An XAFS study of the local structure of Eu$^{3+}$ ions in glasses prepared by a levitation technique

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The local structure around Eu$^{3+}$ ions in Eu-doped glasses prepared by a levitation technique was analyzed by X-ray absorption fine structure spectroscopy. The X-ray absorption near edge structure spectra demonstrated that Eu$^{3+}$ ions in Al$_2$O$_3$–SiO$_2$ binary glasses were partly reduced during high-temperature melting. Extended X-ray absorption fine structure spectra indicated that in La$_2$O$_3$–Nb$_2$O$_5$, La$_2$O$_3$–Al$_2$O$_3$, and La$_2$O$_3$–TiO$_2$ glasses that contained a large amount of La$_2$O$_3$, the bond lengths between Eu and O were distributed from 2.34 to 2.39 Å. The coordinated polyhedra around the Eu ions could be fitted to a single coordination sphere. It was found that the bond lengths tend to become shorter as the optical basicity of the glass increases. In the Al$_2$O$_3$–SiO$_2$ glasses without any network modifiers, the local structure around the Eu was more complex, leading to the broader first correlation peak of radial structure function.

Key-words : Aluminosilicate glass, Borate glass, Aluminate glass, Niobate glass, Titanate glass, Optical basicity

1. Introduction

Rare earth elements are important for applications in many fields, such as the development of high-power glass lasers, white LEDs, and various electronic and optical devices.¹,² The local structure of rare earth ions in the host matrix greatly influences their optical properties.³⁻⁵ However, in glassy materials, the available structural information is generally less than in crystalline materials. The atomic arrangement around rare earth ions in glasses has been studied using a variety of experimental and theoretical methods to better understand the relationship between the local structure of rare earth ions and their physical properties. X-ray absorption fine structure (XAFS) spectroscopy is one of the most powerful techniques used to measure this phenomenon, as it is useful even when the rare earth ion concentration is very low. Not only do these results reveal the oxygen coordination number around rare earth ions, but also the bond length up to the second coordination shell can be acquired from a detailed analysis of the extended XAFS (EXAFS)⁶⁻¹⁰

Recently, glass forming region has been expanded to include new discoveries, using a levitation technique. Some of the glasses obtained in the glass forming regions have exhibited superior physical properties, such as high refractive index and low wavelength dispersion in the visible region, wide transmittance from the ultraviolet to the infrared region, strong fluorescence, high elastic modulus, and crack-resistant properties.¹¹⁻¹⁶ Furthermore, the structure of the glasses has attracted much attention because they do not conform to the conventional glass forming rules. The glasses consisted of not only corner-sharing polyhedra but also edge- or face-sharing polyhedra, and the oxygen coordination number of a polyhedron for a small cation varies between four to six.¹⁷⁻¹⁹ In glasses with these unique local structures, it is expected that rare earth ions are coordinated differently from conventional glasses, which will result in fascinating optical properties.

In this study, the local structure around rare earth ions of glasses prepared by a levitation technique is investigated. The glasses are Al$_2$O$_3$–SiO$_2$ glasses without any modifiers and La$_2$O$_3$–Nb$_2$O$_5$, La$_2$O$_3$–Al$_2$O$_3$, and La$_2$O$_3$–TiO$_2$ glasses that are lacking in conventional network formers. Na$_2$O–SiO$_2$ and La$_2$O$_3$–B$_2$O$_3$ glasses are used as references of conventional glasses. The local structure analysis around rare earth ions is conducted using XAFS spectroscopy. A small amount of Eu$^{3+}$ is added to the glasses as a probe to obtain structural information. Furthermore, the composition dependence of the local structure around rare earth ions in the glasses is discussed on the basis of the optical basicity.
2. Experimental methods

Table 1 summarizes the chemical composition of samples and their abbreviations. The raw materials used were HfBO3 (Kojundo Chemical Lab. Co., Ltd., 99.9%), Na2CO3 (Kojundo Chemical Lab. Co., Ltd., 99%), α-Al2O3 (Kojundo Chemical Lab. Co., Ltd., 99.99%), SiO2 (Kojundo Chemical Lab. Co., Ltd., 99.9%), TiO2 (Kojundo Chemical Lab. Co., Ltd., 99.9%), Nb2O5 (Wako Pure Chemical Industries, Ltd., 99.9%), La2O3 (Wako Pure Chemical Industries, Ltd., 99.9%), Eu2O3 (Wako Pure Chemical Industries, Ltd., 99.9%), and EuS. Eu2O3 of 0.5 mol % was added to the glass composition. Na2CO3, SiO2, and Eu2O3 for Na3Si7 were melted in a Pt crucible at 1,600 °C for 1 h and then quenched to room temperature by pouring on a steel plate. The resulting glasses were ground and molten once again to ensure a good homogeneity. The glasses obtained were annealed at 500 °C for 1 h to relax the thermal stress during quenching. La2O3 and H3BO3 for 2La7B had mixed stoichiometry and were annealed at 400 °C for 1 h in air to remove the H2O from the H3BO3. After re-grinding and melting at 1,300 °C, the glasses were obtained, as in the case of Na3Si7. The glasses obtained were annealed at 600 °C for 1 h to relax the thermal stress during quenching. Other glasses were prepared by a levitation technique. All weighed raw materials were mixed thoroughly and pressed into pellets at 25 MPa then sintered for an aerodynamic levitation (ADL) furnace. Targets were placed on the nozzle of the ADL furnace and levitated by CO2 laser was applied to melt the levitated sample. The melt was rapidly cooled to room temperature by turning off the laser power and then solidified. The synthesized glasses were ground into powders and mixed with high purity hexagonal boron nitride powder to form pellet specimens. Eu LIII-edge XAFS spectra at room temperature were recorded at BL14B2 and BL16B2 at beamlines of SPring-8. The incident X-ray was monochromated with a double crystal, using Si (111) planes, and the higher harmonics were cut off by a Rh-coated mirror. The XAFS spectra of Eu2O3 and EuS were used as references, and Na3Si7 and Al6Si4 were collected in the transmission mode, using two ionization chambers, whereas the fluorescence mode was applied for those of the other glasses, using a 19-element solid state detector released by Canberra Industries. Because these samples contained a large amount of La atoms, the absorption coefficient of the X-ray used here was high. Therefore, it was necessary to measure it with a fluorescence mode. In addition, measurements were taken, which were over 10 to 20 times longer than those of the transmission mode. The spectra that were measured covered the energy range of 6,770–7,620 eV.

