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Structural Study of Lithium, Magnesium, and Barium Vanadate Glasses by Means of Mössbauer Spectroscopy

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All the isomer shifts for Li_2O-, MgO-, and BaO–V_2O_5 glasses containing 10 mol% Fe_2O_3 are in a range of 0.39—0.37 mm s^{-1}, indicating that iron is present as tetrahedral Fe^{3+} ions. This suggests that all the Fe^{3+} ions are present at the substitutional sites of tetrahedral V^{5+} or V^{4+} ions constituting the skeleton of each glass matrix. Distinct decreases in the quadrupole splitting and the glass transition temperatures are observed when Li_2O is incorporated into V_2O_5 matrix, suggesting a gradual change of the glass matrix from the layer structure originally composed of VO_5 tetragonal pyramids to a chain structure composed of VO_4 tetrahedra. This structural change is essentially the same as that of Na_2O- and K_2O–V_2O_5 glasses. On the other hand, simultaneous increases in the quadrupole splitting and the glass transition temperatures are observed with increasing MgO or BaO content in the case of MgO- and BaO–V_2O_5 glasses. This suggests a gradual change of the glass matrix from the original layer structure to a highly complicated three-dimensional network structure composed of VO_4 tetrahedra, similarly to the case of P_2O_5–V_2O_5 glasses.

It is well known that V_2O_5 has a layer structure composed of distorted VO_5 tetragonal pyramids, which can also be viewed as distorted trigonal bipyramids.[1,2] Each V^{5+} (or V^{4+}) ion is known to be present at the center of the tetragonal pyramids, surrounded by five oxygen atoms. An IR study of several vanadate (V_2O_5-based) glasses performed by Dimitriev et al.[3] revealed that introduction of alkali or alkaline earth oxides into the V_2O_5 matrix results in a destruction of the layer structure followed by a formation of tetrahedral VO_4 units. Furthermore, Dimitriev et al.[3] elucidated that only VO_4 units are present in the skeleton of metavanadate glasses having alkali or alkaline earth oxide to V_2O_5 ratio equal to unity. The same conclusion was obtained by Segel and Creel[4] in an NMR study of KVO_3 glass. Considering that alkali metavanadate crystals (e.g. KVO_3 crystal) have a one-dimensional chain structure composed of VO_4 tetrahedra,[5] it is not surprising that alkali metavanadate glasses have a chain structure composed of VO_4 tetrahedra. These results are consistent with the recent Mössbauer results of alkali vanadate (K_2O–V_2O_5[6] and Na_2O–V_2O_5[7]) glasses containing 10 mol% Fe_2O_3, obtained by the present authors. In the K_2O- and Na_2O–V_2O_5 glasses,[6,7] all the Fe^{3+} ions proved to be present at the substitutional sites of the V^{5+} or V^{4+} ions constituting VO_4 tetrahedra. In the recent Mössbauer study of phosphorus vanadate (P_2O_5–V_2O_5) glasses,[8] it was concluded that introduction of P_2O_5 into the V_2O_5 matrix results in a structural change of the glass matrix from the layer structure originally composed of VO_5 tetragonal pyramids to a three-dimensional network structure composed of VO_4 tetrahedra. In contrast to these results, a neutron diffraction study performed by Wright et al.[9] showed that V^{5+} or V^{4+} ion is surrounded by five oxygen atoms in P_2O_5–V_2O_5, BaO–V_2O_5, and PbO–V_2O_5 glasses and that the vanadate glasses are composed of interconnected and distorted VO_5 tetragonal pyramids. A similar conclusion was obtained in EXAFS and XANES[10] and NMR and ESR[11] studies of P_2O_5–V_2O_5 glasses.

The present Mössbauer study was performed in order to elucidate the structural change of lithium, magnesium, and barium vanadate glasses, brought about by incorporating Li_2O, MgO, and BaO into V_2O_5 matrix. DTA measurements were performed in order to examine the structural change, such as a change in the coordination number of V^{5+} or V^{4+} ions and a formation of nonbridging oxygen atoms, through the composition dependency of the glass transition temperatures (T_g).

