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Composition dependence of local structure in lanthanoborate glasses

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Abstract

Lanthanoborate glasses ($(La_2O_3)_x(B_2O_3)_{1-x}$ glasses, where $x = 0.22, 0.25, 0.28, 0.30$) were prepared by rapid-quenching method using twin-roller apparatus. The composition dependence of the local structure in the lanthanoborate glasses was investigated by Raman spectroscopy, XAFS and XPS measurements. The XAFS measurements of La LIII-edge showed that the lanthanum ion is surrounded by nine oxygen atoms and that the La–O distance decreases with increasing of the La_2O_3 content, which shows that the La–O interaction becomes stronger with increasing of the La_2O_3 content. The corresponding result was obtained from XPS spectra for La $3d_{3/2}$ and $3d_{5/2}$. The Raman spectra showed a band at ca. 761 cm^{-1} which is assigned to metaborate chain structure. It is found that the band decreases with increasing of La_2O_3 content. The bands at 635, 835, and 925 cm^{-1} increase with increasing of La_2O_3 content, which are assigned to small anionic units, such as metaborate ring, pyroborate, and orthoborate structure, respectively, which shows that the network structure in the glasses changes to small anionic units as the La_2O_3 content increases.

Keywords: Lanthanoborate glass; Local structure; XAFS; Raman; XPS

1. Introduction

It is well known that alkali borate glasses ($(M_2O)_x(B_2O_3)_{1-x}$, where M is alkali metal) glasses have anomalous composition dependences of the physicochemical properties, such as density and thermal expansion coefficient, which is called as 'boric oxide anomaly' [1,2]. Extensive investigations of alkali borate glasses have been performed by X-ray/neutron diffraction [3,4], Raman spectroscopy [5], B^{11}-NMR [6], molecular dynamics simulation [7], IR spectroscopy [8], and so on. These results indicated that various structural groups, such as boroxol ring, diborate, triborate, metaborate ring, are formed from the tetrahedral BO_4 units and the triangle BO_3 units in the alkali borate glasses [9].

However, there are few works on rare earth borate binary glasses, because the preparation of the glasses is difficult due to narrow glass formation range. No boroxol ring structure has been observed in rare earth borate crystal [10]. It is important to elucidate the structure of rare earth borate glasses to investigate the effect of La ion on the borate glass structure. Lanthanoborate glasses, $(La_2O_3)_x(B_2O_3)_{1-x}$, were developed as low-dispersion, and high-refractive-index optical glasses [11]. The glass formation region and the physicochemical properties have been studied for these glasses. It is known that the density does not change in alignment according to La_2O_3 content [11,12]. Therefore, a precise knowledge on the structure of lanthanoborate glasses is very important from fundamental point of view.

In the present work, we have prepared and characterized lanthanoborate glasses ($(La_2O_3)_x(B_2O_3)_{1-x}$, where $x = 0.22$, 0.25, 0.28, 0.30) by rapid quenching method with a twin-roller [13]. We have studied the variation of borate network in La_2O_3–B_2O_3 glasses with La_2O_3 content by Raman spectroscopy. The valency and local structure of La atoms were investigated by X-ray absorption fine structure (XAFS) and X-ray photoelectron spectroscopy (XPS) measurements.

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2. Experimental

2.1. Preparation of lanthanoborate glasses

For the preparation of lanthanoborate glasses, commercial regent-grade H_3BO_3 and La_2O_3 were used as starting materials. As the glass forming region of lanthanoborate glasses is narrow, the glasses were prepared by using a roller-quenching technique by a twin-roller apparatus. Mixtures of these materials with appropriate compositions were melted from 1523 to 1653 K for 15 min in a platinum crucible in air. The melt was quenched by rotating twin rollers (900 rpm) with quenching rate of 10^3 to 10^4 K/s. The glasses were ground and annealed near glass transition temperature. The amorphicity of the glasses was verified by the absence of any peaks in X-ray diffraction pattern. The composition of each glass was determined by inductivity coupled plasma atomic emission spectroscopy (ICP-AES) (Seiko Instruments Inc., SPS 1500VR).

