step-index fiber (IRF-S-9) sourced from IRflex has a core diameter of 9 μm. The fiber possesses low loss of less than 0.6 dB/m from 2 to 6 μm except at 4.1 μm where a peak due to H-S absorption is present. The loss rises to 1.5 dB/cm at 6.5 μm and the typical transmission range for this fiber provided by the manufacturer is 1.5 to 6.5 μm. The NA of this fiber is relatively small at around 0.3, and the calculated ZDW is longer than 6.5 μm according to the value provided by the manufacturer (the waveguide structure pushes the fiber ZDW to longer wavelengths compared with the ZDW of the material itself), and this is
beyond the range accessible to our MIR femtosecond OPA source. Even if a pump long enough is available, the limitation from the material absorption will inhibit long wavelength extension for this fiber. As a result this fiber could only be pumped in its normal dispersion regime where the main nonlinear effects dominating the spectral broadening were SPM as shown in Fig. 4.1. The length of the fiber was 1.1 m and the coupling loss was around 5 dB. The dips apparent in these spectra were due firstly to the S-H absorption around 4.1 µm and secondly absorption in the optical path of the measurement system due to CO₂ around 4.25 µm. Whilst this spectrum was far narrower than what can be obtained through soliton dynamics when pumping in the anomalous regime, a feature of these spectra was their stability.

![Typical SC spectra obtained from the 1.1 m long IRF-S-9 fiber at a pump wavelength of (a) 4000 nm and (b) 4440 nm respectively. The power marked is the coupled peak power.](image)

An important thing to note is that with the increase of input power, the output didn’t show trend of saturation as SOI or SiGe waveguides did as shown in Fig. 3.7. Specifically, the transmission property of this As-S fiber at 4 µm by using pulses from the femtosecond OPA is shown in Fig. 4.2. The stars show the approximate positions where SC spectra were taken in Fig. 4.1. It is clearly shown that for this chalcogenide fiber made with As-S, nonlinear absorption effects were minor while SC spectral broadening due to SPM was obvious. This backs our choice of chalcogenides as a promising nonlinear photonic material in the MIR.
Fig. 4.2: Normalized output power as a function of the coupled peak intensity for the IRF-S-9 fiber. The stars mark the approximate positions where SC spectra were taken in Fig. 4.1.

Another type of IRflex fiber is made of As-Se glass (IRF-Se-12) and the transmission range is significantly wider than that of the As-S based fiber. However, the ZDW is then moved to ≈8.5 µm for a fiber with a core diameter of 12 µm again meaning we can only pump in the normal dispersion regime. A typical spectrum generated in a 1 m long fiber of this kind pumped with 330 fs pulses at 4586 nm is shown in Fig. 4.3. An advantage of pumping in the normal dispersion regime is good pulse-to-pulse stability and flatness of the spectrum and this reflects different physical processes, particularly the absence of soliton dynamics, in creating the spectral broadening. Interestingly, a piece of a 4 cm long IRF-Se-12 fiber resulted in a SC bandwidth of 2 µm at a dynamic range of -30 dB, which means the long interaction length is not required to achieve the large spectral broadening. For some applications, for example, MIR optical coherence tomography (OCT), such spectral broadening may be sufficient and the high stability becomes a significant advantage.

Fig. 4.3: Typical SC spectra obtained from the 1 m long IRF-Se-12 fiber at a pump wavelength of 4586 nm.
Whilst these kinds of fiber are not ideal for generating a broadband MIR SC, they can be used to stretch and chirp the MIR pulses as they propagate through due to the interaction of nonlinearity with normal dispersion. In theory the output pulses can then be compressed to create pulses that are much shorter than those at the input in a similar manner to the scheme proposed in [163] in which SPM in a single-mode fiber can chirp a pulse and then a grating-pair compressor is used to compress the pulse. This will be further demonstrated in Chapter 6 as a route for obtaining pulses that can lead to a SC produced by a single soliton which can lead to a coherent SC spectrum.

### 4.2 PERFOS Suspended-Core Fibers

The PERFOS company in France offers a suspended core chalcogenide microstructured fiber made from \( \text{As}_{38}\text{Se}_{62} \) with a core diameter of 4.5 \( \mu \text{m} \) fabricated by the casting technique described in [164]. This research into SC generation using this fiber was conducted in collaboration with researchers from the Danish Technical University (DTU) and PERFOS. The ZDW of this fiber was calculated to be close to 3.5 \( \mu \text{m} \) and this was confirmed by measurements [165].

A fiber 18 cm long was pumped using the 330 fs MIR OPA system at various wavelengths and power levels. The experimental setup to collect the SC spectra was similar to the one shown in Fig. 3.22. The total insertion loss of the fiber plus the coupling lenses was measured to be \( \sim 7.5 \text{ dB} \) and thus the power delivered to the fiber was estimated to be 3.75 dB lower than the input power. This corresponded to 59 W of peak power delivered to the fiber for every milliwatt of input average power. Figure 4.4 shows the SC evolution with increasing powers at a pump wavelength of 3.5 \( \mu \text{m} \) for this fiber.

To maximize the bandwidth of the generated SC, the pump wavelength was varied while the coupled peak power was maintained to be approximately 5500 W. A series of SC spectra for different pumping wavelengths are shown in Fig. 4.5. By pumping at 4.4 \( \mu \text{m} \) with a coupled peak power of 5.2 kW, a SC spanning from 1.7 to 7.5 \( \mu \text{m} \) with an average output power of 15.6 mW (after NA=0.56 coupling lens) and an average power of 4.7 mW at wavelengths beyond 5.0 \( \mu \text{m} \) has been obtained. Detailed numerical validations of these experimental results can be found in [165]. The long wavelength end extension was mainly
limited by the rapidly increasing fiber loss after 8 μm [165]. Coupling between polarization states and coupling to higher-order modes were also possible, which effectively reduced the power driving SC generation further. Full analysis of the performance of this fiber was carried out by our colleagues at DTU and hence is not contained in this thesis.

Fig. 4.4: SC spectra evolution as a function of the input power for the PERFOS fiber at a pump wavelength of 3.5 μm. The power levels shown in the legend is the coupled peak power. The curves are offset by 10 dB relative to each other for clarity.

Fig. 4.5: SC spectra obtained at maximum power with various pumping wavelengths. The averaged coupled peak power inferred from insertion and propagation losses is ~5500 W. The curves are offset by 10 dB relative to each other for clarity.

### 4.3 Dispersion Engineered Step-Index Fibers

The fibers used in the preceding sections were commercial fibers where there was no freedom to engineer, in particular, the dispersion properties as is required for SC generation. In collaboration with Jiangsu Normal University in
China, however, we have been able to design dispersion-engineered step-index chalcogenide fibers with ease. Several candidates for the core or cladding materials are shown in Table 4.1. The design freedom we have is the choice of core/cladding materials and the fiber diameter. To be able to maintain good confinement of the light and manipulate the dispersion of the step-index fibers, moderately high index contrast is needed. Similar to the planar waveguide design, a selenide core (Ge-As-Se) and a sulphide cladding (Ge-As-S) structure was firstly attempted using some of the strong glass formers identified from our materials research. For simplicity, we designate these as all-arsenic fibers as both the selenide and the sulphide contain the As element. However, the absorption of the sulphide cladding material is far from negligible at wavelengths close to transmission edge around 9 μm. Intuitively, to solve this problem, both the core and the cladding materials should be made from selenide glasses, for example, Ge-Sb-Se as the core and Ge-As-Se as the cladding. However, the index difference between them is too small to obtain anomalous dispersion at pump wavelengths available from our OPA. To overcome this, a different selenide cladding was employed (Ge-Se). These two types of fibers were designated as all-selenide fibers. It is important to note that the specific compositions of these glasses had to be finely adjusted to obtain appropriate thermal properties for the core and cladding to enable them to be pulled into fibers, and thus the abbreviations, Ge-As-Se and Ge-Se, are only used for simplicity.

Table 4.1 Typical refractive indices and the transmission cut-off wavelengths of chalcogenide candidates to draw the dispersion-engineered step-index chalcogenide fiber.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Refractive index range</th>
<th>Transmission cut-off</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-As-Se</td>
<td>2.59-2.62</td>
<td>16 μm</td>
</tr>
<tr>
<td>Ge-As-S</td>
<td>2.22-2.26</td>
<td>10 μm</td>
</tr>
<tr>
<td>Ge-Sb-Se</td>
<td>2.63-2.67</td>
<td>16 μm</td>
</tr>
<tr>
<td>Ge-Se</td>
<td>2.40-2.43</td>
<td>16 μm</td>
</tr>
</tbody>
</table>

The fibers were generally drawn via a two-step rod-in-tube technique as in [166]. Detailed discussions will follow.

### 4.3.1 All Arsenic Fibers

The core and cladding materials in the all-arsenic fiber were Ge_{12}As_{24}Se_{64} (Ge-As-Se) and Ge_{10}As_{24}S_{66} (Ge-As-S) respectively, and bulk samples were prepared by
the melt-quenching method [143]. The compositions used in planar waveguide design Ge$_{11.5}$As$_{24}$Se$_{64.5}$ and Ge$_{11.5}$As$_{24}$S$_{64.5}$ could not be used in the fiber drawing process, because an air gap formed between the core and the cladding due to their incompatible thermal properties. The new compositions were specifically tuned to have similar glass transition temperatures to achieve the thermal compatibility required for fiber drawing. In detail, the Ge-As-Se core material has a glass-transition temperature $T_g$ of 205 °C while the cladding Ge-As-S has a $T_g$ of 202 °C determined by differential scanning calorimetry (DSC) [167]. The Ge-As-S material with a slightly lower $T_g$ than the Ge–As–Se core glass was intentionally chosen as the cladding because in this case both glasses could be drawn into fibers at the same temperature. No recrystallization was observed from their reheating curves indicating that they had good potential for drawing into low-loss crystallite-free fibers [167]. Their MIR transmission spectra were measured using a Fourier transform infrared spectroscopy (FTIR) spectrometer using a 3.22 mm thick sample of the selenide glass and a 3.45 mm thick sample of the sulphide and are shown in Fig. 4.6. The selenide glass used for the core was transparent to beyond 12 μm whilst the sulphide cladding started to absorb beyond ~8.5 μm.

![Fig. 4.6: Transmittance of core (Ge-As-Se, thickness = 3.22 mm) and cladding (Ge-As-S, thickness = 3.45 mm) glasses used to fabricate the all-arsenic fiber under test.](image)

The detailed procedure of two-step rod-in-tube technique for fiber fabrication was as follows. In the first step, the Ge-As-Se core rod with a diameter of 10 mm was drawn into a uniform cane with a diameter of 2.2 mm using a high
precision fiber-drawing tower. In step 2, the Ge-As-S rod with a diameter of 15 mm was cut into two 40 mm long rods which were then mechanically drilled with a 2.1 mm diameter hole along their axes. The interior walls of the cladding tubes were polished to a final diameter of ~2.2 mm to match the diameter of the Ge-As-Se cane. In step 3 the Ge-As-Se cane was inserted into one of the Ge-As-S glass tubes and drawn into a composite cane again with a diameter of 2.2 mm. In step 4, this composite cane was inserted into the second Ge-As-S tube to create the final preform for fiber drawing. The finished fiber had a slightly elliptical core with axes 4.1 µm x 4.6 µm and an outer diameter of 190 µm. A polyethylenimine (PEI) polymer jacket was coated to improve the mechanical robustness of the relatively fragile chalcogenide fibers to aid handling.

The linear refractive indices of both materials as a function of wavelength were measured using ellipsometry and they are shown in Fig. 4.7. The core and cladding indices were 2.60 and 2.25 respectively at 4 µm and this corresponded to an NA for the fiber of ~1.3. The numerical aperture (NA) here is defined as \( \sqrt{n_{\text{core}}^2 - n_{\text{cladding}}^2} \), and the connection between the NA and the acceptance angle of the fiber becomes only an approximation. This doesn’t disobey the rule that \( \sin \theta_{\text{max}} \leq 1 \). The bigger NA is, the more strongly guiding the fiber is, i.e. it will generally support a larger number of modes which make it harder to couple into the fundamental mode. The fitted Sellmeier equations for the core and cladding material are shown in Eq. 4.1 and 4.2.

![Fig. 4.7](image-url)
Due to the relatively large index contrast between the core and the cladding material, the fiber was only single mode at quite long wavelengths (>7 μm for a fiber with a long axis core radius of 2.3 μm) according to the normalized frequency ( ) calculation. The dispersion parameter \( D \) for the fundamental mode was calculated as a function of long-axis core radius for a group of fibers with the same ellipticity as the fibers that were drawn, using the full vector finite difference method and is shown in Fig. 4.8. The difference between the two polarization states is minor. It is evident that no design allows the ZDW to be shorter than 3 μm which again emphasizes the need for the femtosecond MIR OPA system described in Chapter 3. Anomalous dispersion can be obtained for a wide range of fiber core radii when the pump wavelength is longer than ~3.5 μm. For the experiments here the OPA wavelength was chosen to be 4.0 μm to avoid overlap with the carbon dioxide absorption dip in the atmosphere and the residual H-Se absorption band in the fiber.

\[
n(\text{Ge–As–Se})^2 = 1 + \frac{5.76160\lambda^2}{\lambda^2 - 0.26115^2} + \frac{1.84710\lambda^2}{\lambda^2 - 51.72200^2}.
\]

\[
n(\text{Ge–As–S})^2 = 1 + \frac{4.07080\lambda^2}{\lambda^2 - 0.21642^2} + \frac{0.87816\lambda^2}{\lambda^2 - 28.25800^2}.
\]

Fig. 4.8: Calculated group velocity dispersion of the slightly elliptical core all-arsenic fiber as a function of the long axis dimension.