Experimental

Lithium, magnesium, and barium vanadate glasses containing 10 mol% Fe_2O_3 were prepared by melting the individual mixtures (1 g) of commercially available Li_2CO_3, $MgCO_3$, $BaCO_3$, V_2O_5, and Fe_2O_3, of guaranteed reagent grade. Each of the mixture was melted at 950—1000 °C for 1 h in an electric muffle furnace under the ambient atmosphere. Ten mol% Fe_2O_3 was incorporated into the individual mixture as a Mössbauer probe. After the fusion, each melt in a platinum crucible was quenched with ice-cold water. All the vanadate glasses prepared in the present study are almost black in color, having a metallic luster. Mössbauer and DTA measurements were performed on the pulverized glasses, according to the procedures reported in the previous papers.[6,8] A piece of metallic iron foil enriched with ^{57}Fe was used as a reference for the isomer shift. Powder of Al_2O_3 was used as a standard material in the DTA measurements.

Results and Discussion

A Mössbauer spectrum of Li_2O–V_2O_5 glass measured at room temperature is shown in Fig. 1, which indicates only the presence of paramagnetic Fe^{3+} ions of high spin state.[12,13] No absorption peak due to Fe^{2+} ions nor magnetic species is observed in any of

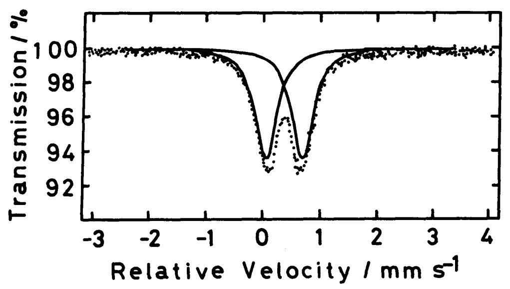

Fig. 1. Mössbauer spectrum of $30Li_2O \cdot 60V_2O_5 \cdot 10Fe_2O_3$ glass measured at room temperature.

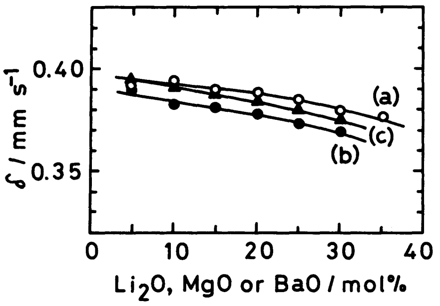

Fig. 2. Composition dependencies of the isomer shift (δ) of Fe^{3+} ions in (a) Li_2O–, (b) MgO–, and (c) $BaO–V_2O_5$ glasses containing 10 mol% Fe_2O_3.

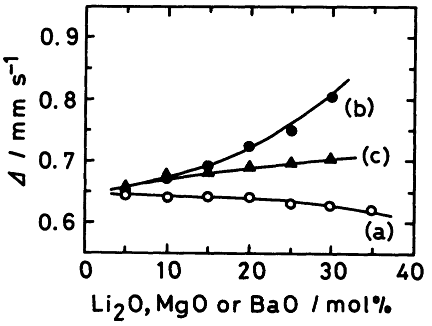

Fig. 3. Composition dependencies of the quadrupole splitting (Δ) of Fe^{3+} ions in (a) Li_2O–, (b) MgO–, and (c) $BaO–V_2O_5$ glasses containing 10 mol% Fe_2O_3.