EXAFS data reduction and analysis were performed with the Athena and Artemis programs in the Demeter software package. The EXAFS spectra were Fourier-transformed (FT) to real space, with k-weighting. Selected FT peaks were fitted by using phases and amplitude functions calculated using the FEFF code.

3. Results and discussion

Figure 1 shows the X-ray absorption near edge structure (XANES) spectra of the glasses, Eu2O3, and EuS. As shown in the reference spectra of EuS and Eu2O3, the peaks that originate from Eu3+ and Eu2+ are located at 6972.8 and 6981.0 eV, respectively. The main peak of all the glasses are due to Eu3+. All glasses except for Al6Si4 have only the Eu3+ peak, whereas the spectrum of Al6Si4 indicates a small amount of Eu2+ in the glass. The fraction of Eu2+ in Al6Si4 was estimated to be approximately 13%, using two Lorentzian functions. Eu3+ is usually stable in silicate glasses when melted under ambient atmosphere. However, even in silicate glasses, Eu2+ was observed in the glass containing Al2O3 with lower basicity. The stabilities of Eu3+ is assumed to be related to the basicity of the glasses. Al6Si4 contains a large amount of Al2O3 and has the lower basicity among the glasses examined, which might cause generation of Eu2+ during melting. In contrast, Eu2+ could not be confirmed in La5Al5 and La3Al7 that contain a large amount of Al2O3 and were

![Fig. 1. Eu LIII-edge XANES spectra of the glasses, Eu2O3, and EuS.](image-url)
prepared in ADL furnace at higher melting temperature. The calculation method of basicity from the chemical composition of the glass was described later.

**Figure 2** shows the $k^3$-weighted EXAFS spectra measured by transmission mode for the Eu$_2$O$_3$ reference sample, as well as the Na$_3$Si$_7$ and Al$_6$Si$_4$ samples. The EXAFS oscillation obtained from the reference sample was clearly observed in the range of 10 Å$^{-1}$. The EXAFS oscillation for Sample Na$_3$Si$_7$ displayed only a single wave frequency, indicating the presence of a single ordered coordination sphere. In contrast, the oscillations for the reference sample and Al$_6$Si$_4$ had distinct frequencies, indicating the presence of higher atomic shells. The radial structure functions obtained by Fourier transformation of $k^3\chi(k)$ over the range from 2 to 10 Å$^{-1}$ are shown in **Fig. 3**. There was a first peak at around 2 Å, which corresponds to the nearest Eu–O pairs. The second peak was around 3.5 Å for the Eu$_2$O$_3$ reference sample due to Eu–Eu correlation in the second-nearest shell. By fitting the EXAFS data, two types of Eu–Eu pairs were confirmed, as shown in **Table 2**. In the Fourier transform of Na$_3$Si$_6$, the contribution of the second shell was very weak. The $k^3\chi(k)$ and radial structural function could be fit with a single Eu–O pair by varying the distance ($R$), the coordination number ($N$) and mean square displacement ($\sigma^2$) in order to obtain the best fit between the experimental and predicted spectra. The estimated coordination number of Eu was 6.2, consistent with the previous reports. In contrast, the first peak of Al$_6$Si$_4$ was broad and could not fit by the single Eu–O pair. In order to reproduce the first peak, at least two kinds of Eu–O pairs were required, and the results here could be fitted using short and long pairs whose bond lengths were 2.25 and 2.45 Å, respectively. In addition, the second shell contributed. Because there is no network modifier in Al$_6$Si$_4$ glass, it is considered that the positive charge of Eu$^{3+}$ is compensated for by three non-bridging oxygen atoms when the concentration of Eu$_2$O$_3$ is low. Thus, it is assumed that the oxygen atoms of the short Eu–O pairs are the non-bridging oxygen ones, and the oxygen atoms of the long Eu–O pair oxygen are the bridging oxygen atoms.