The same SC generation setup as shown in Fig 3.22 was used. The input lens was an NA = 0.57 diamond turned ZnSe lens with an AR coating for the 3.8-5.5 μm band. The SC at the output was collected by an NA = 0.52 reflective
microscope objective to avoid chromatic aberration, although both lenses introduced substantial coupling losses because their NAs were significantly less than that of the fiber. The Newport liquid nitrogen cooled MCT detector was used at the output slit of the monochromator.

Using a pump at 4.0 µm the total insertion loss was measured to be ~15 dB for an 11 cm long fiber including both coupling lenses. Subtracting the excess loss due to the output reflective objective (~3 dB, caused by truncation of the beam by the secondary mirror and its support), the input coupling loss was estimated to be ~6 dB. Thus, an input power of 80 mW corresponded to a peak pulse power of ~3000 W injected into the fiber and an average power of ~2.5 mW exiting the reflective objective.

If the power was further increased, the fiber facet could be damaged once the peak intensity reached ~30 GW/cm² which corresponded to an average power density of ~100 kW/cm². Damage remains the limitation of chalcogenide-based devices and according to our measurements depends significantly on the composition of the glass. We illustrate this in Fig. 4.9 where we have accurately measured the relative surface damage threshold of various glasses in the GeAsSe(S) and GeSbSe(S) systems using CW light at 830 nm focused onto the sample with an infrared-corrected NA=0.55 microscope objective. The uncertainty in the absolute intensity of these measurements was ±50% as the focal spot size could not be measured directly but was estimated from the f-number of the optics. Nevertheless, what is apparent from Fig. 4.9 is that the GeAsSe glass has the lowest damage resistance of ~30 kW/cm² whilst as Se is progressively replaced by S, the damage threshold increases markedly. The same trend is observed in GeSbSe(S) glasses although in this case the damage level was slightly higher than in the case of the GeAsSe(S) glasses. Under current experimental condition, highly S-rich materials could not be damaged even at the highest intensities available.
From our SC experiments, it appears that relative damage thresholds for S and Se-based glasses at 830 nm were mirrored at longer wavelengths. At 4 µm, the core of our fibers could be damaged at average power densities of the same order as at 830 nm, but the S-based cladding was unaffected. We believe that damage was associated with heating and decomposition of the glass surface. In fact at 830 nm bulk samples of GeAsSe glasses “burned” in air once damage has commenced and a large volume of glass was destroyed. In the case of the S-containing selenides, however, the damage remains restricted to the glass surface. The notion that local heating is responsible for onset of damage in selenides is borne out by our observation that planar waveguides made of exactly the same materials damage at a significantly higher threshold. The main difference is that the planar waveguide was deposited on a silicon wafer that acted as a heat sink which can lower the end facet temperature while the fibers are covered by plastic coating. This damage problem also motivates the use of femtosecond rather than picosecond pump pulses to limit the fluence at a given intensity. Figure 4.9 also suggests that other fiber compositions may significantly raise the damage threshold allowing larger pump intensities.

Figure 4.10 shows the evolution of the SC spectrum with increasing pump power. The SC spectrum broadened progressively until the damage threshold of the chalcogenide material was reached. The maximum coverage was from 1.8-9.5 µm at a dynamic range of 15 dB which corresponds to about 2.4 octaves.
Fig. 4.10: Measured SC evolution under increasing pump powers in the step-index chalcogenide fiber. The curves are offset by 30 dB relative to each other for clarity.

To analyze these results, we compared the measured spectra with numerical simulations. For the current fiber, the first ZDW was \( \sim 3.2 \, \mu m \) as shown in Fig. 4.8 and the GVD parameter was 21.77 ps/(nm*km) at the pump wavelength 4.0 \( \mu m \). As the third-order nonlinearity of Ge-As-Se material has not been measured directly, the \( n_2 \) value was assumed to be \( 1/3 \) the value at 1550 nm which is consistent with values inferred from previous experiments and the predictions of models proposed by Dinu \[37\] and Sheik-Bahae \[135\]. Using this value the nonlinear parameter \( \gamma (\gamma = 2\pi n_2 / \lambda / A_{eff}) \) was calculated to be 0.25 W\(^{-1}\)m\(^{-1}\) at 4.0 \( \mu m \). Based on the calculated dispersion and nonlinearity, we solved the GNLSE using the SSFM including up to 20th order dispersion. The linear loss of the fiber at the pump was assumed to be 0.1 dB/cm at the pump wavelength. We also introduced the effect of cladding absorption using the data of Fig. 4.6 in combination with the calculated values of the overlap of the propagating power with the cladding.

From Fig. 4.11 we can see that the simulation accurately reproduced the measured features of the experimental spectra. In particular, dispersive waves were generated in the normal dispersion regions at both short and long wavelengths and were correctly located at \( \sim 2 \, \mu m \) and 8-10 \( \mu m \) respectively as observed experimentally. In the region of the pump there was a general maximum in the spectrum with evidence of a red-shifting soliton peak moving to the zero dispersion point around 6 \( \mu m \). The spectrum decayed rapidly beyond about 9.5 \( \mu m \) because of rising absorption by the cladding. One discrepancy was that peak powers used in simulations are significantly lower than experimentally
estimated possibly due to coupling between two polarization states along the fiber and/or coupling into higher-order modes. For 1700 W pumping, the soliton fission length $L_{\text{fiss}}$ was calculated to be 3.61 cm, which is in the order of the fiber length. Note the fine structure evident in the simulations and arising from interference between multiple solitons was not resolved in the experiments.

![Fig. 4.11](image)

**Fig. 4.11:** Simulated SC evolution under increasing pump peak powers in the all-arsenic step-index chalcogenide fiber. The curves are offset by 30 dB relative to each other for clarity.

There are several issues with the fibers. One is that as the two orthogonal polarization mode states are degenerate in semi-circular fibers, the SC threshold is thus two times higher than would be the case for a polarization maintaining waveguide due to the polarization mode coupling effect [165,168]. This can deteriorate the stability of the spectrum. Moreover, as a relatively large index contrast was used in this fiber, the fiber is multimode at wavelengths shorter than 7.5 μm according to the normalized frequency calculation, which means higher order modes can be present which is detrimental to both the stability and brightness of the SC. In the experiments, efforts were made to optimize the signal at relatively long wavelengths to make sure most power was coupled into the fundamental modes. Thus to compare with experiments, the multi-mode influence on simulations is neglected.

### 4.3.2 All Selenide Fibers

In the last section, it was demonstrated that by choosing a step-index chalcogenide fiber with a selenide core and a sulphide cladding which corresponds to a moderate index contrast, the first ZDW point could be tuned to
be around 3.2 μm. The existence of the second ZDW point benefits dispersive wave generation on the long wavelength end. However, the limitation of this approach is that more energy leaks into the cladding at long wavelengths and the sulphide cladding material absorbs dramatically beyond 10 μm. Intuitively, if both the core and the cladding were made of selenide glasses with longer MIR transmission ranges [39], MIR SC generation can be further extended assuming appropriate dispersion engineering can be achieved.

Based on these considerations, we firstly proposed a Ge₁₅Sb₁₅Se₇₀ (Ge-Sb-Se) core, Ge₁₇As₁₀Se₇₃ (Ge-As-Se₂) clad step-index fiber structure. These compositions were again specifically chosen to make the glass transition temperatures of the two materials compatible to avoid gap formation between the core and the cladding when the fiber was drawn via the rod-in-tube technique [167]. Furthermore, according to Fig. 4.9, the selenide containing antimony has significantly higher damage resistance than the arsenic based materials. Figure 4.12 shows the transmittance measured with a FTIR spectrometer of both bulk materials with a thickness of 5.03 mm and 5.96 mm respectively.

![Transmittance graph](image)

Fig. 4.12: Transmittance of the core (Ge-Sb-Se, 5.03 mm) and the cladding (Ge-As-Se₂, 5.96 mm) glasses used to fabricate the firstly proposed selenide-based step-index fiber.

Due to the smaller refractive index difference between the core and cladding materials, however, the degree of which the dispersion can be engineered is more restricted. Figure 4.13 shows the dispersion parameters D calculated for different fiber dimensions of the Ge-Sb-Se/Ge-As-Se₂ fiber. It is obvious that it is difficult to move the ZDW to below 5 μm which is beyond the wavelengths
attainable by our OPA system. However it is well known that pumping in the normal dispersion regime close to the ZDW can still lead to creation of a broadband SC. It is worth noting that for the fiber to be single mode at around 4 μm, the fiber radius needs to be less than 1.7 μm which is far away from the anomalous dispersion regime and not suitable for long-wave MIR operation. A relatively large dimension was thus chosen mainly for the purpose of dispersion engineering.

Thus, we pumped a 14 cm long fiber with a core radius of 3.75 μm with 4.586 μm, 330 fs, pulses at 21 MHz from our OPA pump in a similar experimental set-up as in Fig. 3.22. SPM in the normal dispersion regime was sufficient to broaden the input spectrum until energy was coupled across the ZDW into the anomalous dispersion regime where solitons effects and dispersive wave generation were able to contribute to spectral broadening to longer wavelengths as illustrated in Fig. 4.14. The coupling loss for this fiber was estimated to be 5 dB per facet. At a peak power of around 4500 W, the SC spanned from 3 μm to 12 μm at a dynamic range of ±15 dB with an output average power of ~9 mW after an NA=0.56 black diamond output lens. The disadvantage of pumping in the normal dispersion regime is that only self-phase modulation contributes to broadening on the short wavelength side and thus the short wavelength extension was limited. The power penetrating into the anomalous regime was only a fraction of the input power. As a result the spectra tended to have a negative slope when
pumping in the normal dispersion regime. Therefore, for a dynamic range of 5 dB, the spectrum covered only from 3.1 μm to 7 μm at best.

![Experimental SC spectra](image.png)

Fig. 4.14: Experimental SC spectra by pumping a 14 cm long Ge-Sb-Se/Ge-As-Se2 step-index fiber at increasing pump power levels at 4.586 μm with 330 fs pulses. The powers shown are peak powers. The curves are offset by 10 dB relative to each other for clarity.

To allow better dispersion management, more index contrast between the core and the cladding material of the step-index chalcogenide fiber is needed. Thus, a selenide glass with a lower refractive index would be needed for the cladding. Our material study has found that by removing the As from the cladding material, the refractive index decreased while the transmission is not significantly affected. Another advantage of higher index contrast between the core and the cladding material is that the fundamental mode will be confined more tightly especially at long wavelengths. Figure 4.15 shows the typical dispersion parameter of a fiber made from a Ge15Sb15Se70 (Ge-Sb-Se) core and a Ge20Se80 (Ge-Se) cladding. It is clearly shown that by using Ge-Se as the cladding material, the first ZDW can be shifted to around 4.22 μm for a fiber with a radius of ~3 μm. Again, the fiber is only single mode outside the anomalous dispersion regime, for example, at a wavelength of 4 μm, the fiber radius should be less than 1.4 μm to guarantee single mode operation. For the purpose of dispersion management, the single mode condition is not satisfied. The loss of a fiber with the same composition but with a much larger core (60 μm diameter) was measured using an FTIR system and reported in [167]. The core of the actual fiber was too small to perform the test by the FTIR. In the 2–9 μm range, this large core fiber exhibited a background loss of <1 dB/m, and a peak loss of ~5 dB/m at 4.6 μm. These results can offer some guidance to the smaller core fiber.
As an example, by pumping an 11 cm long fiber of this kind at 4.485 μm, a SC spanning from 2.2 μm to 12 μm was obtained with obvious dips around both ZDWs and distinct dispersive wave generation features beyond both of them as shown in Fig. 4.16. The wavelength was chosen as 4.485 μm is in the anomalous dispersion regime of the fiber. Also, at this wavelength, the average power from the OPA is relatively high. The total insertion loss was measured to be 8.8 dB and input coupling loss was estimated to be 4.4 dB. At an input average power of 132 mW, the corresponding output average power of the SC source was 17 mW after an NA=0.56 black diamond lens. The obvious advantage of this design is that the spectra extend slightly more at the short wavelength end. By pumping in the anomalous dispersion regime, a comparatively flat spectrum was obtained with a 2.5 μm to 9.5 μm bandwidth at a dynamic range of ± 5 dB with useful energy beyond 10 μm.
Fig. 4.16: Experimental SC evolution as a function of coupled peak power when the 11 cm long Ge-Sb-Se/Ge-Se fiber is pumped at 4485 nm with 330 fs pulses. The curves are offset by 10 dB relative to each other for clarity.