the Mössbauer spectra. The linewidth (FWHM) is characteristic of the absorption peak due to iron in glasses, being in a range of 0.59—0.46 mm s^{-1}. All the isomer shifts of Fe^{3+} ions are located in a small range of 0.39—0.37 mm s^{-1} with respect to metallic iron, as is shown in Fig. 2. Earlier Mössbauer studies of several glasses[14–16] have shown that Fe^{3+} ions are present at tetrahedral environments in borate and silicate glasses. This is the case for the recent Mössbauer results on borate[17–20] and borosilicate[20–22] glasses obtained by the present authors' group. In these glasses,[17–22] all the isomer shift values are located in a range of 0.38—0.22 mm s^{-1} with respect to metallic iron. The experimental error for the isomer shift is usually estimated to be ±0.01 mm s^{-1}. Judging from the experimental results shown in these reviews and papers,[14–22] it is concluded that all the Fe^{3+} ions are present at tetrahedral environments in the Li_2O–, MgO–, and $BaO–V_2O_5$ glasses, forming FeO_4 tetrahedra. This conclusion indicates the presence of tetrahedral VO_4 units, because Fe^{3+} ions should be present either at the substitutional sites of the V^{5+} (or V^{4+}) ions constituting the skeleton of the glass matrix or at the interstitial sites in the glass matrix. (The presence of V^{4+} ions has already been confirmed by ESR measurements of several vanadate glasses, e.g., $P_2O_5–V_2O_5$ glasses.[8]) It is considered that coordination number of metal ions present at interstitial sites is usually larger than that of the metal ions at substitutional sites. The same conclusion on the presence of VO_4 tetrahedra has been obtained in the recent Mössbauer studies of K_2O–, Na_2O–, and $P_2O_5–V_2O_5$ glasses containing 10 or 5 mol % Fe_2O_3.[6–8] The isomer shift values show a distinct decrease with increasing Li_2O, MgO, or BaO content (Fig. 2). Similar composition dependency of isomer shift observed in $K_2O–V_2O_5$[6] and $Na_2O–V_2O_5$[7] glasses was ascribed to a formation of nonbridging oxygen atoms in VO_4 tetrahedra, because a simultaneous decrease in the isomer shift and the quadrupole splitting of Fe^{3+} ions was observed with increasing K_2O or Na_2O content. This is true in the case of $Li_2O–V_2O_5$ glasses studied in the present paper, where a simultaneous decrease in the isomer shift (Fig. 2) and the quadrupole splitting (Fig. 3) is observed with increasing Li_2O content. The experimental error for the quadrupole splitting is estimated to be ±0.02 mm s^{-1}. The decrease in the quadrupole splitting of Fe^{3+} ions is well ascribed to an increased symmetry of the iron–oxygen tetrahedra, because high-spin Fe^{3+} ions have a symmetric electron configuration of $3d^5$ in the outermost orbital and the electric field gradient brought about by the neighboring atoms or ions should primarily cause the nuclear quadrupole interaction. The simultaneous decrease in the isomer shift (Fig. 2) and the quadrupole splitting (Fig. 3) observed in $Li_2O–V_2O_5$ glasses is therefore ascribed to a formation of nonbridging oxygen atoms in VO_4 tetrahedra. Also, it is considered that a structural change of the glass matrix occurs from the two-dimensional layer structure originally composed of VO_5 tetragonal pyramids to a chain structure composed of VO_4 tetrahedra, similarly to the case of $K_2O–V_2O_5$[6] and $Na_2O–V_2O_5$[7] glasses.

On the other hand, increases in the quadrupole splitting are observed in the case of MgO– and $BaO–V_2O_5$ glasses (Fig. 3). A similar phenomenon was observed in $P_2O_5–V_2O_5$ glasses containing 5 mol% Fe_2O_3,[8] where an increase in the quadrupole splitting of Fe^{3+} ions, indicating a decreased symmetry of the FeO_4 (and VO_4) tetrahedra, was ascribed to a gradual change of the glass matrix from the layer structure originally composed of VO_5 tetragonal pyramids to the three-dimensional network structure composed of VO_4 tetrahedra. The same conclusion was drawn from the similar composition dependency of the glass transition temperatures of the P_2O_5–V_2O_5 glasses.[8] The increase in the quadrupole splitting of Fe^{3+} ions, observed in the case of MgO- and BaO–V_2O_5 glasses (Fig. 3), is therefore ascribed to a gradual change of the glass matrix from the two-dimensional network structure composed of VO_5 tetragonal pyramids to a highly complicated three-dimensional network structure composed of VO_4 tetrahedra. In contrast to Li_2O–V_2O_5 glasses, it is considered that nonbridging oxygen atoms are rarely formed in the VO_4 tetrahedra constituting the skeleton of MgO- and BaO–V_2O_5 glasses, because the quadrupole splitting values show a continuous increase with increasing MgO or BaO content. It is therefore concluded that fraction of nonbridging oxygen atoms decreases with increasing MgO or BaO content in the MgO- and BaO–V_2O_5 glasses. It can be seen from Fig. 3 that the quadrupole splitting of Fe^{3+} ions in the MgO–V_2O_5 glasses shows a more distinct composition dependency than that of the Fe^{3+} ions in the BaO–V_2O_5 glasses. This will be due to a large ionic potential of Mg^{2+} ion. (The ionic potential is generally denoted by Z/r, where Z is the charge of cation and r is the ionic radius.) It is speculated that cations having large ionic potential will bring about an increased chemical bond strength between the cations and neighboring oxygen atoms. As a result, the resultant structure will become more complicated.