2.2. Characterization of lanthanoborate glasses

Raman spectroscopy was carried out with a T64000 (Jovin Yvon). The excitation source was the 532 nm line of the Nd:YAG laser, operating at 100 mW. Raman scattering was detected through a triple monochromator with CCD detector (2048 pixels × 512 pixels) in a back scattering geometry. The scattering intensity was accumulated by 10 scans with a collection time of 30 s per scan.

XAFS measurements of the glasses and $La_2O_3{\cdot}3B_2O_3$ crystal were carried out with transmission mode by using R-EXAFS Super (Rigaku Denki Co.) which applies a rotating-anode X-ray source with a tungsten target (13 kV, 200 mA). The incident X-ray was monochromatized by a curved Ge single crystal (2 2 0). The intensities of incident X-ray (I_0) and transmitted X-ray (I) were measured by proportional counter (Ne) and NaI scintillation counter, respectively. X-ray absorption near edge structure (XANES) spectra and X-ray absorption fine structure (EXAFS) spectra of the La L_{III}-edge were measured by step-scanning technique with the fixed time over 100 s at every energy.

XPS measurements were carried out by an ESCA-3400 (Shimadzu) spectrometer using Mg Kα X-ray with 200 W, that is, with 10 kV acceleration potential and 20 mA emission current. The glasses were mounted on carbon adhesive sheet. The ambient pressure in spectrometer was kept below 5×10^{-6} Pa during the XPS measurements. The energy calibration of spectra was performed with the C 1s electron peak (Eb = 284.6 eV) of the carbon adhesive sheets.

3. Results and discussions

3.1. Variation of borate network structure with La_2O_3 content

Fig. 1 shows the Raman spectra collected from lanthanoborate glasses ($(La_2O_3)_x(B_2O_3)_{1-x}$, where $x = 0.22$, 0.25, 0.28, 0.30) in the range from 560 to 1200 cm^{-1}. It is found that the peak area of the band at about 761 cm^{-1} decreases with increasing of La_2O_3 content. The bands are assigned to ladder-type metaborate chain which is composed of BO_3 trigonal and BO_4 tetrahedral units in a 2:1 ratio and is connected by lanthanide ions [14]. The peak areas of the bands at about 1060 and 1100 cm^{-1} decrease with increasing of La_2O_3 content. The bands at about 1060 and 1100 cm^{-1} are assigned to diborate [14]. It is known that the bands of both ladder-type metaborate chain and diborate represents the evidence of three-dimensional glass network in lanthanoborate glasses. It is found that the network structure is broken with the increase of La_2O_3 content.

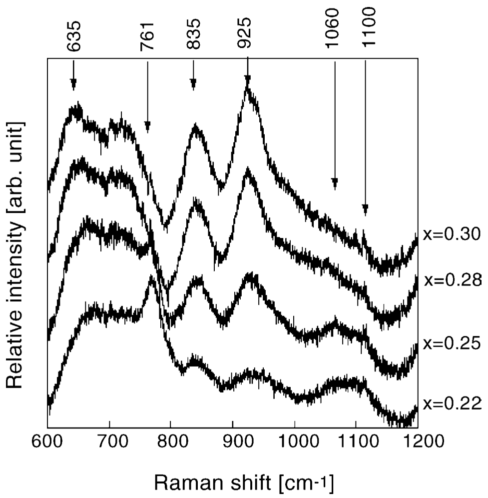

Fig. 1. Raman spectra of $(La_2O_3)_x(B_2O_3)_{1-x}$ glasses.

The peak area of the bands at ca. 635, 835, and 925 cm^{-1} increase with increasing of La_2O_3 content, which are assigned to metaborate ring, pyroborate, and orthoborate, respectively. These structural units take no part in forming three-dimensional glass network. It is clear that the addition of La_2O_3 induces the breaking of the borate network into those units.

