Change in Coordination Number of Barium Ion As a Network-Modifier in Borate and Alminoborate Glasses

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Abstract

The coordination number of barium ion in barium borate xBaO-(100-x)B_2O_3 and barium alminoborate $y$$Al_2O_3$-(100-$y$)[$x$BaO-(100-$x$)$B_2O_3$] glasses was investigated by the EXAFS (extended X-ray absorption fine structure) method at the barium L_{III}-edge. With increasing BaO content in barium borate glasses, the local structure around Ba changes from a single shell structure of 6 coordinated O atoms at a Ba-O interatomic distance of 2.77 Å to a 2-shell structure with distances 2.67 Å and 2.90 Å and coordination numbers 4 and 3-4, respectively. For barium alminoborate glasses, with increasing BaO content similar results to those found for the barium borate glasses were obtained at fixed y equal to 1 and 5 mol%. On the other hand, at constant barium concentration of x = 50 mol%, with increasing Al_2O_3 amount the local structure around Ba changes from a 2-shell structure to a single shell structure of 4 coordinated O atoms at a Ba-O length of 2.71 Å.

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Introduction

The structure of the glasses changes by adding network-modifiers. Barium borate xBaO-(100-x)B_2O_3 glass is well known as one of the binary alkaline-earth borate systems with wide glass-forming range going from x=16.7 mol% to 66.7 mol% [1]. Also, it is well known that an addition of Al_2O_3 to barium borate glasses causes an extension of glass forming range. In such a wide range of barium ion concentrations, it must be interesting to investigate the local structure of network-forming atoms as well as the coordination number of barium ion. In this study we focused on the local structure of barium ion as a network-modifier.

We prepared barium borate glasses xBaO-(100-x)B_2O_3 with x ranging from 10.0 to 65.0 mol%. Barium alminoborate $y$$Al_2O_3$-(100-$y$)[$x$BaO-(100-$x$)$B_2O_3$] glasses were prepared with x ranging from 10.0 to 60.0 mol% at fixed y value of 1 and 5 mol%, respectively. We also examined barium alminoborate glasses by changing y from 1 to 40 mol% at constant barium concentration of x = 50 mol%. The local structures of barium ion in these glasses were investigated by the EXAFS (extended X-ray absorption fine structure) method at the barium L_{III}-edge. Analyzing EXAFS data we obtained interesting results on the change in the coordination number of barium ion in these glasses.

Experimental

Twetve barium borate xBaO-(100-x)B_2O_3 glasses were prepared from extra-regent grade barium carbonate and boric acid by usual quenching method. The samples were heated in platinum crucibles in an electric furnace at temperatures in the range 1073-1623 K for periods of 30 min. Similarly, twenty eight barium alminoborate $y$$Al_2O_3$-(100-$y$)[$x$BaO-(100-$x$)$B_2O_3$] glasses were prepared from extra-reagent grade powder of Al_2O_3, $BaCO_3$ and H_2BO_3. Raw materials were melted in platinum crucibles at 1173-1923 Kfor 20 min and then quenched. All samples were checked by Raman spectroscopy [2,3].

Ba L_{III}-edge EXAFS measurements were carried out at the beam-line BL-4 of the Synchrotron Radiation Center in Ritsumeikan University [4,5]. The stored electron beam energy was 575 MeV, the radius of the beam 0.5 m, and the initial beam current is 300mA. Ba L_{III}-edge EXAFS spectra were measured by transmission mode using an Si(220) double-crystal monochromator. Ionization chambers filled with N_2 gas were employed as detectors for measuring both incident and transmitted X-ray beam intensities. The Ba L_{III}-edge EXAFS data were analyzed using standard software packages, Athena and Artemis [6], REX2000 (Rigaku), and EXAFS (Technos), and they were also checked by FEFF8.2 code

[7]. BaO powder, α- and β-BBO (BaB_2O_4) single crystals and powders (Casix) were used as model compounds.

Results and Discussion

Figure 1 shows the radial structure functions obtained from Ba L_{III}-edge EXAFS spectra for xBaO-(100-x)B_2O_3 glasses. The peaks due to Ba-O bonds at 2.1 Å shift to a shorter

