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## FAST TRACK COMMUNICATION

# Related mechanism of transparency in MgAl<sub>2</sub>O<sub>4</sub> nano-ceramics prepared by sintering under high pressure and low temperature

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## Abstract

We fabricate transparent MgAl<sub>2</sub>O<sub>4</sub> nano-ceramics, which are composed of 40 nm grains, by sintering under high pressure and low temperatures. Analysis of the grain size, differential strains, yield strength and porosity obtained from transmission electron microscopy and x-ray diffraction indicates that the pores at the grain boundary triple junctions can retard grain boundary migration and thus prevent grain growth. It is found that the relatively high density for MgAl<sub>2</sub>O<sub>4</sub> nano-ceramics produced at low-temperature and high pressure is attributed mainly to the large energy in the grain exteriors. The decrease in the transparency with increasing temperature (>700 °C) is therefore a result of the light scattering at large pores. On the basis of these results, we propose a mechanism of transparency in MgAl<sub>2</sub>O<sub>4</sub> nano-ceramics.

## 1. Introduction

Magnesium aluminium spinel (MgAl<sub>2</sub>O<sub>4</sub>) has been considered as an important ceramic material due to its attractive combination of physical, chemical, optical, electrical and magnetic properties. Because of its high melting temperature of 2135 °C [1], MgAl<sub>2</sub>O<sub>4</sub> spinel can be used in harsh environments for, e.g., optical devices such as passive Q-switches of lasers [2]. Furthermore, in combination with its excellent optical properties, it can be used as transparent armour and high temperature lens [3–5]. At present, the conventional ceramics can be fabricated using vacuum sintering/hot isostatic pressure and hot pressure [6–8]. These methods have drawbacks such as low efficiency and high cost,

and a high sintering temperature (>1600 °C) is required. It is known that the transparency of the ceramic depends on both the pressure and the temperature during the sintering process. High-quality transparent ceramics have to be produced by sintering under high pressure and low temperature in order to reduce the defects such as porosity and internal stress. On the other hand, a popularly employed approach for realizing high-quality transparent ceramics is to reduce the grain size of the ceramic, namely, to achieve the nano-ceramic with a grain size of less than 100 nm. Such nano-ceramics, having low residual porosity, should be highly transparent due to low Rayleigh scattering [9]. Nano-ceramic materials show many advantages over conventional ceramic materials, in particular, the improved mechanical properties [10]. Hence, to obtain

high-quality transparent ceramics it is desirable to be able to prepare the nano-ceramics under high pressure and low temperature. Here we intend to contribute a pioneering work in this respect.

Recently, there has been considerable interest in synthesizing nano-crystalline metal oxide particles [11, 12], and the first systems for the sintering of the nano-ceramic under high pressure have been reported by Urbanovich and Shkotulo [13]. However, reliable and low-cost methods for preparing nano-ceramic are still to be developed. In recent years, ultrahigh pressure has been developed and applied to the preparation of new technologically important materials [14]. In particular, very recently we have proposed a novel approach for the fabrication of transparent  $\text{MgAl}_2\text{O}_4$  nano-ceramic under ultrahigh pressure [15]. Compared with other methods, the ultrahigh pressure method is one of the promising technologies because of its unique advantages including ease of fabrication, low sintering temperature (500–800 °C), and so on. An important feature of using this method to produce the nano-ceramic is that no significant grain growth occurs during the sintering process.