Simulations showed good agreement with the experimental spectra as shown in Fig. 4.17 though the powers actually used in simulations were only ~30% of the powers estimated from experiments. We believe this was caused by the severe mode coupling effects among multiple transverse modes and also between two orthogonal polarization states. One parameter to characterize the birefringence performance is the polarization extinction ratio (PER). It is defined by ten times the logarithmic value of the ratio of the TE and the TM output components for a particular linear input polarization state. The basic measurement method was to set a certain TE/TM input using a polarizer in front of the fiber, i.e., the fiber was specially positioned using an in-situ microscope to make sure the oscillation direction of the electric field from the laser was aligned with the slow/fast axis of the fiber, then measure the TE/TM output from the fibers. The average PER measured for TE input to this fiber was only 3.2 dB. To maintain the polarization and thus enhance the effective power coupled into one certain axis, more birefringence is required, for example, by making the fiber asymmetric. Another more important advantage of higher birefringence in the fiber is that the generated SC is supposed to be less affected by polarization mode coupling effects which will benefit the practical applications like MIR absorption spectroscopy.

Fig. 4.17: Simulated SC evolution as a function of coupled peak power when the Ge-Sb-Se/Ge-Se fiber is pumped at 4485 nm with 330 fs pulses. The curves are offset by 20 dB relative to each other for clarity.


4.3.3 Asymmetrical Chalcogenide Fibers

In contrast with planar waveguides which can be made quite birefringent, polarization mode coupling effects can be severe in circular optical fibers as the two linearly polarized components are degenerate. In practice this degeneracy may be broken by imperfections in manufacturing process or from mechanical stress. However the birefringence from this source is not large enough to prevent the polarization mode coupling. More birefringence is necessary to reduce such mode coupling and generally a rather short polarization beat length in the centimeter or millimeter range is required. This can only be obtained by reengineering the fiber to introduce significant birefringence. Typically, the polarization beat length is defined as [169]:

\[
L_b = \frac{2\pi}{\Delta \beta} = \frac{\lambda}{\Delta n_{\text{eff}}} \quad (4.1)
\]

One of the most straightforward ways of creating birefringence in a step-index chalcogenide fiber is via form birefringence, i.e. make the fiber core asymmetric [170]. A rectangular fiber design was developed with the compositions being the same as the all-arsenic fiber discussed in Section 4.3.1 but with a ratio between the long and short axes being ~2:1. The fiber was made by extrusion and special care was taken not to twist the fiber during drawing. For a 5.86 μm by 2.78 μm fiber of this kind, the calculated dispersion profiles for the two orthogonal modes are shown in Fig. 4.18. The first ZDW at the fast axis condition was shifted to 3.8 μm and the ZDW at the slow axis was calculated to be 4.25 μm. The calculated polarization beat length for this fiber at 4 μm is ~0.7 mm, which means high birefringence is realized.

![Dispersion parameter graph](image-url)
Chapter 4 MIR SC Generation in Chalcogenide Optical Fibers

Fig. 4.18: Calculated dispersion parameter for the 5.86 μm by 2.78 μm Ge-As-Se/Ge-As-S fiber. TE0: fast axis, TM0: slow axis.

The SC spectra generated when pumping along the fast axis with 4 μm, 330 fs pulses are shown in Fig. 4.19. Obvious dispersive waves in the normal dispersion regimes clearly show the dominance of soliton-related dynamics. At an input average power of 100 mW, the output power of a 14 cm rectangular fiber after the NA=0.56 lens was around 6 mW. The measured average PER was around 9.1 dB which meant that this fiber reduced the polarization mode coupling effect to some extent although higher PER would be still an advantage.

Fig. 4.19: Experimental SC spectra as a function of coupled peak power from the 14 cm long 5.86 μm by 2.78 μm rectangular Ge-As-Se/Ge-As-S fiber when pumping at 4 μm. The curves are offset by 10 dB relative to each other for clarity.

4.4 Summary

This Chapter focused on MIR SC generation in chalcogenide fibers. Benefitting from the longer integration lengths and lower spectral losses, the generated SC extends more than two octaves if the chalcogenide material is carefully chosen and the dispersion is well engineered in the case of custom fibers. For instance, the selenide core, sulphide cladding step-index fiber managed to deliver SC from 1.8 μm to 10 μm, with the long end extension limited by the cladding material absorption. Also, to solve this problem, two types of all-selenide-based step-index fibers have been designed to overcome the material absorption from the sulphide cladding. In the Ge-Sb-Se/Ge-As-Se2 case, the first ZDW was 5.4 μm for a fiber with a radius of 3.75 μm. By pumping in the normal dispersion regime at 4.586 μm with 330 fs, 21MHz pulses from the OPA system, a SC spectrum
spanning from 3 µm to 12 µm within a dynamic range of ±15 dB with an average power of 9 mW after the NA=0.56 output lens was generated. In the Ge-Sb-Se/Ge-Se case, benefited from more index contrast between the core and the cladding, the first ZDW was shifted to around 4.2 µm. By pumping an 11 cm long fiber with a radius of 3 µm at 4.485 µm in the anomalous dispersion regime, a flat SC spectrum has been obtained from 2.2 µm to 12 µm with the ±5 dB spectrum spanning from 2.5 µm to 9.5 µm. The output average power for an input of 132 mW was 17 mW after the NA=0.56 output lens. Simulations showed good agreement with the experimental results.

This multi-octave spanning flat SC source promises to be a useful tool for MIR spectroscopy. However, due to the fact that the two polarization states in a circular fiber are degenerate, polarization mode coupling is almost inevitable thus the effective power coupled into one of the axis was low and the spectrum was not stable. To solve this problem, rectangular fibers with large axis ratio have been designed and tested and these showed a significant improvement in terms of the polarization.

A significant difficulty with all these dispersion engineered fibers is that they are multimode at shorter wavelengths due to the relative large index contrast between the core and cladding. As a consequence the power can couple into multiple transverse modes reducing the brightness of the source. To solve these issues a different approach is required. In the next Chapter we show that chalcogenide planar waveguides can support single mode operation of the full SC spectrum and also produce a single polarization state.
Chapter 5: MIR SC Generation in Chalcogenide Planar Waveguides

This Chapter discusses the other important geometry for chalcogenides which motivated much of the work for this thesis, namely planar waveguides. The advantages of a planar waveguide structure for nonlinear applications such as SC generation include the possibility of integrating the SC generator with other on-chip functionalities and the ability to maintain polarization through appropriate device design. Moreover, as mentioned in Chapter 3, they can be quasi-single mode for some designs. These features can benefit the overall practicality of the generated SC spectrum.

Two kinds of planar waveguide designs will be discussed in this Chapter: one is the tri-layer buried rib waveguide whilst the other is a simplified design based on a chalcogenide under-cladding and core but with an air cladding on the top. Detailed fabrication and characterization will be discussed together with the use of the femtosecond MIR OPA system to pump these waveguides to generate multi-octave spanning SC spectra with high brightness suitable for MIR spectroscopy.

5.1 Waveguide Fabrication

An appropriate waveguide design was developed in the Chapter 3, hence the next step was to fabricate those waveguides, which proved to be far from trivial. Over the past decade my colleagues within the Laser Physics Centre at ANU have developed effective approaches for the fabrication of chalcogenide waveguides as well as mature recipes for film deposition, etching, etc. Basically to obtain the tri-layer buried all-chalcogenide rib waveguide, four steps are needed as shown in Fig. 5.1.
The first step was to deposit the under-cladding and core films from GeAsS and GeAsSe bulk samples respectively onto a bare wafer. The wafer normally used was a 4 inch silicon wafer with a layer of 550 μm thick thermally oxidized silicon (TOX) to isolate the field from the silicon. The deposition was performed using a customized Ecovac co-thermal chamber from Angstrom Engineering of Canada controlled by SQS-242 software. The high quality bulk materials for evaporation were provided by the Jiangsu Normal University in Xuzhou, China and were prepared by the melt-quenching technique from high purity starting materials [143]. As the TM mode is preferred from the perspective of the dispersion management as discussed in Section 3.3, the surface roughness on the top of the rib waveguide is quite important. To avoid roughening of the top surface of the waveguide core during etching to form the rib, an additional layer of GeAsS was added on top of the core film during deposition. The thickness of this layer was determined by modal calculations to ensure that the field penetrating into the region above this layer in the final structure was negligible. The films were deposited in a vacuum of around 10^{-6} Torr. The typical deposition rate was 2 Å/s and was controlled by the power percentage applied to a buffered boat containing the bulk material. Unfortunately because the layers were quite thick, the chamber had to be vented to replenish the materials in the boat and re-evacuated during the deposition, which is not an ideal procedure since it increases the risk of contamination. Each layer of film deposition had witness wafers that were then used to check the respective film thickness using a Scientific Computing International FilmTek 4000 system.

After film deposition, a thin layer of SU-8 was coated onto the tri-layer to isolate the chalcogenide from the photoresists during development. The wafer
was then cured both thermally and optically to solidify the SU-8. The photoresist was then spin-coated onto the wafer using an Excelteq SVG 8600 coater/developer system and the rib patterns created using UV lithography with an i-line ($\lambda = 365$ nm) contact mask aligner (Karl Suss MA-6). Successive automatic wet development and baking were performed on the SVG track. The upper protective sulphide and the core selenide layer were then etched in an inductively coupled plasma (ICP) reactive ion etcher (Oxford Instruments Plasmalab ICP100) with CHF$_3$ gas flow. The etching was controlled to obtain the required rib structure in the core layer which first involved complete etching of the upper GeAsS layer on the top of the core. The empty chamber was then cleaned with oxygen after the CHF$_3$ etching to remove polymer deposited on the walls normally for a period of 20 minutes. The residual photoresist and SU-8 on the wafer were then removed using wet chemical stripping including Kwik Strip, deionized (DI) water and IPA and/or oxygen plasma etching in the ICP etcher.

After waveguide patterning the upper cladding comprising a layer of sulphide glass had to be deposited in particular to cover the vertical, etched side walls. The geometry for deposition of this layer is critical since if the evaporant struck the etched wafer at normal incidence gaps in the coating would form near the edges of the waveguide core due to shadowing effects. In order to avoid this as much as possible, a jig allowing the wafers to be rotated around an axis angled to the vapour plume was employed as shown in Fig. 5.2. The wafer was rotated constantly at a speed of about 10 rpm. The angle between the incidence flux direction and the surface of the wafer was chosen to minimize shadowing effects. In principle, for angles of incidence around 55° the deposition rate on the vertical and horizontal surfaces on a rotating wafer should be the same, neglecting the inevitable effects of shadowing by the growing film. This was confirmed by a systematic study shown in Fig. 5.2 that demonstrated that at these large angles, adequate side-wall coverage could be obtained without any evidence of gaps forming close to the core because of shadowing.
There are several difficulties with this approach and it took some time to obtain good results. For example, it has been reported that angled deposition can result in high film porosity \cite{171, 172} and this was observed in some instances resulting high waveguide loss. Furthermore, any residual contamination of the sidewalls due to the presence of the passivation layer of fluoropolymer deposited during etching resulted in poor adhesion between over-cladding and core. Thus it took some time to obtain reasonable waveguide losses for these structures and room for improvement remains.

However, work on chalcogenide waveguides for sensing undertaken by a co-worker, Pan Ma, had shown that quite low losses could be obtained in air clad chalcogenide waveguides where the final cladding layer was omitted and replaced by a thin fluorinated polymer coating. In the next section this air-clad chalcogenide waveguide design will be discussed first followed by a successful demonstration of the buried tri-layer chalcogenide waveguide. Among the various optical properties of the waveguide, the dispersion parameter is the most important one. From Fig. 3.10 it can be seen that the first zero-dispersion wavelength remain almost constant when the film thickness is varying from 3.7 to 4.7 µm, which means the fabrication tolerance is large. From our fabrication
experiences, the fabrication variation is 10% which can guarantee that the desired dimension can be reached.

5.2 Air-Clad Waveguide Characterization & Tests

The two-layer rib chalcogenide waveguide comprised a 2.5 μm thick core layer made from GeAsSe glass on a GeAsS under-cladding with a thin (10 nm) protective coating of fluro-polymer that prevented surface contamination from water and adventitious hydrocarbons. A rib waveguide 4 μm wide was produced by etching 50% deep into the core layer using CHF$_3$ plasma in an Oxford Instrument ICP100 etcher. The scanning electron microscope picture of the two-layer chalcogenide rib waveguide is shown in Fig. 5.3.