Regarding the short-range (local) structure of vanadate glasses, all the recent[6–8] and present Mössbauer results are consistent with the IR results obtained by Dimitriev et al.[3] and also with the NMR results obtained by Segel and Creel.[4] (In these studies,[3,4] it was reported that all the vanadate glasses are composed of VO_4 tetrahedra.) Regarding the middle- or long-range structure, it is concluded that structure of the glass matrix (skeleton) strongly depends on the type of so-called "network modifier," and that the glass matrix of alkaline earth vanadate glasses has highly complicated three-dimensional network structure. This structural change is similar to that of P_2O_5–V_2O_5 glasses.[8] It is interesting to compare the present results on MgO- and BaO–V_2O_5 glasses with the previous results obtained by different methods, such as a neutron diffraction[9] result on P_2O_5- and BaO–V_2O_5 glasses, an EXAFS and XANES[10] result on P_2O_5–V_2O_5 glasses, and an NMR and ESR[11] result on P_2O_5–V_2O_5 glasses. In these studies, [9–11] coordination number of V^{5+} or V^{4+} ions was reported to be always 5 irrespective of the composition. It seems that apparently higher coordination number (5) was obtained in those studies[9–11] owing to a highly complicated three-dimensional network structure of the glass matrix.

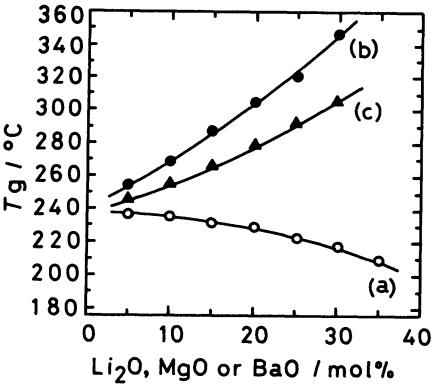

Fig. 4. Composition dependencies of the glass transition temperature (T_g) of (a) Li_2O-, (b) MgO-, and (c) BaO–V_2O_5 glasses containing 10 mol% Fe_2O_3.

Each DTA curve of the Li_2O-, MgO-, and BaO–V_2O_5 glasses containing 10 mol% Fe_2O_3 consists of an endothermic peak due to glass transition and one or a few exothermic peak(s) due to crytallization, similarly to the case of several vanadate glasses studied recently.[6–8] All the glass transition temperatures (T_g) are plotted in Fig. 4 against Li_2O, MgO, or BaO content. Previous Mössbauer and DTA studies of K_2O–V_2O_5[6] and Na_2O–V_2O_5[7] glasses revealed that T_g shows a distinct decrease when coordination number of V^{5+} or V^{4+} ions decreases from 5 to 4 and when nonbridging oxygen atoms are formed in the VO_4 tetrahedra. This is the case for the Li_2O–V_2O_5 glasses studied in the present paper, where the T_g shows a continuous decrease from 236 to 209 °C with increasing Li_2O content (Fig. 4). Considering the NMR result on KVO_3 glass[4] described above, i.e. the glass has a chain structure composed of VO_4 tetrahedra, the present Mössbauer and DTA results on the Li_2O–V_2O_5 glasses lead to the conclusion that a gradual structural change occurs from the two-dimensional layer structure originally composed of VO_5 tetragonal pyramids to the one-dimensional chain structure composed of VO_4 tetrahedra. (This corresponds to the decrease in the coordination number of V^{5+} and V^{4+} ions from 5 to 4.) It can be seen from Fig. 4 that a formation of nonbridging oxygen atoms in the VO_4 and FeO_4 tetrahedra is also reflected as a continuous decrease in T_g of the Li_2O–V_2O_5 glasses. On the other hand, an increase in T_g is observed with increasing MgO or BaO content in the MgO- and BaO–V_2O_5 glasses (Fig. 4). This is in good agreement with the Mössbauer results described above, i.e., a gradual change of the glass matrix occurs from the original layer structure composed of VO_5 tetragonal pyramids to the three-dimensional network structure composed of VO_4 tetrahedra. It should be noted that the T_g shows a distinct increase in spite of the decreased coordination number of V^{5+}or V^{4+} ions from 5 to 4, as described above. Similar results were obtained in the DTA measurements of P_2O_5–V_2O_5 glasses[8)] having a three-dimensional network structure. The difference in the structural change between alkali and alkaline earth vanadate glasses will be caused by the different positive charges of alkali (+1) and alkaline earth (+2) metal ions present at the interstitial sites. It is also considered that higher ionic potential of alkaline earth metal ions (e.g. Mg^{2+} ions) causes the formation of highly complicated three-dimensional network structure.

