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Influence of rare earth additives and boron component on electrical conductivity of sodium rare earth borate glasses

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Abstract

Sodium rare earth borate glasses $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ (RE = Sm, Gd, Dy, Ho, Y, Er, and Yb), were prepared from a mixture of Na_2CO_3, RE_2O_3 and B_2O_3, and their properties as an Na^+ ionic conductor were investigated. Density increased with increasing atomic weight of RE. Crystallization temperature and crystal melting temperature of the present borate system was lower than that of the previously reported silicate and germanate system. Results of the ^{11}B NMR measurement suggested that half of all boron atoms are coordinated by four oxide ions to give a $[BO_4]$ tetrahedral unit and the others are coordinated by three oxide ions to give a $[BO_3]$ planar triangular unit. The electrical conductivity slightly decreased with increasing the ionic radius of RE^{3+}. $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass exhibited the electrical conductivity which is about one order of magnitude lower than those of the previously reported $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ and $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(GeO_2)_{57.1}$ glasses. It was assumed that this lower electrical conductivity is due to the lower content of Na^+ ions as conduction species in the former glass, compared with the latter two glasses.

Keywords: C. Ionic conductivity; C. Thermal properties; D. Glass

1. Introduction

Na-β″-Al_2O_3 ceramics (4.2×10^{-2} S cm^{-1} at 200 °C) and $Na_3Zr_2Si_2PO_{12}$ ceramics (6.7×10^{-2} S cm^{-1} at 200 °C) are well known as high Na^+ ionic conductors, and some of them have been commercialized as solid electrolyte materials in the Na-S cells and the carbon dioxide gas sensors. Besides these, Shannon et al. reported that a series of ceramics, $Na_5RESi_4O_{12}$ (RE = Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), shows the highest Na^+ ionic conductivity (10^{-2}–10^{-1} S cm^{-1} at 200 °C) [1]. However, ceramic materials have some disadvantages that the molding and processing are relatively difficult, and the chemical durability is not so good due to the presence of grain boundaries. In contrast, glass materials have no such disadvantages, and therefore, have been widely investigated to develop the higher Na^+ ionic conductors [2]. Previously, we prepared a series of $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses, the composition of which is similar to the $Na_5RESi_4O_{12}$ ceramics as the high Na^+ ionic conductors reported by Shannon et al. [1], and a series of $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(GeO_2)_{57.1}$ glasses, where Si atoms in the $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses are replaced by Ge atoms, and investigated their electrical properties [3–5]. $(Li_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ and $(K_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses were also prepared, and their physical, chemical and electrical properties were compared with $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses [6,7]. Moreover, we reported response characteristics of all-solid-state pH sensor designed from the $(Li_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ glass as an indicator electrode and Ag/AgCl reference electrode coated with Nafion film [8,9].

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Since the ionic radius of the 4-coordinated B^{3+} (0.012 nm) is much smaller than those of the 4-coordinated Si^{4+} (0.026 nm) and Ge^{4+} (0.040 nm) ions, it can be expected that the interspaces are narrower in the $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ (RE = rare earths) glasses, compared with those in the previously reported $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ and $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(GeO_2)_{57.1}$ glasses. Another interest is the effect of RE^{3+} ions in the network structure on the migration of Na^+ ions. From these points of view, we prepared, in this work, a series of $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses (RE = Sm, Gd, Dy, Ho, Y, Er, Yb), in order to investigate the effect of the B replacement and the ionic size of rare earth on their electrical properties.

