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High-Energy X-ray Diffraction Measurements and Luminescence Properties of Sm$^{3+}$-Doped Borate Glasses

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Citation

Abstract
We carried out high-energy X-ray diffraction (XRD) measurements for Sm$^{3+}$-doped 50ZnO-50B$_2$O$_3$ glass, 25Bi$_2$O$_3$-75B$_2$O$_3$ glass, and 50CaO-50B$_2$O$_3$ glass. The experimental total structure factors of these glasses were different. In the region of $Q < 2.0$ Å$^{-1}$, the diffraction peak was clearly observed in the 50ZnO-50B$_2$O$_3$ glass and in the 25Bi$_2$O$_3$-75B$_2$O$_3$ glass. On the contrary, in the 50CaO-50B$_2$O$_3$ glass, no peak was observed in the region of $Q < 2.0$ Å$^{-1}$. We measured luminescence spectra, luminescence efficiency, Raman spectra, and refractive indexes of these glasses. Luminescence spectra were almost the same in these glasses, while dependence of the modifier oxide on luminescence efficiency was observed. From results of RMC simulation, it is found that medium range order of modifier oxide was important for increasing luminescence efficiency of practical glass phosphor.

1. Introduction

Wideband light sources are used in fiber gyroscopes [1, 2], absorption spectrometry for agricultural applications [3-7], and optical coherence tomography (OCT), which is a recently developed cross-sectional imaging technique for biological tissues [8]. A central wavelength in a near-infrared (NIR) region is suitable for above applications, leading to penetration depths in biological samples larger than that at other wavelength [8]. The wideband light-source is desirable for the absorption spectrometry in order to measure a broader region of an absorption spectrum.

Super luminescent diodes (SLDs) and light emitting diodes (LEDs) in the NIR region and halogen lamps are usually used as NIR wideband light-sources. SLDs and LEDs are small and have longer lifetime. However, a spectral width of SLDs and LEDs is 50 nm at maximum and it is insufficient for most spectroscopic applications. On the other hand, the halogen lamp has the very wide spectral width. Therefore, the absorption spectrometry uses the halogen lamp as the light-source. However, a size of the halogen lamp is much bigger than that of SLDs and LEDs. Moreover, a lifetime of the halogen lamp is much shorter than that of SLDs and LEDs.

Thus, we proposed a novel wideband NIR light-source by combining a wideband NIR phosphor and the LED as an excitation light-source in one package. To realize this light-source, we synthesized a phosphor that emits light at approximately 1000 nm using Bi$_2$O$_3$-B$_2$O$_3$ based glasses doped with Yb$^{3+}$ and Nd$^{3+}$ [9-11]. We successfully obtained a
high power (over 1 mW) NIR light-source with a Gaussian-shape spectrum (spectral width ranging from 950 nm to 1100 nm) using this glass phosphor and a high power amber LED [12]. We achieved a wideband luminescence from 860 nm to 1200 nm by stacking the Sm$^{3+}$-doped glass phosphor between the LED and the Yb$^{3+}$, Nd$^{3+}$ co-doped glass phosphor [13]. A wide spectrum from 760 nm to 1100 nm was achieved by the Pr$^{3+}$-doped glass phosphor stacked on the Sm$^{3+}$-doped glass phosphor excited by a high power blue LED [14]. We successfully achieved the maximum output power of 1.15mW with luminescence from 760 nm to 1100 nm by a Sm$^{3+}$, Pr$^{3+}$ co-doped glass phosphor combined with the blue LED [15]. However the luminescence efficiency of these glasses is lower than that of conventional phosphors. It is well known that luminescence properties of rare-earth ions depend on local structures around the rare-earth ions [16]. And local structures should depend on host-glass structures. Moreover, luminescence properties of rare-earth ions should be strongly affected by heavier atoms in glasses. Therefore, in this paper, we have been investigated the effects of host-glass structures on luminescence properties and carried out high-energy XRD measurements for Sm$^{3+}$-doped borate glasses.