![Fig. 5.3: SEM image of the cross section of the two-layer chalcogenide waveguide.](image)

To measure the wavelength dependent optical losses of the waveguides, the cut-back method was adopted. Several tunable optical sources were used for the loss measurements. The first was a picosecond MIR OPA based on fan-out PPLN grating pumped by a Nd:YVO$_4$ laser using a similar arrangement to that described in [157]. This system could be automatically tuned from ~3 μm to ~4.22 μm and from 4.6 μm to 5 μm under LabVIEW control. The range from 4.22 μm to 4.6 μm is not accessible because in this band a parasitic SHG process in the PPLN crystal was strong, and can lead to crystal damage and, thus, needed to be avoided. The second optical source was a CW high resolution QCL (Daylight Solutions MHF) which covered the range 5.05-5.45μm whilst from 6.2 μm to > 7.5 μm a pulsed QCL laser was used (Daylight Solutions MIRcat). In each case, light was coupled into the waveguides using a Thorlabs NA=0.85 molded black diamond lens with appropriate anti-reflection coatings. The light emerging from the waveguide was collected with a Thorlabs NA=0.56 chalcogenide lens. Both lenses were fixed onto a Thorlabs NanoMax-TS 3-axis stage with Piezo options.
The waveguide was fixed to a vacuum chuck on a three dimensional movable stage. A Xenics Onca InSb camera was used to aid the waveguide alignment. After optimum coupling, the signal was collected by an appropriate detector (PbSe for the ≈3-5 µm sources and MCT for the ≈5-8 µm sources). The measured loss for this waveguide averaged 0.5 dB/cm between 3 µm and 7 µm as shown in Fig. 5.4. Full details of the waveguide characterization and sensing tests can be found in [148].

![Loss vs Wavelength](image1.png)

Fig. 5.4: Loss as a function of wavelength for the two-layer rib waveguide with GeAsSe core on GeAsS bottom cladding with 10 nm tick fluoropolymer coating. The gaps in the spectrum were due to the unavailability of sources in these regions.

The transmission of the 1 cm long waveguide pumped by 330 fs 4 µm pulses is shown in Fig. 5.5. The data were recorded when manually adjusting the input power and collecting the output signals after the focusing lens using a power meter. The uncertainties in the experiment was less than ± 10%.

![Normalized Output Power](image2.png)

Fig. 5.5: Normalized output power as a function of the coupled peak intensity for the air-clad chalcogenide waveguide. The pump condition was 330 fs, 4 µm.
Compared with results of silicon-on-sapphire [140] or Si-Ge waveguides [41,42] which saturate when the coupled light intensity increases as illustrated in Fig. 3.7, this chalcogenide waveguide shows constant transmission even at the highest peak intensity similar to that observed with the chalcogenide fibers. At a coupled intensity of 90 GW/cm², the nonlinear phase change is around 35 radians, which is enough to generate broadband SC as demonstrated below. This experimental observation clearly demonstrates that the nonlinear absorption in chalcogenides is negligible especially when compared to silicon or Si-Ge devices which have a narrower bandgap.

In terms of SC generation, the dispersion of the waveguide is important. The group velocity dispersion was calculated for the lowest order TE and TM mode using the full vector finite difference method. In this case, the dispersion difference between the fundamental TE and TM mode is relatively small. TE mode pumping was chosen at this stage. For a family of such two-layer rib waveguides with 50% etch depth, 4 μm waveguide width and varying film thicknesses, the dispersion map is shown in Fig. 5.6(a) whilst the specific dispersion for the 2.5 μm thick waveguide appears in Fig. 5.6(b). The trajectory of zero dispersion is shown by the green labeled line in Fig. 5.6(a). As is evident, there is no design of waveguide which allows anomalous dispersion at wavelengths shorter than about 3 μm. Specifically the waveguide used in the experiments had a small anomalous dispersion for wavelengths between 3.06 μm and 5.8 μm with a peak value of 19.96 ps/nm/km at 3.9 μm. These waveguides supported propagation of the lowest order TE mode up to a cut-off around 9 μm whilst the cut-off of the first high order TE mode occurred between 3.5 μm and 4 μm.
For SC generation the pump needed to lie in the anomalous dispersion regime and for our experiments we chose the pump wavelength to be 4 μm from the femtosecond MIR OPA described in Section 3.4 which would allow the full functional group band to be covered if the SC could be made to extend about 1 octave on either side of the pump. The insertion loss of the waveguide was measured by placing a large area power meter immediately after the end facet of the waveguide. Since the propagation loss of the waveguide at 4 μm was low at about ≤0.5 dB for the TE mode used in these experiments, the transmission was determined by the coupling loss at the input and reflections from the waveguide facets. The reflection loss contributed ~1.8 dB based on a simple estimate due to Fresnel reflection. The total insertion loss, including the loss of the focussing lens was measured to be 6.7 ± 0.3 dB from which the total coupling loss was estimated to be 5.6 dB. The maximum power that could be launched into the waveguide was ~8 kW above which issues were encountered with damage of the input facet. The output from the waveguide was imaged using the reflective objective with a magnification of ~×36 onto the input slit of a Newport Cornerstone 1/4m monochromator to avoid chromatic aberrations. Using a 0.5 mm wide slit at input and output corresponded to a resolution of about 10(5) nm for the 150(300) l/ mm gratings, respectively, whereas using 50 μm slits improved the resolution to about 1 nm. Either a PbSe or a thermoelectric cooler (TEC) MCT detector was used to record the spectra: the former for the range 1500–4000 nm and the latter from 4000–8500 nm. Filters were used to block the higher order grating reflections from reaching the detectors. The MCT detector had a peak response at 6 μm and its sensitivity dropped significantly to longer wavelengths. For wavelengths less than 2750 nm a 300 l/mm grating was employed and for 2750–8000 nm this was changed to 150 l/mm to maintain good grating reflectance for the p-polarized light emerging from the waveguides. The overall experimental setup has been shown in Fig. 3.22.
The input power to the waveguide could be adjusted using a pair of wire grid polarizers and with increasing power the spectrum showed remarkable spectral broadening. Sample results directly measured by the detectors without correction for the detector sensitivity are shown in Fig. 5.7 spanning from low power to illustrate the laser spectrum, to high power (~3260 W). As is evident with a power of ~3260 W coupled into the waveguide the spectrum extended from about ~1800 nm to beyond 7500 nm—over two octaves in bandwidth. Over this range the power was constant to ±15 dB and full coverage over the whole functional group band was achieved. Typically over 5–10 nm band (~0.1% bandwidth) the SNR available on the detectors exceeded 40 dB.

![Graph showing output spectra](image)

Fig. 5.7: Output spectra of the air-clad chalcogenide waveguide measured as a function of the estimated peak input power. The curves are offset by 10 dB relative to each other for clarity.

Evident in the raw spectra was some “noise” in the range above at 5500-7000 nm and also around 3000 nm. The longer wavelength band was scanned at high resolution by setting the slits on the monochromator to ~50 μm and scanning in 1 nm steps from which it became apparent that the “noise” was in fact due to absorption of the beam by water vapour in the ~1 m path of atmosphere between the output of the waveguide via the monochromator to the detector. The resulting spectrum is shown in Fig. 5.8. With the slits set to 50 μm, only a few percent of the SC power was transmitted into the monochromator and the spectrum was also being recorded in a range where the detector responsivity dropped by as much as 15 dB relative to its peak at 6 μm. In spite of this, by increasing the integration time of the lock-in amplifier and optimising the alignment of the output beam onto the monochromator the SNR in this measurement was >20 dB. Because this measurement involved a slow scan of the
monochromator over more than an hour, it also demonstrated both the good stability of the source and its ability to perform high-resolution spectroscopy. Water absorption also occurs in the region around 3 μm.

![Graph showing water vapor absorption](image)

**Fig. 5.8**: A high resolution scan from 5250 nm to 7000 nm showing clear absorption dips due to water vapour in the laboratory atmosphere. The scanning step of the monochromator is 1 nm.

Figure 5.9 shows the comparison of the water vapour absorption from the simulated HITRAN database [173] and the one taken from our SC scanning experiment. They show good qualitative agreement which proves the source to be an outstanding candidate for spectroscopy applications.

![Graph comparing HITRAN and experimental results](image)

**Fig. 5.9**: Comparison between the experimental result and HITRAN database of H₂O absorption [173]. The vertical axis is in arbitrary unit.

Comparison was also made between the measured SC spectra and the numerical simulations where we solved the GNLSE using the SSFM including up to 12th order dispersion. An accurate dispersion model was essential to obtain satisfactory agreement between the experiments and the simulations. In these calculations we assumed a wavelength independent waveguide nonlinear
parameter of $\gamma = 0.49 \text{ W}^{-1}\text{m}^{-1}$ at 4 \(\mu\)m. This value was estimated from the calculated mode area at the pump wavelength and, since the actual third order nonlinearity, $n_2$, of these chalcogenide glasses has not been measured in the MIR, a value for the $n_2$ based the measured value at 1550 nm with a correction ($\sim \times 0.3$) for dispersion based on the semiconductor models presented by Dinu et al. [37] and Sheik-Bahae et al. [135]. The code used a time resolution of 0.12 fs over a 100 ps window, an adaptive step size and conserved photon number.

The linear absorption was set to be 0.5 dB/cm which represented the average waveguide losses [148] over the whole wavelength range although the exact value of the absorption coefficient had a negligible effect on the output spectrum for this short waveguide. The numerical results are shown in Fig. 5.10 and indicate strong spectral broadening occurs once the input power is $>1500$ W after which the overall spectrum becomes more heavily modulated as the power is further increased. Using 330 fs duration pulses in this particular waveguide we are, in fact, in a regime where soliton fission starts to dominate SC generation.

Fig. 5.10: Simulated SC spectra for increasing input powers. The threshold for broad SC generation falls at about 1500 W. The curves are offset by 20 dB relative to each other for clarity.

The second order dispersion $\beta_2$ was $-0.1$ ps$^2$/m at 4000 nm and this leads to a dispersion length, $L_D = \tau_p^2/|\beta_2|$ of $\sim 1$ m where $\tau_p$ is the laser pulse duration. Using the estimated waveguide nonlinear parameter of 0.49 W$^{-1}$m$^{-1}$ leads to a nonlinear length at 1500 W of coupled power of $L_{NL} = 1/\gamma P = 1.3$ mm. The soliton number $n_{sol} = \sqrt{L_D/L_{NL}} = 27$ and the soliton fission length $L_D/n_{sol} = 35$ mm—which is of the order of the waveguide length. Thus, the SC is in a transient state dominated by soliton fission and this results in more pulses being generated by the fission process as the power is increased which causes the appearance of the
modulation on the SC envelope as a result of interference between individual solitons.

Qualitatively the simulations were in quite good agreement with the experiments as illustrated by comparing Figs. 5.7 and 5.10 which clearly show the correct location of the dispersive wave which creates emission centred at ~2 μm; peaks close to the pump; the relatively flat tail extending up to our measurement limit; and a similar power dependence. A notable difference is that in the experiment the power drops faster to longer wavelength when compared with the simulations. We believe that a large part of this is due to the limited numerical aperture of the reflective objective (NA= 0.52) used to collect the light at the output of the waveguide combined with the increasing mode area in the waveguide with increasing wavelength. In these waveguides the mode area increases with wavelength (from ~6 μm$^2$ to ~17 μm$^2$ between 2 μm and 7.5 μm), but this implies that the NA of the beam emerging from the waveguide increases from ~0.32 to ~0.73 over the same range. Thus, the collection efficiency of the reflective objective drops at the long wavelengths and this would cause the collected power to also drop by ~6 dB between 2 μm and 7.5 μm. In addition at long wavelengths, the size of the MCT detector was smaller than the magnified beam from the waveguide and the sensitivity of the TEC MCT detector dropped, which would further attenuate the signal. Finally, the waveguide losses increase rapidly beyond about 7 μm firstly because of the presence of the thin fluoro-polymer (Teflon) coating on the top of the waveguide which has a strong fundamental absorption around 8 μm, and secondly because the fundamental TE mode cuts-off beyond 9 μm in this asymmetrical rib waveguide.

The total power in the spectrum at the waveguide facet was measured using a power meter and was ~20 mW for an input average power of 160 mW before the focusing lens. This is competitive with that available from a synchrotron source over the same wavelength band. However, because the waveguide is single mode after ~3.5 μm and hence produces a diffraction-limited output, the brightness is high, around ~8 × 10$^{20}$ ph/s/mm$^2$/sr/0.1%BW. This is around 100–1000 times the brightness of a typical synchrotron and, hence, both in terms of average power and brightness this SC source should compare favourably with a synchrotron at least over the 2000–7500 nm bands.
After these initial experiments had been completed we obtained a new liquid nitrogen cooled MCT detector with much better sensitivity at longer wavelengths. This resulted in the spectra shown in Fig. 5.11. In this case, the SC extends to around 9 $\mu$m and here the long wavelength end is still limited by the fundamental absorption of C-F bond of the protective polymer and the mode cut-off due to the asymmetric structure. The data taken here was from a 2 cm long sample.

![Graph showing corrected SC spectra](image)

**Fig. 5.11:** Corrected SC spectra when one liquid nitrogen-cooled MCT detector is substituted for the previous TEC MCT detector. The curves are offset by 10 dB relative to each other for clarity.

### 5.3 Tri-Layer Waveguide Characterization & Tests

In the initial example of waveguide design described in Chapter 3, a tri-layer buried chalcogenide rib waveguide was calculated to be an excellent platform for MIR SC generation. The replacement of the upper air cladding by a chalcogenide sulphide glass (GeAsS) eliminated the mode cut-off present in the air-clad device as well as the need for the fluoropolymer coating. In principle, this should allow the spectrum to extend to wavelengths only limited by absorption by the sulphide cladding itself which starts to increase at 8 $\mu$m and becomes serious at 10 $\mu$m [38].