3.2. Variation of local structure around La with La_2O_3 content in lanthanoborate glasses

The details of the local structure of La in the glasses were studied by XAFS measurement. The La L_{III}-edge XANES spectra of the glasses and $La_2O_3{\cdot}3B_2O_3$ crystal are shown in Fig. 2. Any apparent change in the XANES are not observed for the glasses by La_2O_3 content due to low energy resolution of the XANES measurement. The jumping energy of La L_{III}-edge for the glasses is almost the same as for $La_2O_3{\cdot}3B_2O_3$ crystal. Therefore, it is found that the La ion in the glasses is trivalent (+3).

EXAFS data analysis was carried out by using the commercial software, REX (Rigaku Denki Co.). The EXAFS oscillation curve, $\chi(k)$, is obtained after subtraction of background and normalization, where k is the wave number of

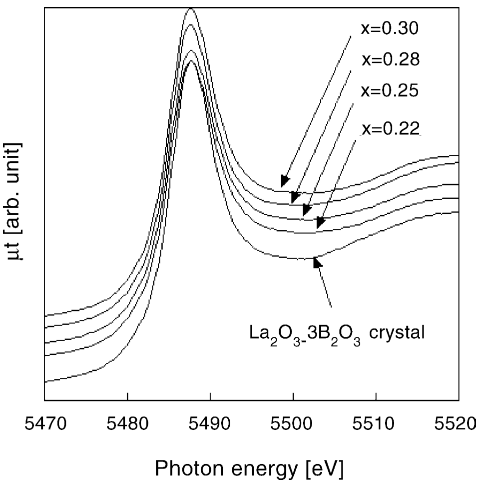

Fig. 2. XANES spectra of $(La_2O_3)_x(B_2O_3)_{1-x}$ glasses.

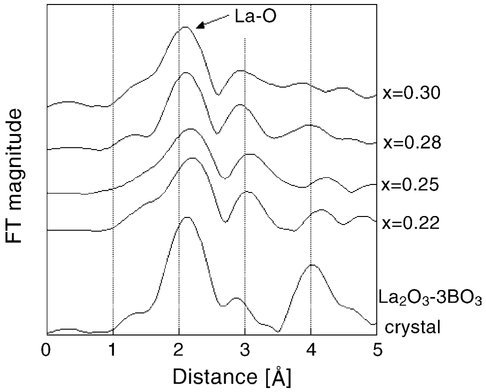

Fig. 3. Fourier transforms of EXAFS for $(La_2O_3)_x(B_2O_3)_{1-x}$ glasses and $La_2O_3{\cdot}3B_2O_3$ crystal.

the photoelectron. Fig. 3 shows the radial structure functions, RSFs, of the glasses, which are calculated by Fourier transformation of k^3 weighted $\chi(k)$s functions, $k^3\chi(k)$s, without correction of phase shift. The RSFs show a large peak around 2.2 Å which is assigned to the La–O correlation and that the La–O distance decreases as the La_2O_3 content increases. The structural parameters for the La–O correlation have been calculated by least square method to reproduce the k^3 weighted $\chi(k)$s functions, $k^3\chi(k)$s, of the La–O correlation with Mckale's parameters [15–17] in the range from 3.5 to 10 Å^{-1} of k, as summarized in Table 1. Table 1 indicates that La ion is surrounded by about nine oxygen ions and that La–O distance decreases with increasing of La_2O_3 content. It is noted that the La–O correlation becomes stronger as the La_2O_3 content increases. The variation of La–O strength with the La_2O_3 content was confirmed with the shift of Raman spectra at ca. 260 cm^{-1}, which is assigned to La–O stretching mode, with the La_2O_3 content.