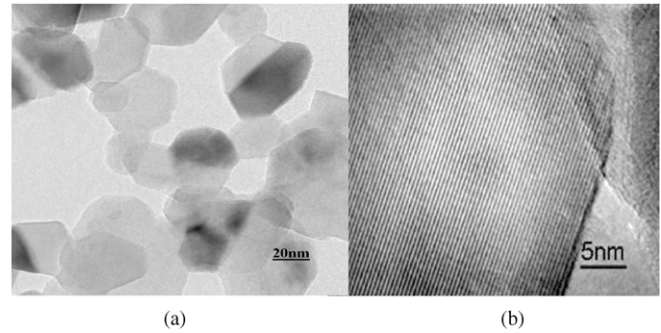
In this study, we conduct an investigation on the transparency mechanism of  $\text{MgAl}_2\text{O}_4$  nano-ceramics. The high-density nano-ceramics are produced using the low-temperature and high-pressure (LTHP) sintering technique. Preliminary work showed the feasibility of  $\text{MgAl}_2\text{O}_4$  nano-ceramics fabrication by means of this technique [15]. The aim of this present work is the investigation of the effect of sintering temperature and pressure on transparency in  $\text{MgAl}_2\text{O}_4$  nano-ceramic materials.

## 2. Experiment and discussion

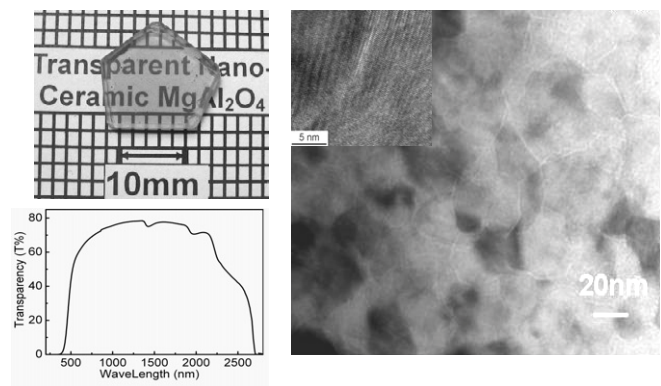
$\text{MgAl}_2\text{O}_4$  powder used as the starting material for nano-ceramic fabrication is prepared by the molten salt baking method [16]. Prior to sintering, pellets are formed from the powder by vacuum heat treatment, which favours getting rid of impurity gases attached to the powder surfaces. The nano-ceramic is fabricated using the LTHP technique that we have developed previously [15]. Briefly, the nano-ceramics can be obtained at 500–800 °C under 3 GPa, 4 GPa and 5 GPa. Under these sintering conditions there is no formation of impurities.

The nanostructure of the powder and of sintered pellets is investigated by means of bright-field TEM (BFTEM), high resolution TEM (HRTEM) and XRD. The transmittance spectra is measured by a Perkin-Elmer Lambda 19 spectrometer.

Figure 1 shows TEM and HRTEM images of well-dispersed nano-sized  $\text{MgAl}_2\text{O}_4$  powders, produced using the low-cost melted-salt method and calcined at 1150 °C for 4 h. The average size of hexagonal particles is about 35 nm. Some larger particles can be 40 nm and some smaller particles can reach up to 25 nm relatively homogeneously. The TEM and HRTEM analyses show that as-prepared powder is well crystallized with few defects, as shown in figure 1. The results indicate that powder with better crystallization and uniform grain size is beneficial to the preparation of transparent nano-ceramics. Highly transparent nano-ceramic ( $T \approx 80\%$ ) can be obtained by sintering at 4 GPa/600 °C, as shown in figure 2.