Following the design parameters, tri-layer waveguides were fabricated. The thicknesses of the three layers were measured using the Filmtek 4000 to be 6.1 $\mu$m, 4.4 $\mu$m and 1.5 $\mu$m respectively from the bottom to the top layer. The relatively thick bottom layer was chosen to avoid power leaking to the absorbing silica of the oxidized silicon substrate. A 3.7 $\mu$m thick layer was removed by the CHF$_3$ etching which was equivalent to total removal of the protective layer of
GeAsS and 50% etching of the GeAsSe core. The change of the core thickness from 4 μm used in the design to 4.4 μm in the actual device and corresponding change in the fractional etch depth from 40% to 50% did not move the waveguide out of the favourable design range in terms of birefringence and quasi-single mode operation. The waveguide was still birefringent ($\Delta n_{\text{eff}} = 0.0019$ @4 μm) and supported only the fundamental TE and TM modes over a wide range of wavelengths (>1 μm) based on the numerically calculated mode profile. Some examples are shown in Fig. 5.12. It also displayed no cut-off before the transmission edge of the core selenide material at 16 μm according to the numerical calculations. The calculated dispersion parameter of this specific waveguide for both TE and TM mode is shown in Fig. 5.13. It is obvious that TM mode is anomalous from ~4 μm to ~6.5 μm whilst TE mode remains in the normal regime. As will be shown later, the birefringence, the quasi-single mode features and distinct TE and TM mode dispersion is helpful for spectroscopic applications.

Fig. 5.12: Calculated mode profile at 1, 4, 8 μm for fundamental and first-order TE and TM modes of the tri-layer waveguide.
After hand cleaving, two samples with a length of 5 cm and 1.8 cm were obtained and the typical cross section under a scanning electron microscope (SEM) is shown in Fig. 5.14. As can be seen, the over-cladding was >2 µm thick over the whole rib. The slightly asymmetric structure may be caused by the fact that the chip was not placed at the exact centre of the wafer holder during the angled deposition. The etching created small pedestals on both shoulders but these did not affect the waveguide properties.

The waveguide losses over the range 3 µm to ≈5 µm were characterized by the cut-back method using 7.5 ps duration pulses from an optical parametric amplifier similar to the arrangement described in [157]. The wavelength range of from 4244 nm to 4647nm was not accessible using this device as indicated earlier. Two 2 mm diameter PbSe detectors were used to measure a reference signal reflected by a beam splitter and the output signal after the waveguide, respectively. Several waveguides with the same width 4 µm were measured and
averaged to make sure that the variations due to cleaving or fabrication errors were minimized. Molded “black diamond” lenses from Lightpath Technologies were used to couple the light in and out of the waveguides. A polarizer was used to select the polarization state and the losses for both TM and TE modes were determined as shown in Fig 5.15. Several different waveguides with the same designed width were measured to average the results and generally the scatter between measurements was less than ± 15%. As is evident, the waveguides typically have a loss around 0.6 dB/cm between 3.8 µm to 5 µm although this rises to around 2 dB/cm for the TM mode around 3.2 µm. This enhanced loss was probably caused by residual O-H and C-H contamination on the etched surfaces of the waveguide, and in fact SEM imaging of the cleaved end faces suggests that cladding adhesion on the side walls was imperfect suggesting that the passivation layer essential for vertical etching was not effectively removed in the subsequent processing. It is not clear, however, why the TM mode was more strongly affected since the field overlap with the sidewalls is similar for both modes. Finally these measurements allowed an estimate of the coupling loss which was around 6 dB per facet. The loss profile beyond this wavelength range is unknown as the previously used MIRcat QCL source was not available for these measurements.

![Fig. 5.15: Measured averaged losses of the fundamental TE and the TM mode for the tri-layer all-chalcogenide rib waveguide.](image)

Based on the measured core film thickness and the calculated dispersion parameters from Fig. 5.13, the ZDWs of this particular waveguide were ≈4 µm and ≈6.5 µm for the TM mode whilst for the TE mode the dispersion was small
but normal. Therefore, we chose a pump wavelength of 4.184 µm delivered in 330 fs pulses from an OPA system described in Fig. 3.15 (note the region between \( \approx 4.2 \) µm and 4.4 µm could not be used because of CO\(_2\) absorption in the air). The chip used for the SC generation experiments was 1.8 cm long.

The experimental arrangement used to couple light into the waveguide and collect the SC spectrum was the same as that depicted in Fig. 3.22. The liquid nitrogen cooled MCT detector with spectral coverage from 2 to 17 µm was used. Three gratings (300 l/mm, 2 µm blaze wavelength; 150 l/mm, 4 µm blaze wavelength; 75 l/mm, 7 µm blaze wavelength) were used depending on the wavelength range. The input and output slit widths of the monochromator were set to be 350 µm and the scanning step of the program was typically 20 nm. The path between the waveguide output and through the monochromator was not purged or evacuated and hence the resulting spectra were affected by absorption in the air due to water vapour and carbon dioxide.

Figure 5.16 shows the evolution of the SC with increasing pump powers. With an average input power of 130 mW delivered by the pump, the corresponding coupled peak power was estimated to be \( \approx 4500 \) W, and the spectrum covered from 2.2 µm to 10.2 µm at a dynamic range of ±15 dB. There was evidence of dispersive waves at around 3 µm and 8 µm beyond both ZDWs as shown in Fig. 5.16. The output average power after the reflective optics objective used to direct the output beam to the monochromator was 6.5 mW and after correction for losses in this lens, the power of the SC itself directly exiting the chip was around 20 mW.
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Fig. 5.16: Experimental SC evolution with increasing powers at a pump wavelength of 4.184 µm. The power legend means the calculated coupled peak power at the input end of the tri-layer chalcogenide chip. The curves are offset by 10 dB relative to each other for clarity.

To validate these experimental results, simulations were performed by solving the GNLSE using the SSFM. The dispersion terms up to 20th order were calculated using the full vector finite difference method. The nonlinear parameter was assumed to be 0.2/W/m at the pump wavelength. The soliton number was calculated to be 59 at a peak power of 4500 W. Simulations show good agreement with the experiments as shown in Fig. 5.17 except that the long wavelength extension was limited in the experiments most probably due to the rising absorption of the sulphide cladding beyond ≈8 µm. To solve this problem, a different cladding material would be needed, for example, a low-index selenide glass. However, this makes it significantly more difficult to obtain anomalous dispersion at wavelength below 5 µm making it difficult to find a suitable pump source.

Fig. 5.17: Simulated SC evolution with increasing powers at a pump wavelength of 4.184 µm and with a pulse duration of 330 fs for the tri-layer waveguide. The curves are offset by 10 dB relative to each other for clarity.

To verify the predictions of our dispersion design, we also measured the spectrum produced by pumping with the TE mode for the same input conditions. This resulted in a narrower spectrum extending from 2.4 µm to 6.5 µm showing characteristics of SPM as would be expected for normal dispersion. However it is worth noting that even in this regime the spectrum was still 1.4 octaves wide with an arguably flatter spectral distribution than in the anomalous regime as
shown in Fig. 5.18. To be able to operate at TE mode but in the anomalous dispersion regime, a thicker core layer would be needed or the width of the waveguides should be increased according to our calculations.

We found that the SC spectrum actually narrowed slightly when using the 5 cm long waveguide most likely because of higher total losses at long wavelengths due to the cladding and due to the contamination responsible for the short wavelength losses evident in Fig. 5.15. The spectra showed better repeatability compared to the experiments in circular fibers most likely due to absence of polarization mode coupling. The polarization beat length of this waveguide is calculated and shown in Fig. 5.19. It is obvious that the polarization beat length is one order of magnitude smaller than the waveguide length at the pump wavelength and even smaller at longer wavelengths, which means the waveguide can be moderately resistant to polarization mode coupling effects.

Another parameter to characterize the birefringence performance of the waveguide is the polarization extinction ratio (PER). It is defined by ten times the logarithmic value of the ratio of the TE and the TM output components for a particular linear input polarization state. For this 1.8 cm long tri-layer waveguide, the average PER was measured to be 20.6 dB and 18.7 dB at the TM and TE pumping condition respectively while the typical value we measured for the circular step-index chalcogenide fiber made of similar materials was only 3.2 dB.

![Comparison SC spectra for both the TM and the TE operation conditions at the same input power of 130 mW for the 1.8 cm long tri-layer chalcogenide rib waveguide at a pump wavelength of 4.184 µm.](image)
At long wavelengths where no TE contribution is present, the PER should be even higher.

![Graph showing beat length vs. wavelength](image)

**Fig. 5.19:** Calculated beat length of the tri-layer chalcogenide rib waveguide.

In summary, a linearly polarized, quasi-single mode 2-10.8 μm spanning SC from a tri-layer rib chalcogenide waveguide was demonstrated experimentally with good stability by pumping with 330 fs, 4184 nm, 4500 W pulses. The chip-based SC source paves the way for practical spectroscopic applications. This demonstration almost reached the transmission limitation of this selenide/sulphide configuration. Improvements can be made by adjusting the waveguide dimension, reducing the waveguide losses and modifying the material compositions to support better transmission beyond 10 μm.

### 5.4 Demonstrations of Spectroscopy

One of the purposes of generating a MIR SC is that it can be used for MIR spectroscopy in a convenient way. Generally to facilitate fast data acquisition, an FTIR spectrometer should be used instead of the scanning monochromator used to record the SC. However, the FTIR we had available was far from state-of-the-art and suffered from low dynamic range and high thermal noise at long wavelengths. Thus for proof-of-principle demonstrations, the monochromator was still used as the dispersing component. One of the most promising SC source is the one generated from the tri-layer buried chalcogenide rib waveguide as discussed in Section 5.3. Benefitted from the quasi-single mode feature and the polarization maintaining property of the rib waveguide structure and the distinct difference between the TE and TM mode dispersion parameters, the generated
SC spectrum should be stable enough to perform practical spectroscopic applications.

To test this, a thin polyethylene (PE, \(-\text{[-CH}_2\text{-CH}_2\text{-]}_n\) membrane was inserted in the beam path before the monochromator and spectra were taken for both TE and TM operation respectively as shown in Fig. 5.20. The experimental setup followed the one used in SC spectrum recording process described in Section 5.3. The acquisition of each spectrum took around 20 minutes at a scanning step size of 20 nm.

![Comparison SC spectra with and without the polyethylene (PE) membrane for both TM and TE operation conditions.](image)

The normalized PE absorption spectra at both TE and TM mode are shown in Fig. 5.21. The SC source resolved C-H and C-C absorption around 3500 nm and 6800 nm with features matching the reference spectrum in [174]. The spectrum is, however, relatively noisy at the shorter wavelength end. This could be due to the relatively longer polarization beat length at these wavelengths which implied stronger coupling between the fundamental TE and TM modes. At the longer wavelengths from 6 \(\mu\)m to 9 \(\mu\)m, the SC source showed good stability for the TM mode.
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This procedure has also been performed on a 0.7 mm thick polystyrene (PS, \([C_8H_8]_n\)) sample using TM mode pumping and the result is shown in Fig. 5.22. Thin-film PS has been widely used as the material for wavenumber calibration in the IR beyond 2.5 μm since at least 1950 [175]. The characteristic C-H absorption peaks around 3.3 μm and the multiple dips from 5 μm to 6 μm were clearly resolved though the resolution after 7 μm was limited by the reduced SNR of the SC. Fluctuations still occurred in the 3.5-5 μm range.

One significant issue with SC spectra are fluctuations in time that may be either characteristic of the nonlinear process itself (due to the break-up of multiple solitons, the modulational instability, etc.), due to polarization effects, or due to small drifts in the pump power coupled into the waveguide. Thus, normalizing two successively recorded spectra generally produces significant
fluctuations (±20%) especially in regions where the spectral intensity changes rapidly with wavelength. In fact, pulse-to-pulse jitter characteristic of the nonlinear process itself could be detected by examining portions of the spectrum filtered by the monochromator or using long pass filters.

Thus, in practice, a dual beam system is needed to compensate these fluctuations. This comprises signal and reference arms that are recorded simultaneously. Unfortunately this may not be straightforward especially if the polarization state also fluctuates, as can occur in the fiber geometry, basically because the reflectivity of a simple angled beam splitter used to create the signal and reference arms is sensitive to polarization.

In this context the tri-layer waveguide SC source has a particular advantage because of it can provide a linearly polarized output. Thus a simple pellicle beam splitter used at 45° angle of incidence and placed after the monochromator can be used to produce correlated sample and reference beams. Additionally, without loss of signal we could further stabilize the polarization of the SC by placing a wire grid polarizer at the input to the monochromator.

The beam paths of the two arms were made of equal length to eliminate the effects from absorption from the atmosphere and the signals detected using a pair of thermoelectric cooled MCT detectors whose response extended to around 6 µm. Using two lock-in amplifiers the transmission spectrum of a sample placed in one of the arms could be determined after normalization against the ratio of the signals from the channels with no sample. Figure 5.23 shows a spectrum of polystyrene obtained in this way compared with an average of 64 scans from a Bruker Vertex 80V FTIR under vacuum with a resolution of 4 cm⁻¹. In addition, the same procedure has been applied to a polyethylene film and the results are shown in Fig. 5.24. These demonstrations show significant improvement compared with the spectra taken without the reference shown in Fig. 5.21 and Fig. 5.22.
Fig. 5.23: Comparison of the normalized polystyrene absorption spectra measured by the generated SC source at the TM mode operation condition together with a monochromator and by a commercial globar fitted FTIR spectrometer.

