Spectrally resolved microprobe cathodoluminescence of intergrowth $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ferroelectrics

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Spectrally resolved cathodoluminescence measurements of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ($x=0-1.50$) ceramics at room temperature showed three distinct luminescence bands located at about 380, 502, and 660 nm, respectively, which were tentatively assigned to F^+ center, oxygen vacancy-related defect and octahedron structure-related luminescence center, respectively. These assignments could be made in light of electron irradiation experiments with different exposure times. Bands related to oxygen vacancies were clearly enhanced by lanthanum doping, indicating that charge compensation occurred by the substitution of Bi for La^{3+} in perovskitelike structured intergrowth ferroelectrics. We observed that, for contents of La^{3+} $x > 0.75$, La^{3+} ions entered the $[\text{Bi}_2\text{O}_2]^{2+}$ layer according to a doping mechanism which is briefly discussed in this letter. © 2007 American Institute of Physics. [DOI: 10.1063/1.2767857]

Since layered bismuth compounds were discovered by Aurivillius in 1949, they have attracted considerable attention due to their interesting crystal structure and potential applications in information technology.¹ Nowadays, it has formed a common understanding that La^{3+} doping can improve the ferroelectric properties of mixed bismuth layer-structured oxides (BLSOs).² The dielectric property and structure of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ferroelectrics could be influenced by different doping contents by dielectric spectroscopy and Raman spectroscopy investigations.³ Although the photoluminescence (PL) properties of some perovskite-type materials, such as $\text{Bi}_2\text{W}_2\text{O}_9$ and BaTiO_3 , have been investigated,^{4,5} however, detailed information about the doping mechanism and about the defect structures present in the compounds were difficult to obtain by those methods.

Recently cathodoluminescence analysis in a scanning electron microscope (SEM-CL) has been applied by our group to study ferro-/piezo- or dielectric materials, since it enables to acquire unique information on band structure, impurities, and point defects on a micro- and a submicrometer scale. Based on the adjusted experimental setup, we studied the CL spectrum of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ($x=0-1.5$), which revealed the defect-related information in detail. Our investigation on the effect of increasing amounts of La^{3+} dopant incorporated in BLSFs clarifies that charge compensation occurred in the perovskite layer due to heteroion substitution of

Bi for La^{3+} and there are two optically active defects: the F^+ centers and the oxygen vacancies. This study not only demonstrates the applicability of the CL technique to characterize the BLSFs with high spectral resolution, but also provides a clear understanding of electronic levels and layered structures in BLSFs.

The investigated specimens of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ($x=0, 0.25, 0.5, 0.75, 1, 1.25$, and 1.5) were prepared by conventional solid-state reaction method. A scanning electron microscopy (SEM) investigation revealed that the materials display a flakelike appearance and the main directions for crystal growth are the a and b axes, while the c plane is observed to be mainly parallel to the free surface.⁶ In this study, CL measurements were performed in a field-emission scanning electron microscope (FEG-SEM) (S-4300SE, Hitachi Co., Tokyo, Japan) at room temperature. The emitted light was collected by a 600-grating monochromator (Triax-320, Jobin-Yvon, Horiba) equipped with a liquid-nitrogen cooled charge-coupled device (CCD) detector.

Figure 1 shows the room temperature CL spectrum of a $\text{Bi}_5\text{TiNbWO}_{15}$. The CL spectrum could be deconvoluted into three distinct bands according to fitting Gaussian curves, with the aid of a commercially available fitting software package (LABSPEC version 4.02, Jobin-Yvon/Horiba, Kyoto Japan). The center positions of the three bands were located at 3.27, 2.47, and 1.87 eV (henceforth simply referred to as bands I, II, and III, respectively). As there was no report available from literature on the origin of these CL bands, we

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FIG. 1. (Color online) Typical CL spectrum of BW-BTN at room temperature. The spectrum could be precisely deconvoluted into three Gaussian curves, I, II, and III, respectively.

attempted here to assign the bands to particular luminescent moieties in the studied structure.

Figure 2 shows the variation of the CL spectrum as a function of doping content in $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ($x=0, 0.25, 0.5, 0.75, 1, 1.25$, and 1.5). It can be observed that with increasing La content, both band I and band II experienced an enhanced intensity, while band III varied within a much smaller range. It is important to notice here that negligible La segregation could be deduced by a spectral mapping study.

According to a previous work on the luminescence property of perovskite-structured materials, the luminescence of such compounds is attributed to radiative deexcitation of the crystalline lattice components, such as the octahedron (e.g., WO_6).⁷ This is applicable to bismuth layer compounds, which are built up of octahedrons between two fluoritelike layers. Because band III is the strongest and is barely affected by lanthanum doping, it must be connected with the octahedron structure, which is the buildup structure component of $\text{Bi}_2\text{WO}_6\text{-Bi}_3\text{TiNbO}_9$ (BW-BTN). In order to minimize instrumental effects and to fairly eliminate the influence of surface roughness, we examined the intensity ratio of

FIG. 2. (Color online) Room temperature CL spectra of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ with different La doping contents.

FIG. 3. (Color online) Relative intensity of band I and band II as a function of La^{3+} doping content.

band I/III and band II/III as the relative intensity of I and II, respectively.

Figure 3 shows the variation of the relative intensity of band I and band II as a function of La^{3+} content, respectively. It can be seen that with increasing La^{3+} doping concentration, both bands I and II became stronger, showing a significant dependence on the doping content, but their intensities reach a saturation point when $0.75 < x < 1.0$. In other words, at high doping levels the bands were nearly intensity invariant.