It is concluded that all the Fe^{3+} ions are tetrahedrally coordinated with oxygen atoms and are present at the substitutional sites of V^{5+} or V^{4+} ions, which constitute the skeleton of vanadate glasses in the form of VO_4 tetrahedra. It is also concluded that introduction of Li_2O into V_2O_5 matrix results in a gradual change of the glass matrix from the original layer structure composed of VO_5 tetragonal pyramids (or trigonal bipyramids) to the chain structure composed of VO_4 tetrahedra. It is considered that VO_4 tetrahedra have some nonbridging oxygen atoms and that the structural change of Li_2O–V_2O_5 glasses is essentially the same as that of Na_2O- and K_2O–V_2O_5 glasses. On the other hand, it is concluded that introduction of MgO or BaO into the V_2O_5 matrix results in a gradual change of the glass matrix from the original layer structure composed of VO_5 tetragonal pyramids to the highly complicated three-dimensional network structure composed of VO_4 tetrahedra, similarly to the structural change of P_2O_5–V_2O_5 glasses.

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References

1) A. Byström, K. A. Wilhelmi, and O. Brotzen, *Acta Chem. Scand.*, **4**, 1119 (1950).

2) K. Jansen and G. Sperlich, *Phys. Status Solidi B*, **55**, 495 (1973).

3) Y. Dimitriev, V. Dimitrov, M. Arnaudov, and D. Topalov, *J. Non-Cryst. Solids*, **57**, 147 (1983).

4) S. L. Segel and R. B. Creel, *Can. J. Phys.*, **48**, 2673 (1970).

5) H. T. Evans, *Z. Kristallogr.*, **114**, 257 (1960).

6) T. Nishida and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **60**, 941 (1987).

7) T. Nishida, M. Ogata, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **60**, 2887 (1987).

8) T. Nishida, M. Ogata, and Y. Takashima, *J. Non-Cryst. Solids*, **94**, 229 (1987).

9) A. C. Wright, C. A. Yarker, P. A. V. Johnson, and R. N. Sinclair, *J. Non-Cryst. Solids*, **76**, 333 (1985).

10) S. Stizza, I. Davoli, O. Gzowski, L. Murawski, M. Tomellini, A. Marcelli, and A. Bianconi, *J. Non-Cryst. Solids*, **80**, 175 (1986).

11) F. R. Landsberger and P. J. Bray, *J. Chem. Phys.*, **53**, 2757 (1870).

12) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy," Chapman and Hall Ltd., London (1971) Chap. 3.

13) R. Ingalls, F. Van der Woude, and G. A. Sawatzky, "Iron and Nickel," in "Mössbauer Isomer Shifts," ed by G. K. Shenoy and F. E. Wagner, North-Holland Pub Co., Amsterdam (1978), Chap. 7.

14) C. R. Kurkjian, *J. Non-Cryst. Solids*, **3**, 157 (1970).

15) J. M. D. Coey, *J. Phys.*, **35**, C6-89 (1974).

16) W. Müller-Warmuth and H. Eckert, *Phys. Rep.*, **88**, 91 (1982).

17) T. Nishida and Y. Takashima, *J. Non-Cryst. Solids*, **37**, 37 (1980).

18) T. Nishida, T. Shiotsuki, and Y. Takashima, *J. Non-Cryst. Solids*, **41**, 161 (1980).

19) T. Nishida, T. Hirai, and Y. Takashima, *J. Non-Cryst. Solids*, **43**, 221 (1981).

20) T. Nishida and Y. Takashima, "Application of Mössbauer Effect on the Crystallization of Several Glasses," in "Industrial Applications of the Mössbauer Effect," ed by G. J. Long and J. G. Stevens, Plenum Press, New York and London (1986), pp. 409—422.

21) T. Nishida, T. Hirai, and Y. Takashima, *Phys. Chem. Glasses*, **22**, 94 (1981).

22) T. Nishida, T. Hirai, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **54**, 3735 (1981).