**Figure 4** shows the $k^3$-weighted EXAFS spectra for La$_3$Nb$_7$, La$_6$Nb$_4$, La$_3$Al$_7$, La$_5$Al$_5$, La$_3$Ti$_7$, and La$_2$B$_7$ (broken line with open circles). The theoretical fits are given as solid lines.

### Table 2. Fitting parameters of the EXAFS data analysis and optical basicity $\Lambda$

| Sample name | Pair  | $R$ (Å) | $N$ | $\sigma^2$ (Å$^2$) | $R$-factor | $\Lambda$ |
|-------------|-------|---------|-----|-----------------|------------|---------|
| Eu$_2$O$_3$ | Eu–O  | 2.345*  | 6.0* | 0.011           | 0.023      |         |
|             | Eu–Eu | 3.612*  | 6.0* | 0.012           |            |         |
|             | Eu–Eu | 4.089*  | 6.0* | 0.014           |            |         |
| Na$_3$Si$_7$| Eu–O  | 2.32    | 6.0* | 0.008           | 0.005      | 0.598   |
|             | Eu–O  | 2.25    | 3.2  | 0.008           | 0.069      | 0.548   |
|             | Eu–O  | 2.45    | 3.4  | 0.008           |            |         |
|             | Eu–Al(Si) | 3.2     | 2.7  | 0.008           |            |         |
| La$_3$Nb$_7$| Eu–O  | 2.39    | 5.6  | 0.007           | 0.015      | 0.616   |
|             | Eu–O  | 2.34    | 10.2 | 0.021           | 0.019      | 0.704   |
| La$_3$Al$_7$| Eu–O  | 2.38    | 5.8  | 0.014           | 0.014      | 0.678   |
|             | Eu–O  | 2.35    | 7.9  | 0.018           | 0.018      | 0.734   |
|             | Eu–O  | 2.38    | 7.3  | 0.011           | 0.007      | 0.705   |
| La$_2$B$_7$ | Eu–O  | 2.37    | 9.0  | 0.018           | 0.014      | 0.537   |

The values with an asterisk are taken from the crystal structure and are fixed values in the fitting.
Because these glasses contained a large amount of La$_2$O$_3$, the coordination number of Eu was much larger than six. In La$_6$Nb$_4$ and La$_5$Al$_5$, however, the coordination number of Eu in glasses in this study was thought to be mostly six. In La$_6$Nb$_4$ and La$_5$Al$_5$, however, the coordination number of Eu was much larger than six. Because these glasses contained a large amount of La$_2$O$_3$, the absorption by La atoms in the measurement of XAFS spectra might have a bad influence on the estimation of the coordination number around Eu. The bond distance is considered to be more sensitive and accurate for EXAFS data analysis. The influence of the glass composition on local structures was discussed using the bond distance data.

The optical basicity is often used to evaluate the effect of glass composition on local structures. The value of optical basicity $\Lambda$ is given by

$$\Lambda = \sum \frac{Z_i r_i}{2 \gamma_i}$$

where $Z_i$ is the oxidation number of the $i$th atom and $r_i$ is the ratio of the cations with respect to the total number of oxides. $\gamma_i$ is the empirical basicity moderating parameter given by

$$\gamma_i = 1.36(\chi_i - 0.26)$$

where $\chi_i$ is the Pauling electronegativity. The Eu–O bond distances in borate and silicate glasses are reported in Ref. 6, and the calculated optical basicity is shown in Fig. 6. It can be observed that the optical basicity of borate glasses varies over a wide range, and the Eu–O distances decrease with increasing basicity. The points of La$_2$B$_7$ and Na$_3$Si$_7$ were located in the data area of a series of borate glasses and silicate glasses, respectively. The other glass data were located on the higher basicity side. Considering the La$_2$O$_3$–Nb$_2$O$_5$ and La$_2$O$_3$–Al$_2$O$_3$ systems, they can be connected with a negative slope line, as in the case of the borate glasses. In other words, the higher the basicity, the shorter the Eu–O bond distance. All the data are not put on the same line but on different lines for each system. These results show that the bond length information obtained by EXAFS analysis represents the local structure of the ions in more detail. Further, as in the case of the Al$_6$Si$_4$, it is possible to analyze the case where a single coordination structure is not used. Guidelines for materials design can be obtained by further examining optical properties based on this local structural information.

### 4. Summary

The local structure around Eu ions in the glasses prepared by the levitation technique was analyzed. The XANES spectra demonstrated that Eu$^{3+}$ ions were reduced during high-temperature melting. In the glasses containing La$_2$O$_3$, the bond lengths between Eu and O were distributed from 2.34 to 2.39 Å. The coordinated polyhedra around Eu ions could be fitted by a single coordination sphere. It was found that these bond lengths tend to become shorter as the optical basicity of the glass increases. In the Al$_2$O$_3$–SiO$_2$ binary glass, which did not contain a network modifier, the local structure around Eu was more complex, and the broader first peak was observed by EXAFS analysis.

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