Since the radius of La^{3+} ($1.22 \text{ \AA}$) is similar to Bi^{3+} ($1.20 \text{ \AA}$), compared with other ions, La^{3+} ions have priority in substituting for Bi^{3+} ions. At the same time, it is widely accepted that, $[\text{Bi}_2\text{O}_2]^{2+}$ is a rigid layer and upon substituting La^{3+} for Bi^{3+} , La^{3+} will preferentially enter the A sites of the perovskitelike layers.⁸ A dielectric and Raman spectroscopy study by Yi *et al.*³ revealed that when $x \geq 0.75$ Bi^{3+} in the $[\text{Bi}_2\text{O}_2]^{2-}$ layer began to be substituted by La^{3+} . Meanwhile, the remnant polarization ($2P_r$) reached its maximum when $x=0.75$. These interesting results seem to be correlated with the present phenomena that the intensity of band I and band II began to reach saturation when $x > 0.75$, although we have no information so far on which structure actually contributes to the formation of the observed bands.

According to previous studies,^{9,10} in the BLSFs there are either intrinsic or extrinsic oxygen vacancies that are introduced by aliovalent doping into the perovskite structure and/or due to the inevitable volatilization of bismuth during sintering of $\text{Bi}_5\text{TiNbWO}_{15}$ at high temperature.³ This gives a hint to clarify the origin of the present CL bands. In a study of ZnO phosphor powders, Vanheusdena *et al.*¹¹ pointed out that the 510 nm green emission is related to the density of paramagnetic isolated oxygen vacancies. Building upon this finding, we conducted irradiation-time-dependent CL experiments, which might help in giving a reliable attribution of substitutional defects (e.g., oxygen vacancies, cation vacancies, etc.). To reduce the influence of surface contamination and heating effects,¹² we plotted I/II and II/III versus the exposure time to electron irradiation, as shown in Fig. 4. It can be seen that increasing the exposure time leads to an

FIG. 4. (Color online) Change of relative intensity for BW-BTN sample as a function of exposure time. A and B represent plots for the intensity ratios of I/III and II/III, respectively.

increase in relative intensity of band I, while band II decreases in about 2 s. On the other hand, both bands stay invariant for additional exposure.

In general, if we neglect electron beam contamination, the exposure process can be divided into two distinct procedures, referred in the Kröger-Vink notation¹³ as

In the first step, when the material is impinged with accelerated electrons, the oxygen vacancy may capture one electron and turns into an F^+ center. In addition, the F^+ center may also capture one electron and turn into an F center, as occurring in a second step. These physical processes may be responsible for the observed behavior with increasing irradiation time. The luminescence intensity of oxygen vacancy-related band depends on the concentration of oxygen vacancies and it decreases with increasing exposure time before oxygen vacancies are annihilated. This process is in accordance with the behavior observed for band II in our experiments. Accordingly, we may make the conclusion that band II may originate from oxygen vacancy-related defect, while band I originates from F^+ or F center. The CL band of F^+ center in the sapphire single crystal was reported to be located at about 330 nm, which is rather close to the present CL band I, despite a different surrounding environment for the F^+ defect.² This seems to support the knowledge that, generally, for an isolated defect, the electronic energy level is not so sensitive to the matrix material.

Since, band II originates from oxygen vacancy-related defects, the phenomena of the enhancement of band I and band II upon doping means that La dopant can introduce extra oxygen vacancy and color centers. In general, La^{3+} ions are regarded to substitute for Bi^{3+} ions in the BLSFs. However, the identical valence state of La^{3+} and Bi^{3+} enables to maintain electric neutrality and there is no extra oxygen vacancies introduced during the substitution, which would contradict the observed behavior. Therefore, it can be deduced that La^{3+} ions have the preference to substitute for Bi^{3+} ions

but they may also substitute for Ti^{4+} and/or Nb^{5+} and form negatively charged defects, $(La_{Ti})^-$ and/or $(La_{Nb})^{2-}$, even though the ionic radius of Ti^{4+} (0.64 Å) and Nb^{5+} (0.70 Å) are significantly smaller than La^{3+} . This means that La will occupy the B site of the perovskite component as well as the A site. In order to allow charge compensation, extra oxygen vacancies as well as F^+ centers will be generated, and hence the CL band II will be enhanced. Because F centers have no contribution to charge compensation, we may conclude that band I is attributed to F^+ defects. For $x > 0.75$, La^{3+} enters the Bi_2O_2 layer, so no more oxygen vacancies are generated, that is why the intensity of band I and band II reach saturation.

There is another possibility since the valence state of Nb, Ti, and Bi are variable and generally Nb^{3+} and Nb^{5+} coexist (e.g., in perovskite-type $KNbO_3$ crystal¹⁴) and Bi^{3+} and Bi^{5+} may also coexist at A sites in perovskite layers in order to maintain electrical neutrality. The substitution of La^{3+} for Bi^{5+} may also introduce extra oxygen vacancies and F^+ centers. However, this hypothesis should be validated by additional spectroscopic assessments on heavily doped samples.

In summary, spectral resolved CL was applied to study the effect of La doping on $Bi_{5-x}La_xTiNbWO_{15}$ ferroelectrics. The observed CL bands located at 3.27 and 2.47 eV were tentatively assigned to F^+ center and oxygen vacancies, respectively. Upon doping, La^{3+} may also substitute other cation ions besides Bi^{3+} at A site in the perovskitelike layers of BLSFs; accordingly, oxygen vacancies and F^+ centers are generated for charge compensation. At the same time, Bi^{3+} in the $[Bi_2O_2]^{2+}$ layer start to be substituted by La^{3+} when $x \geq 0.75$. We hope that this research will contribute to the understanding of defect properties of substituted structures in bismuth layer-structured intergrowth ferroelectrics.

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