2. Experimental

The samples used in this study were synthesized by a melt-quenching method. Powders of Samarium Oxide (Sm$_2$O$_3$, KANTO CHEMICAL, 99.5%), Zinc oxide (ZnO, KANTO CHEMICAL, 99.5%), Bismuth oxides (Bi$_2$O$_3$, KANTO CHEMICAL, 99.0%), Calcium oxide (CaO, KANTO CHEMICAL, 99.5%) and Boric Acid (H$_3$BO$_3$, NACALAI TESQUE, 99.5%) were used as raw materials. Composition design of glass samples are 1mol% Sm$_2$O$_3$-doped 50ZnO-50B$_2$O$_3$ glass, 25Bi$_2$O$_3$-75B$_2$O$_3$ glass, and 50CaO-50B$_2$O$_3$ glass. The mixed powders in alumina crucible were melted at 1250°C in an electric furnace. After keeping 10 min, a molten liquid was poured between two stainless-steel mould plates kept at room temperature for a formation of the glass. As-quenched samples were ground into powder for high-energy XRD measurements.

The high-energy XRD measurements were performed using the horizontal two-axis diffractometer, optimized for structural measurements in glasses and liquids, built at BL04B2 high-energy monochromatic bending magnet beamline of SPring-8 in Hyogo, Japan. The XRD patterns were recorded at 61.4 keV, with a germanium semiconductor detector. The experiment was done in the scattering angle range $0.3 \leq 2\theta \leq 48.2^\circ$.

The room temperature Raman measurements were performed in the range 300–1700 cm$^{-1}$ using laser Raman microscope. An excitation laser (YVO$_4$) of 532 nm was focused on sample. The spectral resolution was less than 2 cm$^{-1}$, and the diameter of the laser spot at the focus point was less than 1 μm.

Photoluminescence (PL) measurements were carried out at room temperature. A Si photodiode mounted on a 0.20 m grating monochromator was adopted for a lock-in detection in the NIR region and an LED with central wavelength of 470 nm was used as the photo-excitation light source. Luminescence efficiency $\eta_p$ was estimated by a spectrum of transmitted LED light through a host-glass, a spectrum of transmitted LED light through a glass phosphor and a luminescence spectrum of the glass phosphor. In this paper, luminescence efficiency $\eta_p$ is denoted as

$$\eta_p = \frac{\text{Photon number detected at outside of glass phosphor}}{\text{Photon number absorbed by rare-earth ions}}$$

and Fig. 1 shows a schematic drawing of three spectra. Detail calculation method was shown in Ref [17].

3. Results and Discussion

Figure 2 shows the experimental total structure factor $S(Q)$ of Sm$^{3+}$-doped 50ZnO-50B$_2$O$_3$ glass, 25Bi$_2$O$_3$-75B$_2$O$_3$ glass, and 50CaO-50B$_2$O$_3$ glass.
are observed. On the contrary, in the 50CaO-50B₂O₃ glass, diffraction peak around $Q = 2.2$ Å⁻¹ is observed, while no peak is observed under $Q$ of 2.0 Å⁻¹. Figure 3 shows Raman spectra of these samples. Raman spectra are different in these samples. These glasses have many peaks that indicate unit structures and various borate groups. $S(Q)$ under $Q$ of 2.0 Å⁻¹ and Raman spectra of these glasses suggest the differences of intermediate range structures of host-glasses.

Figure 4 shows experimental PL spectra of Sm³⁺-doped 50ZnO-50B₂O₃ glass, 25Bi₂O₃-75B₂O₃ glass, and 50CaO-50B₂O₃ glass in the NIR region. Luminescence spectra were almost the same in these samples. We estimated the luminescence efficiency using Eq. (1). Luminescence efficiency of Sm³⁺-doped 50ZnO-50B₂O₃ glass, 25Bi₂O₃-75B₂O₃ glass, and 50CaO-50B₂O₃ glass were 0.96 %, 0.86 %, and 0.75 % respectively.

It is well known that phonon energy or refractive index of glass affects the luminescence properties. Therefore, maximum phonon energy was estimated from Raman spectra shown in Figure 3. The maximum phonon energy of 50ZnO-50B₂O₃ glass, 25Bi₂O₃-75B₂O₃ glass, and 50CaO-50B₂O₃ glass were 1584 cm⁻¹, 1540 cm⁻¹, and 1575 cm⁻¹ respectively. Maximum phonon energy was almost the same with these samples. The refractive index of Sm³⁺-doped 50ZnO-50B₂O₃ glass, 25Bi₂O₃-75B₂O₃ glass, and 50CaO-50B₂O₃ glass are 1.9, 1.6, and 1.5 respectively. We estimated these values by Duc de Chaulnes method and the maximum error of these measurements are estimated to 9\%.