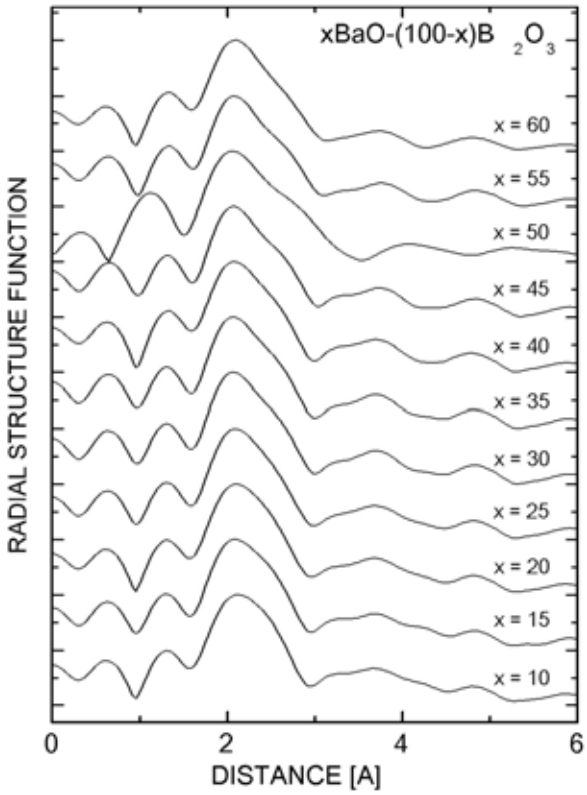

Figure 1 The radial structure functions obtained Ba L_{III}-edge EXAFS spectra for xBaO-(100-x)B_2O_3 glasses.

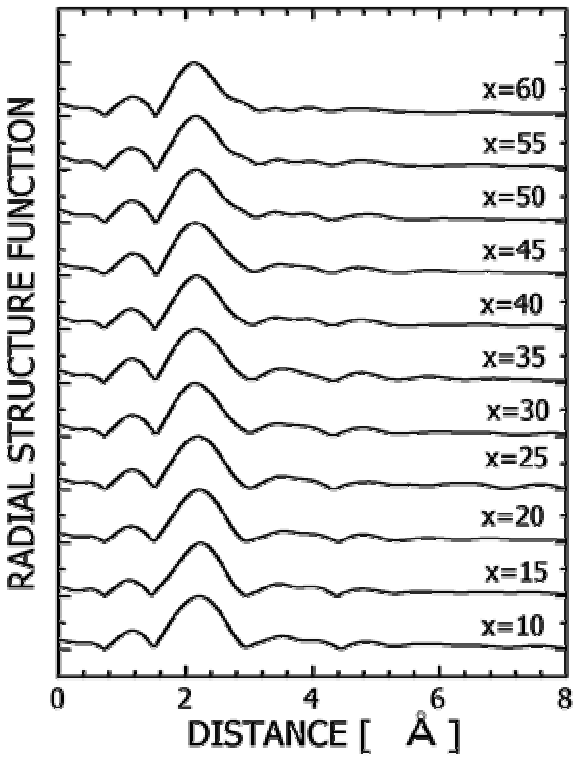

Figure 2 The radial structure functions obtained Ba L_{III}-edge EXAFS spectra for Al_2O_3-99[xBaO-(100-x)B_2O_3] glasses.

distance with increasing BaO content to 25 mol%. A shoulder then appears at 2.7 Å at 30 mol% of BaO. With further increase of BaO amount to 60 mol%, the peak positions at 2.1 Å move to a longer distance and shoulders grow gradually. The obtained structural parameters are listed in Table 1. The local structure around Ba of the systems with low BaO content is similar to that of crystalline BaO where the Ba-O interatomic distance is 2.77Å with 6 nearest neighbor oxygen atoms. With increasing the BaO content in BaO-B_2O_3 glasses, two Ba-O distances are observed one at 2.67 Å with 4 oxygens and 2.90 Å with 3-4 oxygens. The

structure around Ba changes becoming similar to the structure of BBO crystals at high BaO content.

Table 1 Structural parameters for barium ion in xBaO-(1-x)B_2O_3 and $y$$Al_2O_3$-(100-$y$)[$x$BaO-(100-$x$)$B_2O_3$] glasses.

y = 0 mol%			y = 1 mol%			y = 5 mol%		
x/mol%	N_{Ba-O}	R_{Ba-O}/ Å	x/mol%	N_{Ba-O}	R_{Ba-O}/ Å	x/mol%	N_{Ba-O}	R_{Ba-O}/ Å
10	6.1	2.77	10	6.0	2.76	10	6.0	2.76
15	5.7	2.76	15	6.0	2.76	15	6.0	2.76
20	5.9	2.76	20	5.8	2.75	20	6.0	2.75
25	5.6	2.74	25	6.1	2.75	25	3.5	2.74
30	5.7	2.74	30	6.1	2.74	30	2.7	2.69
							3.5	2.88
35	3.4	2.68	35	3.5	2.68	35	2.8	2.68
	2.8	2.89		2.8	2.89		3.5	2.89
40	3.6	2.68	40	3.6	2.69	40	2.8	2.68
	3.0	2.89		2.7	2.89		3.4	2.88
45	3.4	2.67	45	3.4	2.68	45	2.9	2.68
	3.2	2.88		2.9	2.90		3.6	2.90
50	3.7	2.68	50	3.5	2.68	50	2.9	2.68
	3.1	2.90		3.0	2.90		3.6	2.90
55	3.6	2.67	55	3.4	2.68	55	3.0	2.68
	3.2	2.90		2.9	2.90		3.5	2.91
60	3.8	2.68	60	3.6	2.68	60	3.0	2.68
	3.1	2.90		2.9	2.91			2.90
65	3.9	2.69						
	3.4	2.92						