2. Experimental

Reagent grade Na_2CO_3 and B_2O_3, (Wako Pure Chemical Industries Ltd.) and RE_2O_3 (Shin-Etsu Chemical Co. Ltd.; 99.9% purity, RE = Sm, Gd, Dy, Ho, Y, Er, Yb) were used as starting materials. After mixing them in the molar ratio of $Na_2O:RE_2O_3:B_2O_3 = 5:1:8$, the mixture was melted in a platinum crucible at 1100 °C for 1 h in an air atmosphere using an electronic furnace. The melt was quenched on the iron plate and press-molded. The rare earth doped sodium borate glasses were obtained by annealing at 500 °C in order to prevent the distortion and crack. The density was calculated by the Archimedes method. Powder X-ray diffraction (XRD), nuclear magnetic resonance spectroscopy (NMR), and differential thermal analysis (DTA) were performed using the glass sample powders obtained after grinding in a zirconia mortar. The XRD measurement was carried out using CuKα radiation in the 2θ range of 10°–80° with Rigaku MiniFlex. The ^{11}B NMR spectrum was measured for $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass with a Bruker MSL-300 spectrometer, using the standard HBO_3 aqueous solution. The DTA measurement was carried out by heating the glass sample powders (20 mg) at a heating rate of 10 °C min^{-1} in an air stream (50 ml min^{-1}) from room temperature to 800 °C. Glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) were estimated from the DTA results. Electrical properties were measured in the temperature range of 200–400 °C and in the frequency range of 100 Hz to 10 MHz with an impedance analyzer (HP4194A), putting the Ag electrodes on both sides of samples. Electrical conductivities were estimated by the complex impedance analysis.

3. Results and discussion

3.1. Appearance, X-ray diffraction and density

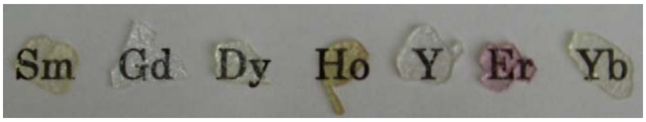

Fig. 1. Appearance for $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ (RE = Sm, Gd, Dy, Ho, Y, Er and Yb) glasses.

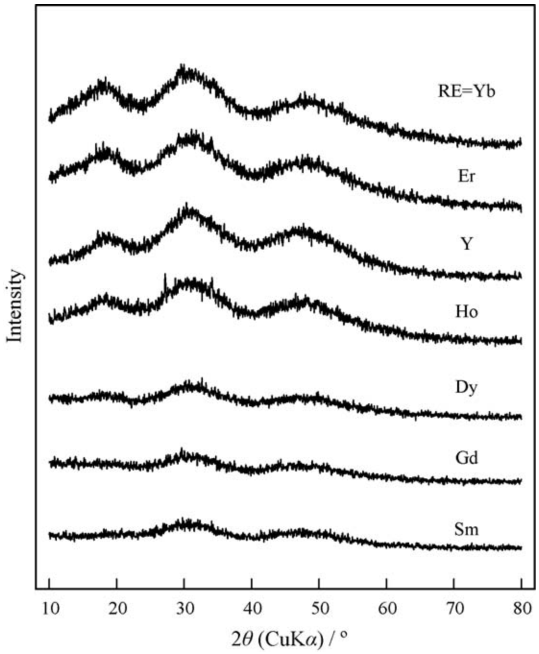

Fig. 2. XRD patterns for $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses.

As shown in Fig. 1, all the prepared glass samples were transparent and no inhomogeneous phases were visually recognized after the crystallization was completed. Each sample exhibited the characteristic color of rare earth ion as a component: yellow for the Sm, pale yellow for the Dy, orange for the Ho, pink for the Er and colorless for the other samples. The XRD patterns are given in Fig. 2. Three halo patterns caused by interatomic distances such as B–O and B–B (B–O–B), etc. were observed around $2\theta = 20°, 30°, 50°$ for all the glass samples [10], and no other diffraction peaks attributable to the crystalline phases were recognized, indicating the formation of amorphous $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses by quenching on an iron plate after melting at 1100 °C. Density of the borate system glasses, which increased almost linearly with increasing the atomic weight of RE as shown in Fig. 3, was