The refractive index of Sm³⁺-doped 25Bi₂O₃-75B₂O₃ glass is the highest in the samples. Sm³⁺-doped 50ZnO-50B₂O₃ glass and 50CaO-50B₂O₃ glass were almost the same. Table 1 shows the luminescence efficiency, maximum phonon energy, and refractive indexes of Sm³⁺-doped 50ZnO-50B₂O₃ glass, 25Bi₂O₃-75B₂O₃ glass, and 50CaO-50B₂O₃ glass, respectively. There are no relationships between the luminescence efficiency and maximum phonon energy or refractive indexes in table 1.
Table 1. Luminescence efficiency, maximum phonon energy, and refractive indexes of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Luminescence efficiency [%]</th>
<th>Maximum phonon energy [cm⁻¹]</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>50ZnO-50B₂O₃</td>
<td>0.96</td>
<td>1584</td>
<td>1.0</td>
</tr>
<tr>
<td>25Bi₂O₃-75B₂O₃</td>
<td>0.86</td>
<td>1540</td>
<td>1.9</td>
</tr>
<tr>
<td>50CaO-50B₂O₃</td>
<td>0.75</td>
<td>1575</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The error of luminescence efficiency is 0.03%. The maximum error of refractive index is 9%.

Therefore, in order to analysis the detail of host glass structure, measured S(Q) was simulated by RMC simulation [18]. To characterize the goodness of fit between experimental and calculated data series, $R_w$ was used in this study. The calculation of $R_w$ is follows:

$$R_w = \frac{\sqrt{\sum (S^\text{Exp}(Q_i) - S^\text{Cal}(Q_i))^2}}{\sqrt{\sum (S^\text{Exp}(Q_i))^2}}$$  (2)

where, $S^\text{Exp}(Q_i)$ is the experimental structure factor, $\delta$ is a parameter related to the convergence of the simulations and to the experimental errors, and $\chi$ is represented by

$$\chi^2 = \sum_{i=1}^{m} \frac{(S^\text{Exp}(Q_i) - S^\text{Cal}(Q_i))^2}{\delta^2}$$  (3)

where, $S^\text{Cal}(Q_i)$ is the estimative of $S(Q)$ obtained by RMC simulations.

For the RMC starting model, a disordered atomic configuration was built up with a simulation box containing 2800 atoms in these samples. We estimated the density of samples as follows. The glass former oxide A and the modifier oxide B are synthesized to be XA-(100-X)B glass (X is molar fraction). Then, the density of XA-(100-X)B glass is calculated as:

$$d = \frac{(X \times M_A) + ((100-X) \times M_B)}{(X \times \rho_A) + ((100-X) \times \rho_B)} \left[ \text{g/cm}^3 \right]$$  (4)

where $d_A, d_B$ are density and $M_A, M_B$ are molecular weight of glass A, glass B respectively. The number density of the investigated Sm⁺³-doped 50ZnO-50B₂O₃ glass, 25Bi₂O₃-75B₂O₃ glass, and 50CaO-50B₂O₃ glass were 0.0805 atoms Å⁻³, 0.0726 atoms Å⁻³, and 0.0774 atoms Å⁻³ respectively. The closest distance between atoms were decided refer to crystal structure of Zn₄B₆O₁₃ crystal [19], Bi₃B₆O₁₆ crystal [20], and CaB₂O₄ crystal [21]. To increase accuracy of simulation, the N₄ ratio (the ratio of BO₄ to BO₃ unit) was estimated in these glasses by ¹¹B NMR experiments. The N₄ ratio of Sm⁺³-doped 50ZnO-50B₂O₃ glass, 25Bi₂O₃-75B₂O₃ glass, and 50CaO-50B₂O₃ glass are 0.23, 0.48, and 0.28 respectively, and we constraint both 3-hold and 4-hold oxygen coordinated boron atoms in the 1.0-1.95 Å interval in these simulation. The converge of the RMC calculation was good and the final S(Q) matched very well with the experimental S(Q), as illustrated in Fig. 5. $R_w$ value and the actual set of constraints used in the final RMC run are collected in Table 2.