**Figure 1.** TEM (a) and HRTEM (b) images of nano-sized  $\text{MgAl}_2\text{O}_4$  powder calcined at 1150 °C for 4 h.

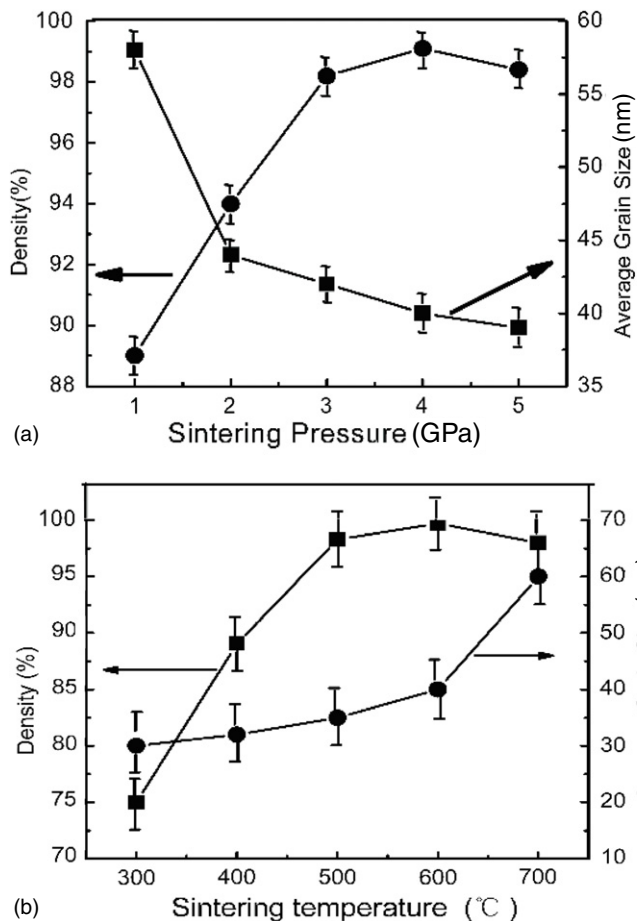


**Figure 2.** Transparent  $\text{MgAl}_2\text{O}_4$  nano-ceramic prepared at 600 °C/4 GPa, a transmission spectrum and TEM images of sample.

In figure 2, we show images obtained from the bright-field TEM and HRTEM for highly transparent nano-ceramic ( $T \approx 80\%$ ) prepared at very low temperature (600 °C). These results can be used to understand the effect of the surface properties on nano-powder. It is well known that the sintering temperature for the ultrafine powder is substantially below that for the usual powder. The difference in the sintering temperature can be up to several hundred degrees due to increased capillary forces induced by the Gibbs–Thomson effect and by the more favourable particle structure for the ultrafine powder. A noticeable feature for the ultrafine powder particles is the presence of high surface energy. According to the Coble [17] theory, the relative densification rate of the  $\text{MgAl}_2\text{O}_4$  nano-ceramic is defined as

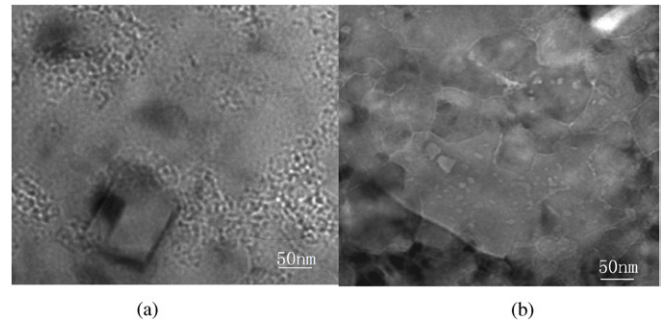
$$\frac{1}{\rho} \cdot \frac{\partial \rho}{\partial t} = \frac{\Omega}{k \cdot T \cdot d^2} \cdot \left[ \frac{40D_1}{3} + \frac{47.5W \cdot D_b}{d} \right] \cdot \left[ \frac{p}{\rho} + \frac{\gamma_s}{r} \right], \quad (1)$$

where  $\rho$  is the relative density,  $T$  is the sintering temperature,  $D_1$  and  $D_b$  are diffusion coefficients for crystal lattice and grain boundary, respectively,  $W$  is the grain boundary width,  $d$  is the grain size,  $p$  is the sintering pressure,  $\gamma_s$  is the surface energy and  $r$  is the pore radius. In this study of relative density, we only deal with the surface energy and the sintering pressure. From this equation, we see that the high surface energy ( $\gamma_s$ ) is related to the atomic driving force which leads to the shrinkage of the pores and removal of the porosity. As a result, the density increase in the samples is obviously a