Fig. 5.24: Comparison of the normalized polyethylene absorption spectra measured by the generated SC source at the TM mode operation condition together with a monochromator and by a commercial globar fitted FTIR spectrometer.

On this basis the performances of the SC monochromator duo and the globar-fitted FTIR spectrometer are similar, and hence one could argue little has been gained. However, the globar has a spectral brightness that is at least $10^4$ times smaller than that of the SC source. Because the SC is emitted from a single mode waveguide it can be concentrated to a diffraction-limited spot around a wavelength in diameter without a loss of signal meaning that the same SNR and dynamic range would be obtained when examining wavelength scale structures, making the SC source vastly superior for micro-spectroscopy. In a practical implementation the monochromator would need to be replaced by a FTIR for rapid spectral acquisition. Unfortunately, the lack of suitable hardware prevented
us from implementing such a solution here, but there is no reason why it should be problematic.

To further emphasize the benefits of the waveguide SC source we compared its performance with a SC source based on a circular step-index chalcogenide fiber. In this case the PS transmission measurements were repeated using the SC generated by the all selenide fiber (Ge-Sb-Se/Ge-Se, 3 μm radius, 11 cm long, 4 μm, 120 mW pump). Figure 5.25 shows the raw ratio between the reflected and the transmitted signals collected by the MCT detectors when no sample was inserted in the beam path. The case with and without a polarizer in front of the monochromator are included for both the waveguide and the fiber.

![Figure 5.25: Raw ratio between the reflected and the transmitted signal collected by the amplified MCT detectors when no sample was inserted in the beam path. WG: waveguide. TM means a vertically polarized polarizer was inserted in the beam path before the monochromator.](image)

Overall the ratio varied slowly with wavelength which was characteristic of the beam splitter. However, it is quite clear that the addition of the polarizer greatly improved the stability of the ratio which means there were significant mode-coupling effects especially in the circular fiber case. In fact the fluctuating features were imprinted in the final spectra so the output polarization controller is indeed necessary. In general the waveguide performed much better which can be explained by its much higher PER (20.6 dB) compared to the circular selenide fiber (3.2 dB).

In conclusion, the combination of the high quality MIR SC generated by the chalcogenide rib waveguide and the two-arm approach enables excellent
spectroscopy application demonstrations with competing performance with the commercial globar-FTIR spectrometer duo. The high birefringence of the SC source is shown to be a necessity when high repeatability and stability of the spectroscopy performance is required.

5.5 Summary

In this Chapter, the design, fabrication, characterization and SC tests of two-layer and tri-layer chalcogenide waveguides have been presented in detail. In the air-clad two-layer rib waveguide, the first ZDW is tuned to be around 3 µm and by using a pump wavelength of 4 µm, a SC spanning from 1.8 µm to 9 µm has been obtained. As for the tri-layer all chalcogenide waveguide, the first ZDW is around 4 µm and at a pump wavelength of 4.184 µm, the SC spectra cover from 2 µm to 10.8 µm. These two sets of SC sources possess high brightness benefited from the spatial coherence property of the waveguide structure and they hold great promise for MIR micro-spectroscopy. Especially for the tri-layer waveguide, due to the distinct difference of the dispersion between the TE and the TM mode, the quasi-single mode feature and the relatively short beat length, the generated SC spectrum was stable and allowed dual beam spectroscopy. This offers some insight about the important of high birefringence in the design of realistic chalcogenide platforms.

The waveguide platform solved the issues of multi-mode and degenerate polarization state present in fiber geometries; however, the soliton numbers in the waveguides were still relatively large at power levels that allowed broad SC generation which means multiple solitons can still be present for the SC spectrum, and this can reduce the coherence of the SC. The next Chapter discusses SC coherence in detail and provides solutions for improving coherence by reducing the pump pulse duration.
Chapter 6 Coherence Characterization & Pulse Compression

The goal of this PhD project was to develop broadband (2-10 µm and beyond) SC sources that can be applied to practical applications such as MIR spectroscopy, microscopy and imaging. Until the work described in this thesis, there had been relatively few practical experimental demonstrations [176-178] though papers on the potential for MIR SC generation were abundant [141,142,155,179-181]. In many of the other experiments that led to a broadband MIR SC, the average power was low because high peak power (>MW) low repetition rate (kHz) sources were used as the pump. Secondly, the coherence from these SC sources was limited. For many applications, for example, the generation of frequency combs, completely coherent SC sources are essential.

In this Chapter, coherence will be discussed in the context of the SC sources described in the previous Chapters. In particular, the pump pulse duration is chosen to optimize the coherence, since other quantities such as the nonlinearity and dispersion are fixed, at least to a degree, by the device designs that in turn are determined by the available materials. For the all-arsenic fibers it will be shown that pulses less than <100 fs in duration are required to produce a coherent SC, but even then there remain the issues of the multimode nature of the fibers and their polarization properties that have the effect of reducing the coherence from the ideal case. In the case of the tri-layer waveguide somewhat longer pulses in the 100-200 fs range are predicted to lead to a coherent SC. In either instance these are shorter than those delivered by our 330 fs (or 200 fs) MIR OPAs used in most of the experiments.

To overcome this, we demonstrate that shorter pulses can be generated by using a length of commercial chalcogenide fiber to chirp the OPA pulses allowing them to be compressed in a short length of bulk material that has anomalous dispersion. By this means pulses compressed down to around 60 fs were created which are suitable for generation of a coherent SC using any of our dispersion-engineered waveguides.
6.1 Coherence Characterization

6.1.1 Coherence Calculations

In addition to the spectral bandwidth of the SC, coherence is an important parameter when considering its performance as a radiant source. A lot of theoretical and experimental studies have been undertaken to characterize the coherence of a SC [182-188]. Among the various coherence parameters, the normalized degree of spectral coherence originally introduced by Dudley and Coen [182] is the mostly widely used and is the one adopted in this thesis.

The inclusion of noise in numerical modelling of SC generation is necessary to understand how fluctuations of the pump influence the wavelength-dependent intensity and phase stability characteristics of the generated SC spectrum. The approach used here is to perform multiple simulations in the presence of random noise to generate an ensemble of output SC spectra. Then in order to characterize fluctuations in the spectral phase of the SC, an interferometric measurement is performed between successive SC spectra in the ensemble. The modulus of the complex degree of first-order coherence is defined by [29]:

$$\left| g^{(1)}_{12}(\lambda,0) \right| = \frac{\langle |E_1(\lambda,t)E_2(\lambda,t)| \rangle}{\sqrt{\langle |E_1(\lambda,t)|^2 \rangle \langle |E_2(\lambda,t)|^2 \rangle}}$$

(6.1)

This is introduced to quantify the overall coherence across the SC spectrum in which $t$ is the time measured at the scale of the temporal resolution of the spectrometer used to resolve these SC spectra. This modulus can be seen as the fringe visibility at zero path length in Young’s two-source experiment and mainly a measure of phase stability.

This calculation was performed for the all-arsenic fiber (GeAsSe/GeAsS) with a dimension of 4.6*4.1 µm as described in Section 4.3.1 and the tri-layer rib waveguide (GeAsSe/GeAsS) as described in Section 5.3. The ensemble contains 200 samples under the influence of white Gaussian noise with an FWHM width of 7 µm and a SNR of 50 dB.
For the all-arsenic fiber, the pump was chosen to be 4000 nm with a peak power of 1700 W while for the tri-layer waveguide, the pump was chosen to be 4184 nm with a peak power of 4500 W. In both cases, the pump pulse duration was chosen to be 330 fs, 200 fs or 100 fs respectively as shown in Fig. 6.1.

It is obvious that the coherence is significantly improved in both examples as the pulse duration is reduced. In the case of the fiber though, the coherence is
not perfect even for 100 fs duration pump pulses whilst the waveguide is more tolerant with pulses of around 200 fs being acceptable, at least for these pump powers. Shorter pulses reduce the soliton number in the anomalous pumping condition and this is known to improve the coherence of any SC [29]. In some cases, spectrograms that show the correlated time and frequency features of SC are used to illustrate the dynamics of SC generation. Spectrograms for the case of the all-arsenic fiber are shown in Fig. 6.2 using a gate function of a 50 fs FWHM Gaussian pulse. This emphasizes that only for pulses around 60 fs is a single soliton created in the spectrogram. These numerical results motivate the need for shorter MIR pulses as the SC pump than available directly from our OPAs. In Section 6.2 we will discuss an approach to pulse compression that shows these short pulses can be generated using relatively simple hardware.

Fig. 6.2: Calculated SC spectrogram for the all arsenic fiber at a peak power 1700 W at 4000 nm pump. (a) 330 fs; (b) 200 fs; (c) 100 fs; (d) 60 fs.
6.1.2 Coherence Measurements

Most of the experimental measurements of the coherence of a SC reported so far were performed in the NIR using SC sources that had relatively narrow spectra [185-188]. To extend the measurements into the MIR does not require any new science, but does introduce a number of technical challenges that are not necessarily present in NIR measurements.

To measure MIR SC coherence experimentally, we adopted the approach based on an asymmetric Michelson interferometer as described in [188]. The method relies on measuring the spectral interference between consecutive pulses in the quasi-continuous train of SC pulses at the repetition rate of the pump. To obtain fringes the pulse train is launched into a Michelson interferometer whose two arms differ in length by a distance \( L = \frac{c}{F_p} + \Delta \), where \( F_p \) is the repetition frequency of the pump pulses and \( \Delta \) is a small offset that results in a frequency-dependent change of phase between the interfering beams and superimposes fringes on the spectrum measured at the output of the interferometer. In order to obtain large fringe visibility, which is the measure of coherence, the resolution, \( \delta \lambda \), of the monochromator used to measure the spectrum has to be chosen so that \( \delta \lambda \ll \frac{\lambda^2}{c T_p} \) where \( T_p \) is the pulse duration. Typically a resolution of a few nm is required particularly to resolve the depth of the minima in the spectrum. Considering the wide bandwidth (8000 nm) of the SC spectrum, along with its high dynamic range, a scanning monochromator becomes the most practical way of measuring the spectrum, especially since low noise detector arrays for the MIR are non-existent. Compared with the NIR, this introduces the following practical difficulties.

1. The small angular dispersion of gratings used in the MIR means that a very narrow slit widths are necessary to obtain the required resolution from the monochromators and this compromises the throughput of the monochromator reducing signal levels;

2. Because MIR detectors have vastly inferior noise performance compared with NIR detectors, signal averaging is essential to obtain large dynamic range, such as the lock-in techniques used throughout this thesis;
3. The need for a combination of signal averaging with high resolution means that the data acquisition time for a spectrum is at least several tens of minutes;
4. The interferometer and the source itself should be free from drift on this timescale.
5. The atmosphere absorbs significantly in the wavelength range emitted by our SC sources, particularly due to water vapour and CO₂. Thus the interferometer becomes unbalanced because of stronger absorption in the long arm again causing a change in fringe visibility. This could be overcome by placing the apparatus in a vacuum chamber or flooding with dry nitrogen but this was impractical at present.

This fourth issue proved to be extremely challenging. Firstly, for an asymmetric interferometer mounted on a stainless steel optical table and configured for a source with a repetition rate of 63 MHz, the path difference between the arms will drift at a rate of ≈50 µm/℃. This implies that the temperature must be stabilized to <<0.1 ℃, which was not possible in our environment. Secondly, the frequency of the OPA pump source is sensitive to the frequency of both its Yb pump laser and the seed laser. Our OPA was initially seeded with a CW beam from a Santec TSL510 external cavity diode laser. Whilst this laser has a linewidth specified to be <500 kHz, implying that the coherence time is much longer than the inter-pulse time, the absolute frequency of the seed laser was found to drift on the millisecond timescale by more than 10 MHz due to acoustic noise in the environment. A change of frequency of ≈30 MHz is all that is required to shift the fringes at the interferometer output by 2π, and hence these drifts adversely affected the fringe visibility that could be achieved.

The setup of the spectral interferometer is shown in Fig. 6.3. It consisted of a pellicle beam splitter that diverted the beam of the MIROPA™ (seeded by Santec tunable laser) into two arms of the unequal path length Michelson interferometer. The ~200 fs MIROPA™ was chosen as its repetition rate was higher (63 MHz) compared to the 330 fs OPA (21 MHz) and thus the difference in path lengths was only 4.76 m rather than 14.28 m. Both beams need return to the interference plane with identical phase fronts and intensities in order to obtain
deep fringes from which the fringe visibility \( V = \left( I_{\text{max}} - I_{\text{min}} \right) / \left( I_{\text{max}} + I_{\text{min}} \right) \) can be extracted as the measure of coherence. This proves to be rather challenging in the MIR in particular because MIR optical components (high NA lenses for example) are inferior in terms of both chromatic and spherical aberrations. To mitigate this as much as possible, both arms were configured to contain the equivalent of a two lens 1:1 imaging telescope. These were formed by a 1.25 m focal length concave mirror in the long arm and a 10 cm focal length concave mirror in the short arm. When perfectly aligned to image a beam from the beam splitter back to that beam splitter, this combination does not provide the exact delay corresponding to 4.76 m, rather the relative round trip distances differ by 4.6 m. However by shifting the effective source point a small distance beyond the beam splitter and lengthening the effective separation of the concave mirror from the planar end mirror in the long arm, near perfect re-imaging could be obtained with the correct difference in arm length.