Table 1
Structural parameters of $(La_2O_3)_x(B_2O_3)_{1-x}$ glasses and $La_2O_3{\cdot}3B_2O_3$ crystal by curve fitting method

	$x = 0.22$	$x = 0.25$	$x = 0.28$	$x = 0.30$	$La_2O_3{\cdot}3B_2O_3$ crystal
$r_{La\text{–}O}$	2.60(1)	2.59(1)	2.57(0)	2.54(0)	2.52(0)
$N_{La\text{–}O}$	9.3 (5)	9.2(8)	9.1(1)	9.1(1)	10.1(1)
$\sigma_{La\text{–}O}$	0.089(6)	0.085(7)	0.086(5)	0.087(2)	0.054(2)

$N_{La\text{–}O}$: coordination number of La–O correlation, $r_{La\text{–}O}$: La–O distance (Å), and σ: Debye–Waller factor (Å).

Fig. 4 shows the XPS spectra of lanthanoborate glasses and $La_2O_3{\cdot}B_2O_3$ and $La_2O_3{\cdot}3B_2O_3$ crystals in the range from 835 to 865 eV. The peaks at ca. 855 and 840 eV are assigned to La $3d_{5/2}$, La $3d_{3/2}$, respectively, and satellite peaks are observed at ca. 843 and 860 eV. The peak positions of the La $3d_{5/2}$ and La $3d_{3/2}$ for the glasses shift to lower energy with increasing of La_2O_3 content. The decrease in the binding energy of the La 3d main lines comes from the increase of the effective electronic density around the La atoms.

As shown in Fig. 4, the binding energies of La 3d of $La_2O_3{\cdot}B_2O_3$ crystal is lower than those of the $La_2O_3{\cdot}3B_2O_3$ crystal, respectively. In $La_2O_3{\cdot}3B_2O_3$ crystal, ladder-type metaborate chain are connected by La^{3+} ions, and the local structure of La^{3+} is distorted because La ion is inserted by large chain structures [18]. In $La_2O_3{\cdot}B_2O_3$ crystal, borate anion is composed of orthoborate units and the mean La–O distance is shorter than that of $La_2O_3{\cdot}3B_2O_3$ crystal [14,19], which shows the La–O correlation is stronger than $La_2O_3{\cdot}3B_2O_3$ crystal. The XPS peak shift of the glasses is related to the local structural change from metaborate chain to orthoborate units.

Through Raman spectroscopy, XAFS, and XPS measurements of the lanthanoborate glasses, it was concluded that the borate network structures such as ladder-type metaborate chain change to small structures such as orthoborate with increasing of La_2O_3 content. When La_2O_3 content is low, La ion is inserted among large borate units and the local structure of La^{3+} is distorted. With increase of La_2O_3 content, La ion is surrounded by small anionic units and the local structure of La^{3+} shows a well-organized structure.

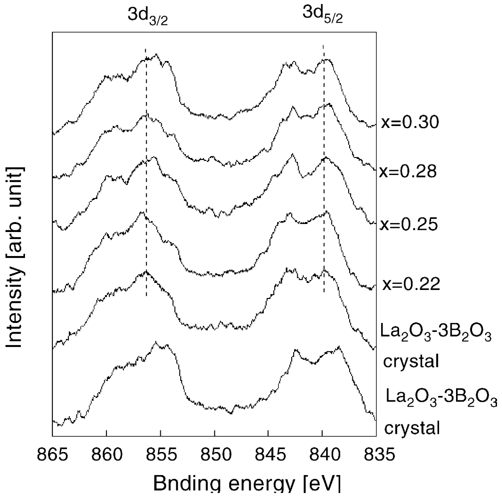

Fig. 4. XPS spectra of $(La_2O_3)_x(B_2O_3)_{1-x}$ glasses and $La_2O_3{\cdot}3B_2O_3$ and $La_2O_3{\cdot}B_2O_3$ crystals.

4. Conclusions

From Raman spectroscopy and XPS measurement of the lanthanoborate glasses, glass network structure of the ladder-type metaborate chain significantly decreases and small units of orthoborate units increases as the La_2O_3 content increases. From XAFS measurement, it was found that the coordination number of La–O is about nine and the La–O distance decreases with increasing of La_2O_3 content.

The detailed structure around boron will be clarified by further studies such as high-energy X-ray diffraction measurements (HEXRD) and XANES measurements of boron absorption edge, neutron diffraction measurements.

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