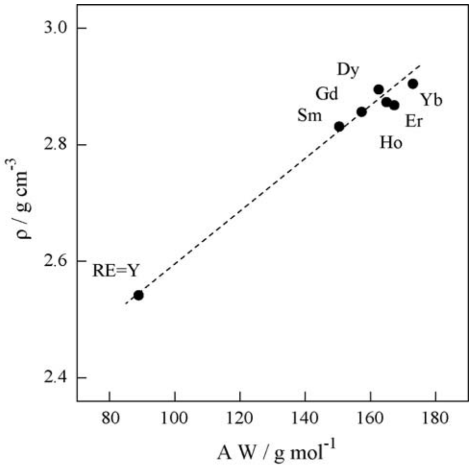

Fig. 3. Relationship between atomic weight of RE and density of $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses.

approximately 0.35 and 0.70 g cm^{-3} lower than those of the previous $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ and $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(GeO_2)_{57.1}$ glasses, respectively [3–5].

3.2. ^{11}B NMR

Fig. 4 shows ^{11}B NMR spectrum for the $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass. The spectrum consists of two types of resonance signals; a sharp one around −20 ppm attributable to the four-coordinated boron atoms (marked by N_4), and two broad ones around −10 and −30 ppm attributable to the three-coordinated boron atoms (marked by N_3). Peak separation in the spectrum was done by considering the asymmetry of nuclear quadrupole, and the atomic ratio of N_4 to N_3 was estimated to be 50/50 from the area of each peak. This indicates that half of all boron atoms are coordinated by four oxide ions to give a $[BO_4]$ tetrahedral unit and the others are coordinated by three oxide ions to give a $[BO_3]$ planar triangular unit.

3.3. DTA

Fig. 5 shows a typical DTA result for the $(Na_2O)_{35.7}(Er_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass. An endothermic peak (T_g) due to the glass transition was observed around 497 °C. Exothermic (T_c) and endothermic peaks (T_m) due to the crystallization and the melting of the crystal appeared around 562 and 789 °C, respectively. Relationship between the ionic radius of RE^{3+}, and T_g, T_c, T_m determined from the DTA curve is shown in Fig. 6. T_c values of the present $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses were about 40 and 220 °C lower than those of the previous $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(GeO_2)_{57.1}$ glasses, and the $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses, respectively. Similarly, T_m values were about 200 and 350 °C lower than those of the corresponding germanate and silicate system glasses. Generally, T_g, T_c and T_m are important, not only in determining the limit of working temperatures of the glass materials but also in estimating the bond strength between rare earth and oxide ions.

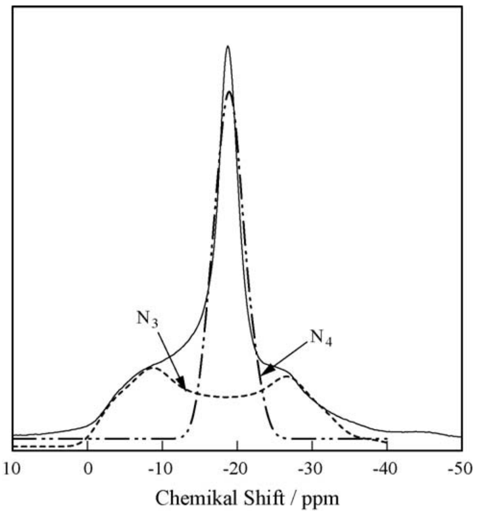

Fig. 4. ^{11}B NMR spectrum of $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass.

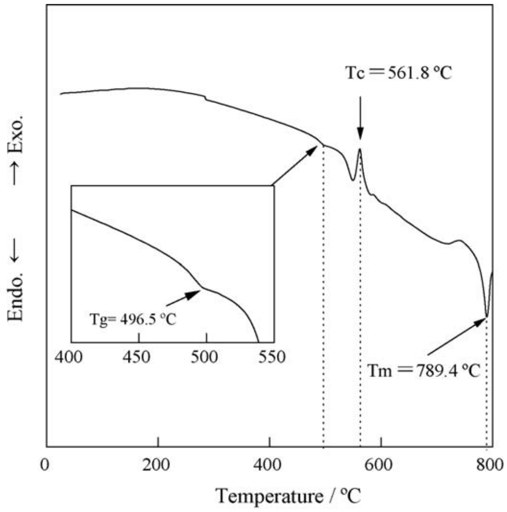

Fig. 5. DTA curve of $(Na_2O)_{35.7}(Er_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass. T_g: glass transition temperature, T_c: crystallization temperature, T_m: crystal melting temperature.