Fig. 6.3: Schematic of the spectral interferometer. M: gold mirror, P: polarizer pair, C: chopper, A: aperture, BS: beam splitter, C1, C2: concave mirror, L: lens.

To assess the best fringe contrast achievable in the MIR, we firstly modified the interferometer so that it had equal arm lengths and measured the interference between the same pulse directly from the MIROPA™ pump. The result is shown in Fig. 6.4. The arm offset was set to approximately 200 µm and the spectra recorded with the scanning monochromators with a resolution of 1 nm. The resulting fringes were up to 20 dB deep corresponding to a fringe visibility >0.98. It was evident during these measurements that it was difficult to obtain perfect extinction between the arms possibly due to the beam splitter not
being perfectly flat, or due to residual vibrations affecting the interferometer. Nevertheless a fringe visibility of >0.98 is generally considered to provide a measure of good coherence.

![Fig. 6.4: Same pulse interference pattern of the MIROPA™ pump seeded by Santec laser. The data represents the ratio of the output from two symmetric arms after normalization by the output from a single arm.](image)

By returning the interferometer to its unbalanced state, we then attempted to measure the coherence of the MIROPA™ pump via the interference of adjacent pulses. The results are shown in Fig. 6.5. The fringes obtained were only ~11 dB deep corresponding to a fringe visibility of ~86%. By examining the real time signal from the detectors, we could identify fluctuations due to noise and vibrations that particularly affected the frequency of the Santec tunable seed laser and affected the depth of the minima adversely.

![Fig. 6.5: Normalized interference pattern of the MIROPA™ pump seeded by the Santec laser. The data represents the ratio of the output from two asymmetric arms after normalization by the output from a single arm.](image)
In spite of this, we did attempt a coherence measurement using the SC generated from the all-arсенic fiber as discussed in Section 4.3.1. The results indicated that the SC was partially coherent, especially in the anomalous dispersion regime between about 3 μm and 6 μm, though the best fringe visibility was only ~81% as shown in Fig. 6.6 almost certainly limited by the issues discussed above. In the normal dispersion regime where dispersive waves reside, the coherence was poor. However, these regions also correspond to those where strong differential absorption caused by water vapor exists and this may induce the strong fluctuation in the traces between 5.5 and 7 μm and below 3 μm. The carbon dioxide absorption at around 4.2 μm can be seen to also distort the fringes in this coherence measurement. Finally polarization mode coupling and the multimode nature of this fiber would also limit the coherence.

![Fig. 6.6: Measured normalized interference pattern of SC generated by the all arsenic fiber pumped by the MIROPA™ seed by the Santec laser.](image)

Thus, many issues existed in the MIR SC coherence measurement system. In particular, the Santec seed laser was an external cavity laser whose frequency was not stable and sensitive to environmental perturbations. To demonstrate that the Santec tunable laser was a significant source of instability, a distributed feedback laser (DFB) was replaced as the seed and the resulting interference spectrum of the pump is shown in Fig. 6.7. It is obvious that the fringe contrast is much better than the results in Fig. 6.5 with the corresponding fringe visibility ~0.95. The problem, however, that the only available DFB had a relatively long wavelength of 1527 nm which corresponded to the idler output at a short
wavelength of 3.26 μm, and this is not optimum for SC generation. Furthermore, whilst the DFB laser proved more stable than the external cavity laser on the millisecond timescale and was not affected by acoustic noise in the environment, it revealed a general drift of the output of the interferometer on the timescale of the data acquisition (10s minutes). Such drift can be due to small drifts in temperature of the DFB laser or in the laboratory.

Ultimately these tests revealed that a much more elaborate experimental system would be needed to obtain a meaningful measurement of fringe contrast for our MIR SC sources. Specifically we would need to lock the source to the asymmetric interferometer in order to compensate for drifts in both the source frequency and thermal changes in the interferometer itself. Ideally we would also need a vacuum or dry nitrogen enclosure to eliminate differential absorption in the two arms. Unfortunately these could not be implemented in the timescale of this thesis.

A final issue that was identified was that the beam splitter only had a working wavelength range of 3-5 μm, beyond this range, the transmission or reflectance of the membrane changed significantly and this had the effect of reducing the SNR at long and short wavelength in the measurements.

These combined issues stopped us from pursuing the coherence measurements further at this stage.
6.2 Pulse Compression

It is evident from the simulation presented above, that pump pulses shorter than we had available (<200 fs) were more ideal to create a coherent MIR SC, which should eliminate pulse-to-pulse the fluctuations in the spectrum and lead towards the creation of a frequency comb. This section discusses how to generate shorter pulses by chirping and compressing the output pulses from our MIR OPA pumps.

6.2.1 Simulations & Design

When pumping a fiber or waveguide in the normal dispersion regime, the spectrum is narrower than that produced in the anomalous dispersion regime, but it is coherent and contains an approximately linear chirp. In principle, it can, therefore, be compressed by a dispersive delay line. Conventionally, dispersive delay lines are made of gratings or prisms and these can be used to compensate the chirp on a pulse of many picoseconds in duration. This kind of dispersion compensation technique was proposed in [163]. We adopted a similar approach for our MIR pulses but used a short length of commercial step index chalcogenide fiber from IRFlex with normal dispersion to chirp the pulses from the OPA so that they could then be compressed by propagation though a short length of calcium fluoride (CaF$_2$) that has anomalous dispersion in the MIR.

The IRflex fibers have already been discussed in Chapter 4 and have normal dispersion in the 3-5 μm range which overlaps with the pump wavelengths used for SC generation. The spectra generated by such fibers are relatively smooth which is characteristic of spectral broadening via SPM in the presence of normal dispersion. To test the feasibility of using this kind of chalcogenide fiber to chirp and stretch pulses from our OPA, we first performed numerical simulations calculating the properties of the output pulses as a function of the fiber length.

Both IRF-S-9 and IRF-Se-12 fibers were studied. Two different input parameters were used: 1) 330 fs, 15 kW pulses at a pump wavelength of 3800 nm which is achievable in the femtosecond MIR OPA system depicted in Fig. 3.15 and used in most of the experiments reported earlier; and 2) 200 fs, 10 kW pulses at a pump wavelength of 3800 nm which is generated by a commercial device, the
MIROPA™-fs system from Hotlight Systems that employs a Spectra-Physics HighQ2 pump laser [162]. The power levels were calculated based on the typical coupling efficiency for these fibers from experiments in Section 4.1.

An example for the 330 fs, 15 kW input pulse and the IRF-Se-12 fiber is shown in Fig. 6.8. Within the first few centimetres of fiber, the spectral broadening expands to its maximum due to the influence of the nonlinearity. Afterwards, the pulse just undergoes temporal broadening due to the influence of dispersion since as the pulse spreads, its peak power drops lowering the influence of the nonlinearity. Calculation of the instantaneous frequency shows that a nearly linear chirp is present as shown in Fig. 6.8(c).

Based on these calculations, only about 3 cm of IRF-Se-12 fiber is necessary to chirp and stretch the pulse and the next step is to identify the requirements for the compressor. Similarly calculations for the IRF-S-9 fiber showed about 4.5 cm was suitable to produce a chirped pulse.

As was evident from these calculations the maximum spectral broadening is reached when the pulse duration was has only increased by a factor of 2-3 and still lies in the range of several hundred fs. This is rather short for a grating or conventional prism compressor to be used. However, a simple and effective approach is to pass the pulses through an appropriate length of bulk material that has anomalous dispersion at the pump wavelength and negligible nonlinearity. Sapphire and YAG bulk materials were first studied for this purpose as they have relatively large anomalous dispersion around 4 µm. Only around ~1 cm of these materials would be required to compensate for the normal dispersion induced by the IRflex fiber. Although thin (0.5 mm) sapphire and YAG samples have reasonable transmission to 5 µm, a 1cm thick sample decreases the transmission significantly. For example, 4 mm sapphire transmits only 65% of the power [189]. Thus, materials with better MIR transparency are needed. It turns out that readily available bulk CaF$_2$ has near ideal properties although its dispersion is smaller than YAG or Sapphire, but it has negligible linear loss in the 3-5 µm range.
Fig. 6.8: (a) Time domain and (b) wavelength domain of the SC evolution and (c) chirp as a function of the IRF-Se-12 fiber length under the 330 fs, 15 kW pulses at 3800 nm.
Simulations of the behaviour of a bulk CaF$_2$ compressor are shown in Fig. 6.9 which assumes linear propagation. We propagated the output calculated for the 3 cm long IRF-Se-12 fiber through bulk CaF$_2$ and this demonstrated that 330 fs, 15 kW input pulses, could be compressed down to ~70 fs in duration with the maximum output peak power increased to 51.73 kW by 5.25 cm of CaF$_2$. For the 200 fs, 10 kW pump, the pulse is compressed to ~75 fs, whilst the peak power would be increased to 22.64 kW by using 4.5 cm of CaF$_2$.

![Fig. 6.9: Simulated time domain pulse evolution as a function of the length of the calcium fluoride bulk after the stretching from a 3 cm IRF-Se-12 fiber under the input condition of (a) 330 fs, 15 kW; (b) 200 fs, 10 kW.](image)

### 6.2.2 Experimental Validation

Experimentally, this compression scheme was demonstrated in two conditions. One used a 4.4 cm long sample of the sulphide fiber (IRF-S-9); the other used a 3.2 cm long sample of the selenide fiber (IRF-Se-12). These fibers were hand-cleaved after stripping the polymer coating with dichloromethane (DCM). The end facets were examined under a microscope to ensure the quality of the cleaved surface, although it proved difficult to achieve end surfaces perfectly normal to the fiber axis by this technique. The typical total insertion loss of these fibers was 3.5-5 dB depending on coupling lens and fiber type. Note that this could have been reduced by around 1.8-1.9 dB by AR coating the fiber end facets and can also probably be reduced by further optimization of the coupling optics.

In practice the length of the bulk CaF$_2$ needed to be variable and this was achieved by fabricating two calcium fluoride wedges that were moved against each other to vary the path length. These were placed after the IRflex fibers with
the light collimated using a NA=0.56 molded chalcogenide lens. After collimation the beam intensity is too low to produce any nonlinear effects in the CaF$_2$. The wedges used in the experiments were designed so that the path length could be varied from $\approx 40$ mm to $\approx 60$ mm. The CaF$_2$ wedges were also not AR-coated and so their insertion loss was around 0.5 dB. Again this could be reduced by AR coatings.

The pump wavelength was tuned to $\sim 3700$ nm to avoid absorption by atmospheric CO$_2$ from affecting the spectrum. It was confirmed experimentally that these short fibers provided similar spectral broadening as the much longer ($\sim 1$ m) fibers used in Section 4.1 as predicted by the simulations. For the sulphide fiber, using the 330 fs pulses from out MIR OPA and an input pump power of 160 mW (23.8 kW), $\sim 41$ mm of CaF$_2$, was required to produce the shortest pulses. The pulse durations measured using a SHG autocorrelator are shown in Fig. 6.10. For the shortest pulse the autocorrelation trace had a width of around 100 fs (FWHM) equivalent to a pulse of about 70 fs in duration. The length of CaF$_2$ was close to the minimum available at the time and not all the available OPA power could be used, so further optimization should produce slightly shorter pulses.

![Normalized autocorrelation traces for the 4.4 cm IRF-S-9 fiber when the CaF$_2$ thickness was varied.](image)

To examine the pulse in more detail the autocorrelator was reconfigured to record SHG-FROG traces, and the pulse measured with and without the 41 mm thick CaF$_2$ wedges. The results are shown in Fig. 6.11. Here the approximately linear chirp in the uncompressed output is clearly evident from the V-shape of
the FROG trace, whilst after compression the pulse is much shorter and shows no evidence of residual chirp.

Fig. 6.11: SHG-FROG traces for the 4.4 cm IRF-S-9 fiber when (a) no CaF$_2$ was present; (b) when CaF$_2$ thickness was ~41 mm. Note that the delay scale is different in these two pictures.

The retrieval was performed as described in Section 3.4.2.2. Figure 6.12 shows the retrieved pulse intensity and phase. In this instance the pulse width was found to be 75 fs with a small residual chirp of about 1 radian which could be corrected by making a shorter compressor, which was not available during these experiments.

Fig. 6.12: Retrieved compressed pulse information from the combination of the 4.4 cm IRF-S-9 fiber and ~41 mm of CaF$_2$ bulk material.

The same measurements were made using the 3.2 cm long selenide fiber. The FROG traces for this case are shown in Fig. 6.13. Using 53 mm of CaF$_2$ and 152 mW (22.6 kW) of input power, the optimum compression was obtained with a final FWHM pulse width of ~63 fs as shown in Fig. 6.14. This is around 5 optical cycles. Again there appears to be a small residual chirp which could be corrected,
although in this case a more pronounced pedestal exists on the edge of the pulse, possibly due to the influence of higher order dispersion terms.