Table 2. The $R_w$ value and closest distances applied in the final RMC run.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rw [%]</th>
<th>The closest distances [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M-M</td>
</tr>
<tr>
<td>50ZnO-50B₂O₃</td>
<td>7.09</td>
<td>3.40</td>
</tr>
<tr>
<td>25Bi₂O₃-75B₂O₃</td>
<td>6.54</td>
<td>3.24</td>
</tr>
<tr>
<td>50CaO-50B₂O₃</td>
<td>6.19</td>
<td>3.66</td>
</tr>
</tbody>
</table>

M: Zn, Bi, Ca

Figure 5. X-ray structure factor S(Q) of Sm⁺³-doped 50ZnO-50B₂O₃ glass, 25Bi₂O₃-75B₂O₃ glass, and 50CaO-50B₂O₃ glass: experimental data (solid lines) and RMC simulation (dotted lines). (The curves are shifted vertically for clarity.)
Several partial pair correlation functions, \( g_{\text{M}-\text{O}}(r) \), have been revealed from this RMC simulation. Since Boron has smaller interaction for the X-ray than Zinc, Bismuth or Calcium, we focused on M-O bonding (M = Zn, Bi, Ca) in this paper. Figure 6 shows partial pair correlation functions of \( g_{\text{Zn}-\text{O}}(r) \), \( g_{\text{Bi}-\text{O}}(r) \), and \( g_{\text{Ca}-\text{O}}(r) \) obtained from RMC simulation. As a reference, partial pair correlation functions of \( g_{\text{M}-\text{O}}(r) \) in \( \text{Zn}_{25}\text{B}_{75}\text{O}_{13} \) crystal, \( \text{Bi}_{25}\text{B}_{75}\text{O}_{13} \) crystal, and \( \text{Ca}_{25}\text{B}_{75}\text{O}_{13} \) crystal are also illustrated in Fig. 6. First neighbor atom group in these glasses should related to first neighbor atom group in these crystals (yellow zone). Second neighbor atom group in the \( 50\text{ZnO}-50\text{B}_{2}\text{O}_{3} \) glass and \( 25\text{Bi}_{2}\text{O}_{3}-75\text{B}_{2}\text{O}_{3} \) glass may related to second neighbor atom group in these crystals (green zone). However, \( 50\text{CaO}-50\text{B}_{2}\text{O}_{3} \) glass is different from others. The \( \text{CaB}_{2}\text{O}_{4} \) crystal has a peak at 3.8Å related second neighbor atoms, while \( 50\text{CaO}-50\text{B}_{2}\text{O}_{3} \) glass has no peak around 3.8Å.

In Fig. 2, small peak of \( S(Q) \) under \( Q < 2.0 \) Å\(^{-1}\) were observed in \( 50\text{ZnO}-50\text{B}_{2}\text{O}_{3} \) glass and \( 25\text{Bi}_{2}\text{O}_{3}-75\text{B}_{2}\text{O}_{3} \) glass. From these results, it is found that host-glass structure may effect on luminescence efficiency. Especially, random structure in the medium range (\( 50\text{CaO}-50\text{B}_{2}\text{O}_{3} \) glass) may decrease the luminescence efficiency. Therefore, the medium range order should be important for development of practical glass phosphor. To reveal detail structures, neutron diffraction measurements, local structure analysis around \( \text{Sm}^{3+} \) are now in progress.

4. Conclusions

We have been investigated the effects of host-glass on luminescence properties by high-energy XRD measurements, Raman measurements, and Duc de Chaulnes method for \( \text{Sm}^{3+} \)-doped \( 50\text{ZnO}-50\text{B}_{2}\text{O}_{3} \) glass, \( 25\text{Bi}_{2}\text{O}_{3}-75\text{B}_{2}\text{O}_{3} \) glass, and \( 50\text{CaO}-50\text{B}_{2}\text{O}_{3} \) glass. Luminescence spectra are almost the same in these samples, on the other hand, the dependence of luminescence efficiency on host glass was observed. We compared luminescence efficiency and maximum phonon energy, refractive indexes, medium range order of host-glass. From these results, it was found that medium range order of host-glass structure would affect the luminescence efficiency of \( \text{Sm}^{3+} \). These findings are useful for development of practical glass phosphor.

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