As shown in Fig. 6, T_g, T_c and T_m values linearly decreased with an increase of ionic radius of rare earth. It can be presumed that the RE^{3+} ions, as well as Na$^+$ ion, doped into the glass system behave as a charge compensator for the $[BO_4]^-$ tetrahedral units, and also play a role for forming the nonbridging oxygen sites. Therefore, when the larger RE^{3+} ions are introduced into the glass system, the glass network structure based on the B–O bonds becomes less sturdy, resulting in the lowering of T_g, T_c and T_m with the increase of RE^{3+} size. This was also the case in the $(R_2O)_x(B_2O_3)_{1-x}$ (R = Li, Na, K, Rb, Cs) glasses and the $(MO)_x(B_2O_3)_{1-x}$ (M = Mg, Ca, Sr, Ba) glasses reported by Yiannopoulos et al. [11].

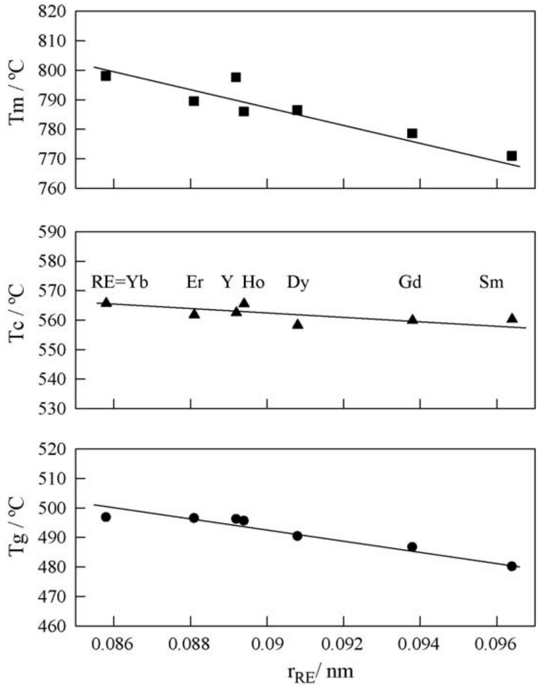

Fig. 6. Relationship between ionic radius of RE^{3+} and glass transition (T_g), crystallization (T_c) and crystal melting (T_m) temperatures of $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses.

3.4. Electrical conductivity

Electrical conductivity was estimated by the complex impedance analysis. A typical complex impedance plot at 200 °C was represented by a semicircle, probably corresponding to the bulk component, which passed through the origin in the higher frequency region, and by a spike, probably arising from the electrolyte-electrode behavior, in the lower frequency region. The semicircle was extrapolated to the real axis in the lower frequency region, and the electrical conductivity at 200 °C was determined from the intersection at the real axis. As the temperature was increased, the semicircle was diminished, and only a spike became observed at 400 °C. In this case, the electrical conductivity at 400 °C was determined from the intersection of the real axis and the spike.

Plots of the electrical conductivities of $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses at 25, 200, 300 and 400 °C against the ionic radii of rare earths (RE^{3+}) are shown in Fig. 7. Values at 25 °C were estimated by the extrapolation from the conductivities at 200, 300 and 400 °C shown in Fig. 7, because the resistances at 25 °C were very high and impossible to measure using our impedance analyzer. Electrical conductivities at each temperature were very slightly decreased with increasing the ionic radius of RE^{3+}, and the glass of RE = Yb showed the highest electrical conductivities which were 3.59×10^{-9}, 1.57×10^{-5}, 2.20×10^{-4} and 1.21×10^{-3} S cm^{-1}, at 25, 200, 300 and 400 °C, respectively. Similar tendency was recognized in the previously reported $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses [3,4]. In contrast to the $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ and $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses, the RE^{3+} size dependence of electrical conductivity was not observed for the $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(GeO_2)_{57.1}$ glasses [5]. Since the ionic radius of the 4-coordinated Ge^{4+} (0.040 nm) is much larger than those of the 4-coordinated B^{3+} (0.012 nm) and Si^{4+} (0.026 nm) ions, the interspaces necessary for the migration of Na^+ are satisfactorily enlarged by the Ge^{4+}, and hence electrical conductivity of the $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(GeO_2)_{57.1}$ glasses may not be affected by the introduction of RE^{3+} ions into the network structure [5,12].

