Electrical conductivity and local structure of iron-containing lithium barium vanadate glass

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Abstract. A relationship between the local structure and electrical conductivity of lithium barium iron vanadate glass with a composition of \(x\)Li\(_2\)O·(20-x)BaO·10Fe\(_2\)O\(_3\)·70V\(_2\)O\(_5\), abbreviated as \(x\)LBFV glass, was investigated by means of \(^{57}\)Fe-Mössbauer spectroscopy, differential thermal analysis (DTA), as well as DC four-probe method. When the Li\(_2\)O content increased from 0 to 20 mol\%, a constant isomer shift (\(\delta\)) value of 0.35±0.01 mm s\(^{-1}\) and a decreasing quadrupole splitting (\(\Delta\)) value from 0.71 to 0.67±0.01 mm s\(^{-1}\) were observed in the Mössbauer spectra. From the DTA curves, decrease in both glass transition temperature (\(T_\text{g}\)) and crystallization temperature (\(T_\text{c}\)) was confirmed from 317 to 236±5 °C and from 374 to 299±2 °C, respectively. A large slope value of 1560 °C/mm s\(^{-1}\) was estimated from ‘\(T_\text{g}-\Delta\) plot’, showing that the Fe\(^{3+}\) acts as a network former (NWF). When the \(x\)LBFV glass with ‘\(x\)’ of 20 was heated up to 125 °C, a larger increase in the electric conductivity (\(\sigma\)) was observed from 3.2×10\(^{-5}\) to 1.3×10\(^{-3}\) S cm\(^{-1}\). It was found that replacement of Li\(^+\) for Ba\(^{2+}\) reduces the local distortion of FeO\(_4\) (\(T_\text{d}\)), and increases the temperature dependence of electrical conductivity.

1. Introduction

Vanadate glass is known as a semiconducting oxide glass with an electrical conductivity (\(\sigma\)) of 10\(^{-7}\)-10\(^{-5}\) S cm\(^{-1}\), caused by 3d electron hopping from V\(^{VI}\) to V\(^{V}\) [1]. Nishida et al. reported that a drastic increase in \(\sigma\) was observed after annealing of K\(_2\)O-V\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) and Li\(_2\)O-Fe\(_2\)O\(_3\)-V\(_2\)O\(_5\)-P\(_2\)O\(_5\) glasses [2,
3]. Barium iron vanadate glass, BaO-Fe$_2$O$_3$-V$_2$O$_5$, has already been registered as a Japanese patent [4], with a trade mark of ‘NTA glass$^{TM}$’. Recently, Kubuki et al. revealed that ‘NTA glass$^{TM}$’ has a $\sigma$ of 1 S cm$^{-1}$ after a prolonged heat treatment, owing to a structural relaxation [5].

In the present study, substitution of Li$^{+}$ for Ba$^{2+}$ in NTA glass$^{TM}$ was investigated in order to achieve higher electrical conductivity. A relationship between the local structure and electrical conductivity of iron-containing lithium barium vanadate glasses was investigated by means of $^{57}$Fe-Mössbauer spectroscopy, differential thermal analysis (DTA) and electrical conductivity measurement.

2. Experimental

New vanadate glass expressed by $x$Li$_2$O·(20-$x$)BaO·10Fe$_2$O$_3$·70V$_2$O$_5$, hereafter abbreviated as xLBFV glass, was prepared by a conventional melt-quenching method. Li$_2$O content ($x$) was changed from 0 to 20 mol %. Weighed amounts of Li$_2$CO$_3$, BaCO$_3$, V$_2$O$_5$ and Fe$_2$O$_3$ of a reagent grade were well mixed in an agate mortar and heated at 1100 °C for 1 h with a platinum crucible. Dark brown glass samples were obtained by dipping the bottom of the crucible into ice-cold water. For Mössbauer measurement, enriched isotope of $^{57}$Fe$_2$O$_3$ ($^{57}$Fe = 95.54 %) was used. Mössbauer spectra were recorded by a constant acceleration method with a source of $^{57}$Co(Rh). DTA was conducted from RT to 500 °C by changing the heating rate from 5 to 10, 15, 20 and 30 K min$^{-1}$. $\alpha$-Al$_2$O$_3$ was used as a reference of the temperature. The electrical conductivity ($\sigma$) was measured by a dc-four probe method at temperatures ranging from RT to 125 °C.

3. Results and Discussion

Mössbauer spectra of xLBFV glass with ‘$x$’ of 0, 5, 10, 15 and 20 were shown in Figure 1. All the spectra were composed of paramagnetic doublet due to the tetrahedral Fe$^{III}$. When the Li$_2$O content increased, a constant isomer shift ($\delta$) value was obtained for 0.35 (±0.01) mm s$^{-1}$, together with a small decrease in the quadrupole splitting ($\Delta$) value from 0.71 to 0.69, 0.68, 0.67 and 0.66 (±0.01) mm s$^{-1}$. These results indicate that Fe-O bond strength remained constant, and that the local distortion of FeO$_4$ tetrahedra became smaller by substituting Li$^{+}$ for Ba$^{2+}$.