Fig. 6.13: SHG-FROG traces for the 3.2 cm IRF-Se-12 fiber when (a) no CaF$_2$ was present; (b) when CaF$_2$ thickness was ~53 mm. Note that the delay scale is different in these two pictures.

Fig. 6.14: Retrieved compressed pulse information from the combination of the 3.2 cm IRF-Se-12 fiber and ~53 mm of CaF$_2$ bulk material.

The pulse compression module was integrated with the commercial MIROPA™ system that delivered shorter 200 fs duration MIR pulses. Its performance using the 3.2 cm selenide fiber is shown in Fig. 6.15 where the compressed pulse width was ~55 fs at a center wavelength of 3.78 μm (bandwidth ~200 nm) and average power after the compressor around 80 mW.
These experiments clearly demonstrate the feasibility of the pulse compression scheme which can offer the possibility to generate ≈5-cycle MIR pump source for coherent SC generation. In an optimized system which would include AR coatings on all elements in the compressor system, average output powers of ≈65\% of the power from the OPA should be achievable.

### 6.2.3 Secondary Pumping

The output from the IRF-Se-12 fiber installed into the MIROPA™ chassis and compressed by the two CaF\(_2\) wedges was coupled into a sample of the circular core all-arsenic fiber tested in Section 4.3.1. The SC spectra using direct pumping from MIROPA™ and the compressed pulse are shown in Fig. 6.16. Firstly in spite of the reduced average power in the compressed pulses, a similar SC bandwidth was obtained. However, the spectrum created by the compressed pulses shows clearer signatures of a soliton at around 6 µm and dispersive waves at 2.1 µm and 8.5 µm separated with deeper dips in the power at 2.7 µm, 5 µm and 7 µm. This is a qualitative indication that fewer solitons and dispersive waves were generated compared to the case of the 200 fs pulses where extra features exist at 3.2 µm, 5 µm and 7 µm. Of course in the single soliton case the spectra would also be expected to be smooth, (see Fig. 6.1 and Fig. 6.2d) which is not particularly the case for these spectra. There are several reasons for this. Firstly these spectra were recorded in a normal laboratory atmosphere contain around a meter of air and hence spectral signatures of CO\(_2\) at around 4.2 µm and water vapor around...
2.5-3.2 μm and 5-7 μm are present. Secondly, these fibers have strong polarization mode coupling that leads to fluctuations in the output pulse. Finally the output of the pump system itself was not completely coherent due to the pulse-to-pulse fluctuations demonstrated above. The issues with the measurements system also prevented meaningful measurements of the coherence, which in any case would not be expected to be ideal for this circular symmetry fiber, because of coupling between the polarization modes and the overall multimode nature of this fiber at short wavelengths.

Fig. 6.16: Measured SC spectra from the direct MIROPA pump (~200 fs) and the compressed pulse (<100 fs) at a center wavelength of 4000 nm. Note that the input power for the compressed pulse case was lower due to the insertion of the IRF-Se-12 fiber and CaF₂ wedges.

6.3 Summary

In this Chapter, the coherence properties of the SC have been numerically characterized which confirms the relatively good coherence of the generated MIR SC across the spectrum especially when short pulses are applied. This demonstrates the importance of generating few-cycle MIR pump sources. An asymmetric interferometer was configured to measure the SC coherence experimentally. However, fit suffered from many challenges and major improvements on the experimental setup would be needed before meaningful coherence measurements can be performed.

The pulse compression was realized in a scheme that chirps the pulses from the OPA using a short length of large core step-index chalcogenide fiber and then compensates the dispersion using bulk CaF₂ wedges with anomalous dispersion at the pump wavelength. Both simulations and experiments were performed and
the resulting pulses can be as short as ~ five optical cycles when the thickness of the CaF$_2$ was optimized. This compressed output can serve as a pump source of SC generation itself, which can enable better coherence and applications in frequency comb generation etc.
Chapter 7 Conclusions & Outlook

The goal of this thesis was to explore the potential of chalcogenide platforms for generating broadband MIR SC sources. As discussed in detail in the above Chapters, this goal has been successfully achieved with a series of octave-spanning SC generated either in bulk chalcogenides, planar waveguides or optical fibers. This Chapter summarizes the achievements in those chalcogenide geometries and offers some insight on future work of this field. In the end, an epilogue will be given.

7.1 Summary

This thesis has provided a systematic study of MIR SC generation in chalcogenide platforms. Three kinds of geometries were used: bulk materials, planar waveguides and optical fibers. The advantages of chalcogenides as an almost ideal candidate for MIR SC generation include their good MIR transparency, high MIR nonlinearity and negligible nonlinear absorption. Two of the chalcogenides, Ge_{11.5}As_{24}Se_{64.5} (GeAsSe) and Ge_{11.5}As_{24}S_{64.5} (GeAsS) were initially selected as the core and cladding materials for waveguides. Bulk SC generation experiments were performed in GeAsS with a spectral coverage of 2.5->7.5 µm which showed the potential of chalcogenides as a promising platform for generating broadband MIR SC. The disadvantage as they having relatively long ZDWs (7 µm for GeAsSe) can be overcome by engineering the total dispersion with waveguide confinement and by using a longer pump wavelength. Both approaches were taken in this thesis.

In terms of dispersion management, the 4 µm wide, 2.5 µm thick, half-etched two-layer rib waveguide made from GeAsSe core and GeAsS cladding managed to shift the ZDW to approximately 3 µm; the 4 µm wide, 4.4 µm thick and half-etched tri-layer rib waveguide with the same composition as the two-layer waveguide shifted the ZDW to around 4 µm. For step-index fibers, the compositions of the ternary chalcogenides were adjusted slightly to make the glass-transition temperature compatible. With a 4.6 µm by 4.1 µm diameter Ge_{12}As_{24}Se_{64} (Ge-As-Se) core and a Ge_{10}As_{24}S_{66} (Ge-As-S) cladding, the anomalous dispersion regime covered from 3.2 µm to 6 µm. The rising absorption from the
sulphide cladding limited the longest wavelength that could be generated to about 10 µm. To overcome this problem, two selenides with moderate index contrast were chosen as both the core and the cladding materials though the degree of which the ZDW could be shifted was reduced due to the smaller index contrast. For example, the ZDW for the Ge\textsubscript{15}Sb\textsubscript{15}Se\textsubscript{70} (Ge-Sb-Se)/Ge\textsubscript{17}As\textsubscript{10}Se\textsubscript{73} (Ge-As-Se2) combination was longer than 5 µm and the ZDW for the Ge\textsubscript{15}Sb\textsubscript{15}Se\textsubscript{70}/Ge\textsubscript{20}Se\textsubscript{80} (Ge-Se) combination was longer than 4 µm.

In terms of pump configuration, as most of the anomalous dispersion regimes fall in the range of 3-5 µm, it was necessary to develop a femtosecond MIR pump source that operated in this range. A 330 fs, 21MHz MIR optical parametric amplifier (OPA) system was developed, characterized and used as the pump for SC generation. The pump laser for the OPA was a 1040 nm Ytterbium laser and the seed laser is a semiconductor continuous wave laser which could be tuned from 1590 nm to 1345 nm. Thus the resulting idler was tuneable from 3 µm to ~4.6 µm. The maximum average power was 250 mW at around 4 µm and this corresponded to 37.5 kW of peak power.

The combination of an efficient MIR OPA pump and the dispersion engineered chalcogenide platforms enabled a series of multi-octave spanning SC sources with reasonable average powers and high source brightness to be demonstrated. The physical mechanisms leading to the SC mainly include self-phase modulation, group-velocity dispersion, soliton fission and the dispersive wave generation. The optimum bandwidth for the two-layer rib waveguide was from 1.8 µm to 9 µm whilst the symmetrical tri-layer rib waveguide generated SC from 2 µm to 10.8 µm [190,191]. For the Ge-As-Se/Ge-As-S fiber, the SC spectrum spanned from 1.8 µm to 10 µm [192]; for the Ge-Sb-Se/Ge-As-Se2 fiber, the spectral bandwidth was from 3 µm to 12 µm; whilst for the Ge-Sb-Se/Ge-Se fiber, a flat SC spanning from 2.2 µm to 12 µm was generated [193]. These SC spectra were all taken by liquid-nitrogen cooled MCT detector with the aid of the LabVIEW controlled scanning monochromator and lock-in amplifier.

These SC spectra were among the widest SC reported to date and numerical simulations by calculating the mode distribution with the finite difference method and by solving the generalized nonlinear Schrödinger equation with the split-step Fourier method showed good agreements with the experimental
results. In terms of the source brightness, for example, the total power of the 1.8-9 \( \mu \text{m} \) spectrum from the two-layer rib chalcogenide waveguide was \( \sim 20 \) mW and the source brightness was \( > \times 100 \) that of current synchrotrons.

One of the most important applications of broadband MIR sources like the SC sources we have generated and the driving force for this PhD project is that bright MIR SC can be used for efficient and convenient detection of almost every organic compound via molecular fingerprint spectroscopy. This has been realized, in principle, by splitting the SC source generated in the birefringent, single mode waveguide into two arms one of which contains a test sample (polyethylene or polystyrene). High dynamic range and high resolution absorption spectra were obtained and compared with those obtained with a globar and FTIR spectrometer. This demonstration is one of the first unequivocal examples of MIR SC spectroscopy with a broadband coverage. The advantage of the SC is that it can be used for large sample lengths or can be focused to a diffraction-limited spot for high spatial resolution without loss of signal.

During my work, teams in Denmark (DTU) and Japan have reported slightly wider spectra (up to 13 \( \mu \text{m} \) and 15.1 \( \mu \text{m} \), respectively) by pumping large core fibers with MW pulses at kHz repetition rates \([179,181]\). However, these are not practical due to their low average powers (<1 mW), poor coherence, and the extreme cost and complexity of the pump laser.

Some other content in the thesis included the experimental measurement of multi-photon absorption and free-carrier absorption coefficients of crystalline silicon, which explains the superiority of chalcogenides over silicon in this regard; the coherence characterization of the generated SC; and the use of the normal dispersed chalcogenide fiber as the stretcher in the dispersion compensation pulse compression scheme to generate few-cycle MIR pulses.

All in all, this thesis has comprehensively explored the potential of chalcogenides as an ideal platform for broadband MIR SC generation and the important application values of these demonstrations.
7.2 Future Work

The theoretical background for MIR SC generation in chalcogenides has been quite mature as articulated in [29]. Most of advances that can be made in the future are mostly technical or are in the respects of detailed designs. For example, chalcogenides with better infrared transparency and higher nonlinearity like tellurides can be a route of pursuit [194]. Also, pumps further into the MIR can be sought after. The relatively low damage threshold of chalcogenides can be improved by doping [195] or changing the compositions. Various structural designs that have been applied to conventional silica fibers can also be used for chalcogenides as the techniques to fabricate chalcogenide-based waveguides continue to mature [196-198]. The pursuit of good polarization maintaining property is also another direction in which the performance of SC can be enhanced. Currently we are only getting around 10% of the pump power into SC due to poor coupling. If better optics and waveguides can be applied to improve this efficiency to around 50%, the generated SC source will be much more useful. For example, anti-reflection coatings can be used and in the case of the in-house chalcogenide rib waveguide, the increase of waveguide dimension would help improve the power handling properties of the waveguide and lower the losses in general.

In terms of the improvement for applications, an FTIR spectrometer with better performance can replace the monochromator which will significantly reduce the data acquisition time and allows for multiple scans. Also, the vacuum environment which is typically adopted in commercial FTIR should also be applied to eliminate the effects of the laboratory atmosphere. The use of the SC source for MIR micro-spectroscopy should be straightforward, but substantial investment in hardware is required.

It is hard to deny that this MIR SC approach for the generation of broadband MIR source is complicated. If we want to reduce the cost and the complexity of the whole system, the possible way out could be by design of waveguide laser/OPA source plus on-chip SC generator which still demands a lot of technology to come together.
7.3 Epilogue

The development of every technology experiences an initially crude stage. Compared to globars, synchrotrons or quantum cascade lasers which are technologically mature, the achievements using SC generation are in many respects in their infancy. In many cases the fibers or waveguides used in our experiments were prototypes: the first of their kind and there is room for much improvement in their losses, in the optimization of materials and methods for fabrication. The pump source itself is quite complex but for MIR SC long wavelength pumps seem inevitable. The OPA based source we employed is certainly much simpler than the alternative in the form of synchronously-pumped OPOs, however, it remains a rather costly component in the overall system. Fortunately there are some ways ahead. The MIR OPA can be operated as a waveguide device and this has been confirmed in our laboratory. Combined with a fiber laser and integrated planar waveguide for SC generation such an approach could lead to substantial reductions in cost and complexity. Nevertheless, such developments are far from trivial and will take much effort to achieve. However, no gain is achieved without effort, and perhaps the results presented here show that the effort is justifiable. That is how we as the human race advance.

I feel lucky that I was part of this pursuit for creating something bigger than myself. For the love of mid-infrared, supercontinuum and chalcogenides.
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