In Figure 2 are shown the radial structure functions obtained from Ba L_{III}-edge EXAFS spectra for $y$$Al_2O_3$-(100-$y$)[$x$BaO-(100-$x$)$B_2O_3$] glasses with varying BaO content at a constant Al_2O_3 concentration of 1 mol%. The change in positions and shapes of peaks at 2.1 Å due to the Ba-O bonds are very similar to that observed for xBaO-(100-x)B_2O_3 glasses. The structural parameters of barium ion for Al_2O_3-99[xBaO-(100-x)B_2O_3] glasses are also summarized in Table 1 together with those for 5Al_2O_3-95[xBaO-(100-x)B_2O_3] ones. The numbers and lengths of the Ba-O bonds are virtually the same as those for the xBaO-(100-x)B_2O_3 system at the same BaO concentration.

Figure 3 depicts the radial structure functions obtained from Ba L_{III}-edge EXAFS spectra for $y$$Al_2O_3$-(100-$y$)[$x$BaO-(100-$x$)$B_2O_3$] glasses with varying Al_2O_3 content at constant BaO

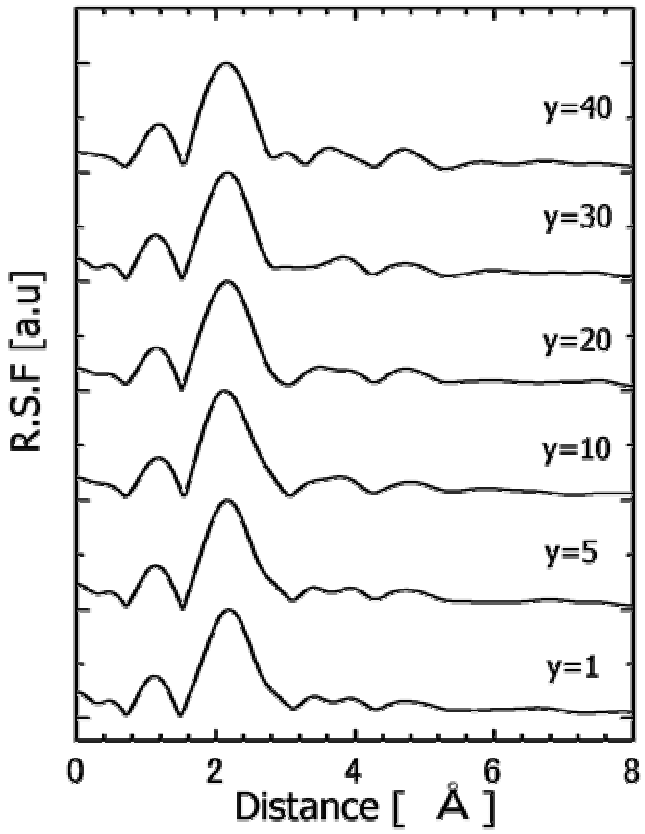

Figure 3 The radial structure functions obtained Ba L_{III}-edge EXAFS spectra for Al_2O_3-99[50BaO-50B_2O_3] glasses.

Table 2 Structural parameters for barium ion in $y$$Al_2O_3$-(100-$y$)[50BaO-50$B_2O_3$] glasses.

x/mol%	N_{Ba-O}	R_{Ba-O}/ Å
1	3.5	2.68
	2.9	2.90
5	3.7	2.69
	2.9	2.91
10	3.7	2.68
	2.9	2.90
20	3.7	2.68
	2.8	2.89
30	4.1	2.71
40	4.3	2.71

concentration of 50 mol%. It is seen from Figure 3 that the peaks due to the Ba-O bond are asymmetric in glasses involving 1-20 mol% Al_2O_3, while with further increase of Al_2O_3 concentration the peak shapes become symmetric. The structural parameters for barium ion are summarized in Table 2. At low Al_2O_3 content the barium ion has a 2-shell structure with distances 2.68 Å and 2.90 Å and coordination numbers 4 and 3-4, respectively. With increasing Al_2O_3 amount the local structure around Ba changes to a single shell structure of 4 coordinated O atoms at a Ba-O length of 2.71 Å. It has been shown that the structure of Al changes from AlO_4 to AlO_6 with increase Al_2O_3 concentration in Al_2O_3-(K_2O-2B_2O_3) and Al_2O_3-(CaO-2B_2O_3) glasses [8]. The Al-O bond is stronger than the Ba-O one and Al takes the larger coordination number at the high Al_2O_3 content. This fact causes the reduction of coordination number of barium ion.

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