**Figure 3.** The relative density/crystallite sizes of  $\text{MgAl}_2\text{O}_4$  nano-ceramics are plotted as a function of sintering pressure and temperature.

result of a decrease in the porosity of the pellets at very low temperature. Our results clearly show that the applied high pressure can significantly reduce the densification temperature during sintering, as revealed in figure 3(a). Another interesting feature exhibited in the TEM images of the  $\text{MgAl}_2\text{O}_4$  nano-ceramics is that the average grain size of the ceramics is  $\sim 40$  nm under the applied pressure. Here we notice that nano-ceramics have been fabricated by the direct combination of nano-sized powder particles and no significant grain growth is observed during the sintering process. It is generally accepted that application of mechanical pressure can help to remove the pores from compacts [18, 19]. The pores of the samples move with grain boundary and are gradually concentrated in the triangular region between grains, under high pressure. Pores at grain boundary triple junctions can retard the grain boundary migration and thus prevent the grain growth. Obviously, the grain growth is restrained during LTHP sintering [20]. However, the grain boundary is a crystal defect so the structure is relatively loose. As a result, the pores are easily removed from the grain boundary during the LTHP sintering developed by us. We find that no extra grain boundary phase is present near the grain boundary. The densification of samples increases, or the inter-grain pore volume decreases, with increasing pressure. The  $\text{MgAl}_2\text{O}_4$  transparent nano-

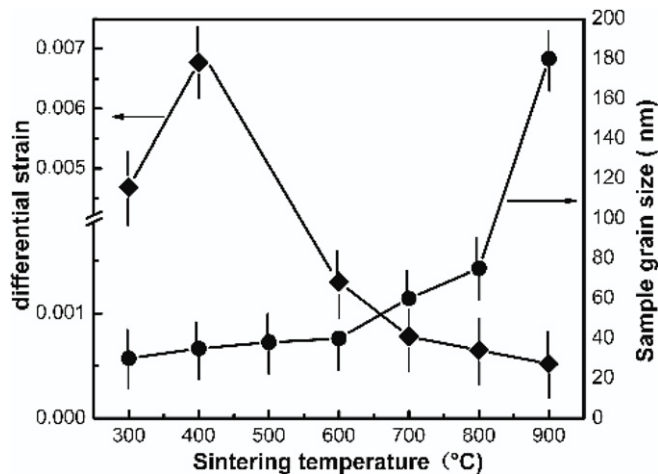


**Figure 4.** SEM and HRTEM image of  $\text{MgAl}_2\text{O}_4$  nano-ceramics prepared at  $500^\circ\text{C}$  (a) and  $700^\circ\text{C}$  (b).

ceramic exhibits a fine-grained and fully crystalline feature with coherent dense grain boundaries.

It is interesting to note that the transparency mechanism for nano-ceramic can be different from that for traditional ceramics. A model for transmission properties of fine-grained, fully dense and polycrystalline  $\text{Al}_2\text{O}_3$  ceramic based on the Rayleigh light-scattering theory for geometrical optics was proposed by Apetz [21]. In general, the scattering can depend both on pores and on their concentration. However, when the pore sizes are below some critical value (depending on a light wave length) the concentration of very small nanopores should affect the scattering very weakly [22, 23]. The light scattering therefore depends only on the size of scattering objects and very little on their concentrations, as assumed by Braun and Pilon [24]. When the pore size is less than 10 nm, the effect of the pore size on the scattering is negligible [24]. Consequently, the high transparency of nano-ceramics can be obtained by controlling the pore size. Closing of the pores was observed during sintering for SiC nano-ceramic under pressures of above 2 GPa [25]. It was found that the pores were closed under high pressure as the size of the pores decreased. The effect of the light scattering can be neglected if the size of individual inhomogeneities dispersed in an otherwise homogeneous matrix is much smaller than the wavelength of the incident radiation [26]. A quantitative criterion requires that the size parameter  $\chi = \pi D/\lambda$  be much less than unity, where  $D$  is the pore diameter and  $\lambda$  is the incident wavelength [27]. According to the condition for the Rayleigh scattering coefficient of the sample  $\chi \ll 1$ , we find that the pore size for negligible scattering is  $D < 12$  nm for a wavelength of 400 nm. This is in good agreement with the theoretical predication that the nano-pore of highly transparent sample is less than 10 nm, as can be seen in figure 2. Moreover, as  $\text{MgAl}_2\text{O}_4$  is a cubic crystal which does not show birefringence, it is not subject to the loss of transparency due to birefringence.