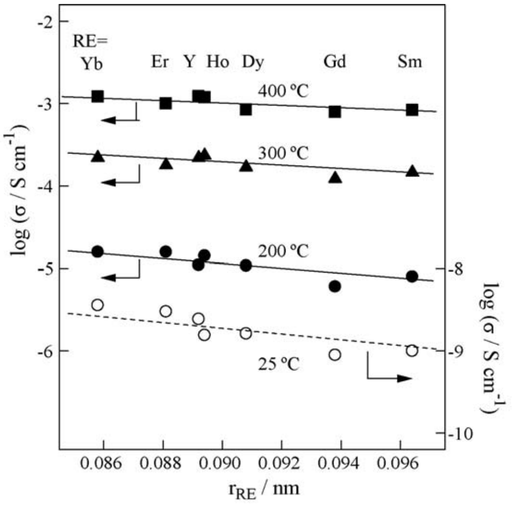

Fig. 7. Relationship between the ionic radius of RE^{3+} and electrical conductivity of $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses.

The electrical conductivity data are parameterized by the Arrhenius equation:

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

where σ, σ_0, E, k and T are the electrical conductivity, pre-exponential factor, activation energy, Boltzmann constant and absolute temperature, respectively. Arrhenius plots of log (σT) versus $1/T$ for the $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$, $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$, and $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(GeO_2)_{57.1}$ glasses are shown in Fig. 8. The electrical conductivity of the borate system glass was about one order of magnitude lower than those of the silicate and germanate system glasses [3–5]. This may be because the content of Na^+ ions as electrical conduction species in the borate system glass is lower, compared with those in the silicate and germanate system glasses; value of Na/(Na + Y + B) is 0.357, whereas that of Na/(Na + Y + Si) and Na/(Na + Y + Ge) is 0.500. In order to confirm whether this discussion is reasonable or not, we prepared further sodium yttrium borate glasses with the different Na_2O contents from the $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass. Results showed that the glass materials cannot be obtained when x-values in the $(Na_2O)_x(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass are higher than 35.7. Instead, the $(Na_2O)_{10.0}(Y_2O_3)_{10.0}(B_2O_3)_{80.0}$ and $(Na_2O)_{25.0}(Y_2O_3)_{8.3}(B_2O_3)_{66.7}$ glasses were able to be prepared, and their electrical conductivities were determined. From an extrapolation of the electrical conductivities for the $(Na_2O)_{10.0}(Y_2O_3)_{10.0}(B_2O_3)_{80.0}$, $(Na_2O)_{25.0}(Y_2O_3)_{8.3}(B_2O_3)_{66.7}$ and $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses, the electrical conductivity of an imaginary

