Electrical Properties of $(\text{K}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ (RE = Sm, Gd, Dy, Ho, Y, Er, Yb) Glasses

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$(\text{K}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ (RE = Sm, Gd, Dy, Ho, Y, Er, Yb) ガラスの電気特性

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Seven kinds of potassium rare earth silicate glasses, $(\text{K}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ (RE = Sm, Gd, Dy, Ho, Y, Er, Yb), were prepared by melting a mixture of K_2CO_3 , RE_2O_3 and SiO_2 . Density increased with increasing atomic weight of RE. An exothermic peak attributable to crystallization was observed in the range between 720 and 800°C. Powder X-ray diffraction analysis showed the formation of two distinct phases, KREO_2 and K_2SiO_3 , above crystallization temperature. The conductivity of $(\text{K}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass was similar to those of $\text{K}_5\text{YSi}_4\text{O}_{12}$ ceramics with the same composition and $(\text{K}_2\text{O})_{36}(\text{SiO}_2)_{64}$ glass not containing Y_2O_3 .

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1. Introduction

Since Shannon and his coworkers found that the rare-earth doped sodium silicate ceramics, $\text{Na}_5\text{RESi}_4\text{O}_{12}$ (RE = Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), exhibit a high Na^+ ionic conduction in 1978, various alkali metal rare earth silicate ceramics such as MRESiO_4 (M = Li, Na, K, Rb, Cs) and $\text{K}_{10}\text{NdSi}_{14}\text{O}_{39}$ have been reported.^{(1)–(5)} However, ceramics have some disadvantages of the deterioration of chemical durability due to the presence of grain boundaries and the difficult molding and mechanical processing. In order to overcome these disadvantages, glasses and crystallized glasses without grain boundaries have been actively developed. Among them, $(\text{Li}_2\text{O})_{43.4}(\text{Y}_2\text{O}_3)_{5.3}(\text{SiO}_2)_{51.3}$ and $(\text{Na}_2\text{O})_{37.9}(\text{Y}_2\text{O}_3)_{7.6}(\text{SiO}_2)_{54.5}$ glasses, and crystallized $\text{Na}_{3.9}\text{RE}_{0.6}\text{P}_{0.3}\text{Si}_{2.7}\text{O}_9$ glass were reported to show high ionic conduction.^{(6)–(11)} Recently, we successfully prepared a series of alkali-metal rare-earth silicate glasses, $(\text{R}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ (R = Na, Li; RE = Sm, Gd, Dy, Ho, Y, Er, Yb), with the same composition as the Shannon's ceramics, $\text{Na}_5\text{RESi}_4\text{O}_{12}$, and investigated their ionic conductivities.^{(12),(13)} Our results showed that the conductivity of $(\text{Li}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass ($8.0 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ at 200°C) was about 2.5 orders of magnitude higher than that of the corresponding $\text{Li}_5\text{YSi}_4\text{O}_{12}$ ceramic ($3.0 \times 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ at 200°C) consisting of Li_2SiO_3 and $\text{Y}_2\text{Si}_2\text{O}_7$ phases, whereas $(\text{Na}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass ($1.3 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 200°C) was about two orders of magnitude lower than that of the corresponding $\text{Na}_5\text{YSi}_4\text{O}_{12}$ ceramic ($4 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 200°C).

In this work, a series of potassium rare earth silicate glass, $(\text{K}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ (RE = Sm, Gd, Dy, Ho, Y, Er, Yb), was prepared and their some properties including the electrical conductivity were compared with those of the previous sodium and lithium system glasses.

2. Experimental

Reagent grade K_2CO_3 and SiO_2 , and RE_2O_3 (99.9% purity, Shin-Etsu Chemical Co., Ltd.) were used as the starting materials. After mixing them in the molar ratio of $\text{K}_2\text{O}:\text{RE}_2\text{O}_3:\text{SiO}_2 = 35.7:7.2:57.1$, the mixture was melted in a platinum melting crucible at 1450°C for 1 h in an air atmosphere using an electric furnace. The melt was quenched on the iron plate and molded with pressing. The potassium rare earth silicate glass was obtained by annealing at 500°C in order to prevent the distortion and crack. The density was calculated by the Archimedes method. The crystallization temperatures were measured by the differential thermal analysis (DTA, Rigaku TG8110) of the ground glass powder (20 mg) at the heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ in an air stream ($50 \text{ ml} \cdot \text{min}^{-1}$). The formation of glass state and crystallization were confirmed by the powder X-ray diffraction analysis (XRD; Rigaku MiniFlex). The electrical conductivities were measured in the temperature range of 200 to 400°C and in the frequency range of 100 Hz to 10 MHz with an impedance analyzer (YHP4194A), using the $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ shaped sample with putting Ag electrodes on both sides.

3. Results and discussions

All of the present potassium system glass samples were transparent and homogeneous as well as the previous sodium and lithium system glasses. Only a halo XRD pattern was observed near $2\theta = 30^\circ$ and no other diffraction peak was observed, suggesting that these samples are in glass state, i.e. amorphous. Each sample assumed the characteristic color of rare earth ion as a component: colorless for the Gd, Dy, Y and Yb glasses, pale yellow for the Sm glass, greenish yellow for the Ho glass and pink for the Er glass. The potassium system glasses were more hygroscopic, compared with the sodium and lithium system glasses.