Figure 4 shows the TEM images for non-transparent ceramics prepared at  $500^\circ\text{C}$  and  $700^\circ\text{C}$ , however, using uniform powder calcined for 4 h. We see that the density of the nano-ceramic depends on the sintering temperature (figure 3(b)). This implies the presence of the nanoporosity even in the samples obtained under high pressure (4 GPa) (figure 4(a)). Another interesting behaviour associated with the TEM results is that at a temperature of  $700^\circ\text{C}$  large pores ( $>20$  nm) can be observed (figure 4(b)). As expected, the



**Figure 5.** The calculated differential strain/crystallite sizes of  $\text{MgAl}_2\text{O}_4$  nano-ceramics are plotted as a function of sintering temperature under high-pressure of 4 GPa.

grains grow quicker with increasing temperature and the grains are non-uniform. We also find that the large pores in the grain are easily observed. As a result, the porosity of the large pore nano-ceramic samples can enhance the light scattering and, in such a case, the decrease in transparency due to the porosity cannot be neglected.

To further investigate the transparency mechanism of the  $\text{MgAl}_2\text{O}_4$  nano-ceramics, we analyse the differential strains observed in the broadening of the x-ray diffraction peaks. During high-pressure compression experiment, the differential strains exist in an aggregate polycrystal because of the grain-to-grain contact [28]. The crystallite sizes were determined by Scherrer's method based on the measurement of diffraction peak broadening given by  $B(2\theta) = 0.9\lambda/L \cos\theta$ , where  $B(2\theta)$  is the full width at half-maximum intensity of a diffraction peak,  $\lambda$  is the x-ray wave length,  $L$  is the crystallite size and  $\theta$  is Bragg's angle. The differential strain  $\varepsilon$  is calculated by the Scherrer and Wilson equation [29]. The calculated differential strains/crystallite sizes are plotted as a function of sintering temperature under the high pressure of 4 GPa in figure 5. With increasing temperature, the differential strain first increases, then decreases and the peak appears at  $T = 400^\circ\text{C}$ . This result implies different crystalline orientations relative to the loading direction and particularly to the stress concentration at grain-to-grain contacts during the powder compaction. The differential strain present in the sample (due to grain-to-grain contact) reduces with increasing temperature (400–900°C) (figure 5). Therefore, the yield strength decreases with the increasing temperature. Once the entire bulk yield, i.e. the loading pressure on the sample, is equal to the materials' yield strength, the local high-stress concentration is expected to diminish in terms of increasing total contact area between the individual particles. This could be a reasonable explanation for the reduction of the transparency in the samples synthesized at 700°C/4GPa. Moreover, the overgrowth of grain size at high temperature can lead to more imperfections at the grain boundaries such as more growth-pores. This effect can further reduce the transparency

of the samples in spite of the stress relaxation during the grain growing.

### 3. Conclusion

In summary, in this paper we have examined the mechanism of transparency in  $\text{MgAl}_2\text{O}_4$  nano-ceramics. For high transparent nano-ceramic ( $T \approx 80\%$ ) prepared at very low temperature (600°C), the effects of the surface properties on nano-particles under high pressure have been studied. We have also investigated the dependence of the transparency of nano-ceramic on density, differential strains and porosity of the sample systems. We have found that the transparency losses in the samples sintered at temperatures  $>700^\circ\text{C}$  are induced mainly by the light scattering at large pores.

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