![Figure 1. Mössbauer spectra of xLBFV glass with ‘$x$’ of 0, 5, 10, 15 and 20.](image)

DTA curves of xLBFV glass are depicted in Figure 2. Both glass transition temperature ($T_g$) and crystallization temperature ($T_c$) decreased from 317 to 284, 274, 258 and 236 (±5) °C, and from 374 to 346, 331, 314 and 299 (±2) °C, respectively. These results show that the thermal durability was
lowered by the introduction of Li$_2$O. A linear relationship between $T_g$ and $\Delta$ for oxide glasses, discovered by Nishida [6], and denominated as ‘$T_g$-$\Delta$ rule’, is expressed by:

$$T_g = a \Delta + b$$

When Fe$^{3+}$ ion is located at a network former (NWF) site, slope ‘$a$’ becomes more than 680 $^\circ$C/mm s$^{-1}$. While a smaller ‘$a$’ value of 35 $^\circ$C/mm s$^{-1}$ is obtained when Fe$^{3+}$ acts as a network modifier (NWM).

As shown in Figure 3, a large ‘$a$’ value of 1560 $^\circ$C/mm s$^{-1}$, obtained from the ‘$T_g$-$\Delta$ plot’, indicates that the Fe$^{3+}$ plays a role of NWF. The activation energy for crystallization ($E_a$) can be calculated by Kissinger equation [7], i. e.,

$$\ln \left( \frac{T_c^2}{\alpha} \right) = \frac{E_a}{R} T_c + \text{const.}$$

where, $\alpha$ and $R$ are heating rate and gas constant, respectively. The $E_a$ value of xLBVF glass was varied from 2.3 to 1.7, 1.6, 1.9 and 2.3 ($\pm$0.2) eV with an increase of Li$_2$O content. Because the chemical bond energy of V-O is reported to be 3.9-4.9 eV [8]. It can be considered that the glass skeleton structure composed by VO$_4$ and VO$_5$ was not affected by the introduction of Li$_2$O.
A temperature dependence of the electric conductivity ($\sigma$) of the xLBFV glass is shown in Figure 4. Along with an increase in the measuring temperature from RT to 125 °C, $\sigma$ value was increased from $3.2 \times 10^{-5}$ to $1.3 \times 10^{-3}$ S cm$^{-1}$ in xLBFV glass with ‘x’ of 20 (figure 4(c)), while a smaller increase in $\sigma$ value was observed from $2.8 \times 10^{-5}$ to $2.4 \times 10^{-4}$ S cm$^{-1}$ when ‘x’ was 0 (figure 4(a)). It is noteworthy that the temperature dependence of $\sigma$ value is increased by substituting Li$^+$ for Ba$^{2+}$ because of higher ionic mobility of Li$^+$. Temperature dependence of electric conductivity can be expressed as Arrhenius equation, i.e.,

$$\sigma = \sigma_0 \exp \left( -\frac{W}{kT} \right)$$

(3)

where $W$ and $k$ are activation energy for electric conduction and Boltzmann constant, respectively. When the Li$_2$O content was increased from 0 to 10 and 20, $W$ value gradually increased from 0.19 to 0.25 and 0.34 eV, as represented in Figure 5. This result shows that the temperature dependence in the $\sigma$ value of xLBFV glass is enhanced by the introduction of Li$^+$. It can be concluded that the temperature dependence of the electrical conductivity is strongly affected by the decrease in local distortion of FeO$^4$ tetrahedra, as reflected in the as $\Delta$ value of Mössbauer spectra.

4. Summary
A relationship between the local structure and electric conductivity of lithium barium iron vanadate glass with a composition of $x$Li$_2$O・(20-x)BaO・10Fe$_2$O$_3$・70V$_2$O$_5$ (xLBFV) was investigated. When the Li$_2$O content was increased, local distortion of FeO$_4$ tetrahedra was decreased; a decrease of $\Delta$ value was observed from 0.71 to 0.67 mm s$^{-1}$ in the Mössbauer spectra. In addition, both $T_g$ and $T_c$ values respectively decreased from 317 to 236 °C and from 374 to 299 °C, showing that the thermal durability was lowered by the introduction of Li$^+$. From the ‘$T_g$-\Delta’ plot, a large slope value of 1560 °C/mm s$^{-1}$ was estimated, indicating that the Fe$^{3+}$ acts as a NWF. A larger increase in the electrical conductivity from $3.2 \times 10^{-5}$ to $1.3 \times 10^{-3}$ S cm$^{-1}$ was observed when xLBFV glass with ‘x’ of 20 was heated from RT to 125 °C. This result indicates that the temperature dependence of the electrical conductivity was increased by substituting Li$^+$ for Ba$^{2+}$.

It is concluded that the electric conductivity is strongly affected by the local distortion of FeO$_4$, VO$_4$ and probably VO$_5$ units.

Acknowledgement
One of the authors (SK) expresses his great gratitude for the support by Electric Technology Research Foundation of Chugoku.

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