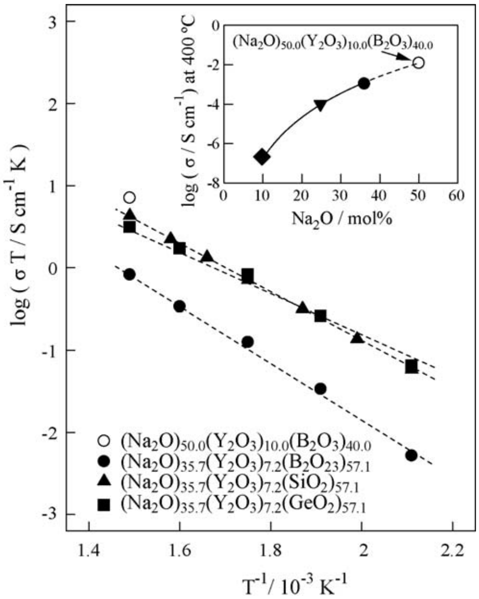

Fig. 8. Arrhenius plots of log(σT) vs. $1/T$ for $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$, $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ and $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(GeO_2)_{57.1}$ glasses. The log(σT) value at 400 °C for the imaginary $(Na_2O)_{50.0}(Y_2O_3)_{10.0}(B_2O_3)_{40.0}$ is also shown as an open circle (○), where the electrical conductivity was estimated from the extraplorated curve shown in the insert.

$(Na_2O)_{50.0}(Y_2O_3)_{10.0}(B_2O_3)_{40.0}$ glass was estimated to be 1.21×10^{-2} S cm^{-1} at 400 °C, as shown in the insertion of Fig. 8. This extrapolated electrical conductivity of $(Na_2O)_{50.0}(Y_2O_3)_{10.0}(B_2O_3)_{40.0}$ glass is close to those of the $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ glass and the $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(GeO_2)_{57.1}$ glass (see Fig. 8). Here, it should be noted that the Na:Y:B atomic ratio (5:1:4) in $(Na_2O)_{50.0}(Y_2O_3)_{10.0}(B_2O_3)_{40.0}$ is very close to the Na:Y:Si and Na:Y:Ge atomic ratio (4.96:1:3.97) in $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ and $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(GeO_2)_{57.1}$, i.e., the Na^+ contents in these three glasses are similar. From these results, it is assumed that the present type of Na–RE–B, Na–RE–Si and Na–RE–Ge system glasses exhibits almost the same electrical conductivity, even if ionic radii of the 4-coordinated B^{3+} (0.012 nm), Si^{4+} (0.026 nm) and Ge^{4+} (0.040 nm) ions forming the network structure should be different, when the contents of Na^+ ions responsible for the ionic conduction are similar to each other.

4. Conclusions

A series of rare earth doped sodium silicate glasses $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ (RE = Sm, Gd, Dy, Ho, Y, Er, and Yb), were prepared by melting a mixture of Na_2CO_3, RE_2O_3 and B_2O_3 at 1100 °C and then quenching the melts on an iron plate. Their properties were summarized as follows:

1. XRD results suggested that all the prepared glass samples are amorphous.
2. All the glasses were transparent, and showed the characteristic color of the component rare earth ion.
3. Density of the glasses was almost linearly increased with an increase of atomic weight of RE.
4. The ^{11}B NMR spectral measurement revealed that the content of the $[BO_4]$ tetrahedral unit is almost equal to that of the $[BO_3]$ planar triangular unit in the $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass.
5. Glass transition (T_g), crystallization (T_c) and crystal melting (T_m) temperatures showed a tendency to decrease with an increase of ionic radius of RE^{3+}.
6. The highest electrical conductivity was achieved for $(Na_2O)_{35.7}(Yb_2O_3)_{7.2}(B_2O_3)_{57.1}$ glass. Electrical conductivities of $(Na_2O)_{35.7}(RE_2O_3)_{7.2}(B_2O_3)_{57.1}$ glasses were very slightly decreased with an increase of ionic radius of RE^{3+}.
7. Electrical conductivity of the present borate system glass ($(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$) were about one order of magnitude lower than those of the previously reported silicate system glass ($(Na_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$) and germanate system glass ($(Na_2O)_{35.7}(Y_2O_3)_{7.2}(GeO_2)_{57.1}$). This may be because the content of Na^+ ions as electrical conduction species in the borate system glass is lower, compared with those in the silicate and germanate system glasses. It was assumed that almost the same electrical conductivity will be obtained in the present type of glasses $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(B_2O_3)_{57.1}$, $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ and $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(GeO_2)_{57.1}$, if the contents of Na^+ ion as an ionic conduction species are similar to each other.

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