Fig. 1. Relationship between the atomic weight and the density of $(R_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ ($R=Li, Na, K$) glasses.

Fig. 2. DTA curves of $(R_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses.

The densities of potassium $(K_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses are plotted against the atomic weights of rare earths in **Fig. 1**, together with the previous data of sodium and lithium system glasses.^{12),13)} The density was increased with increasing the atomic weight of rare earth element (RE) and apparently lower than the lithium and sodium system glasses, where the sodium system was somewhat lower than the lithium system except for the Y glasses. This can be explained by the increase of molar volume with the increase of ionic radius of alkali metal, as was pointed out in the R_2O-SiO_2 system glass ($R=Na, K, Cs$) by Hakim and Uhlmann.¹⁴⁾

Figure 2 shows the typical DTA curves of $(R_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses ($R=Li, Na, K$). The present potassium system glass gave an exothermic peak around 770°C. This peak is attributed to the crystallization from glass state, in analogy with the result obtained in the sodium system glass.¹²⁾ The DTA profiles of these two glasses are different from that of the lithium system glass which shows three exothermic peaks ($T_c(I)$, $T_c(II)$ and $T_c(III)$) in the range of 650 to 870°C due to the crystallization and two endothermic peaks due to the melting of crystals above 950°C, where

Fig. 3. XRD results for $(R_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses treated at 1000°C. ● Li_2SiO_3 (JCPDS No. 29-828), ○ $Y_2Si_2O_7$ (No. 38-440), ▲ $Na_5YSi_4O_{12}$ (No. 32-1204), □ KYO_2 (No. 21-717) and ■ K_2SiO_3 (No. 31-1077).

Li_2SiO_3 , $(Li_2SiO_3 + RE_2Si_2O_7 + RE_2SiO_5)$ and $(Li_2SiO_3 + RE_2Si_2O_7)$ were confirmed to form around $T_c(I)$, $T_c(II)$ and $T_c(III)$, respectively.¹³⁾ The glasses of other rare earths except for Y gave the similar DTA curves to each other for the same alkali metal system. Taking these observations into consideration, three crystallized XRD samples were prepared by heating the $(R_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ ($R=Li, Na, K$) glasses to 1000°C at the rate of 10°C min⁻¹ in an air stream, holding this temperature for 5 min and then cooling to the room temperature. As shown in **Fig. 3**, the formation of KYO_2 and K_2SiO_3 phases is confirmed in the crystallized $(K_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ glass. The crystallized $(Li_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ glass also consists of two phases (Li_2SiO_3 and $Y_2Si_2O_7$), consistent with the previous report.¹³⁾ All of the diffraction peaks for the crystallized $(Na_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ glass were assigned to those of $Na_5YSi_4O_{12}$, as previously reported.¹²⁾

The crystallization temperatures of $(K_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses are plotted against the ionic radius of rare earth in **Fig. 4** which includes the plots for $(R_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ ($R=Li, Na$) glasses.^{12),13)} The first crystallization temperature ($T_c(I)$) for the $(Li_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glasses and the crystallization temperatures for the $(R_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ ($R=Na, K$) glasses were almost linearly decreased with increasing the ionic radius of rare earth. This may be rationalized by the stability of the glass network structure: the stability becomes lower by the introduction of larger RE ion to make the crystallization easier. Similar relationship was also reported in the crystallized $Na_2O-RE_2O_3-P_2O_5-SiO_2$ glasses.¹⁰⁾

The conductivity was estimated by the complex impedance analysis. **Figure 5** shows the typical complex impedance plot obtained for $(K_2O)_{35.7}(Y_2O_3)_{7.2}(SiO_2)_{57.1}$ glass at 200°C. The plot 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. As the temperature was increased, the semicircle was diminished and only a spike became observed. From these results, the conductivity was determined by the extrapolation

Fig. 4. Relationship between the ionic radius of RE^{3+} and the crystallization temperature (T_c) of $(\text{R}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ (R=Li, Na, K) glasses.

Fig. 5. Complex impedance plot of $(\text{K}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass at 200°C.

to zero reactance of the complex impedance plot in the lower frequency region.

The arrhenius plots of $\log(\sigma T)$ vs. $1/T$ for the $(\text{R}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ (R=Li, Na, K) glasses and the related $(\text{R}_2\text{O})_{36}(\text{SiO}_2)_{64}$ glasses (R=Li, Na, K) without yttria are shown in Fig. 6.^{13,14} The conductivity of $(\text{K}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass at 350°C was $6.2 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ which is close to that ($1 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$) of potassium silicate $(\text{K}_2\text{O})_{36}(\text{SiO}_2)_{64}$ glass.¹⁴ Here, the K^+ concentration in the $(\text{K}_2\text{O})_{36}(\text{SiO}_2)_{64}$ glass is almost the same as the $(\text{K}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass, indicating that there is no effect of the rare earth addition on the conductivity enhancement as was in the lithium and sodium system glasses.^{12,13} The $\text{R}_5\text{YSi}_4\text{O}_{12}$ ceramics (R=Li, Na, K) were prepared by sintering the mixture of R_2CO_3 , Y_2O_3 and SiO_2 at 1100°C, in order to compare the conductivity in ceramic state. The XRD patterns of $\text{R}_5\text{YSi}_4\text{O}_{12}$ ceramics (R=Li, Na, K) were very similar to those of the corresponding alkali metal system glasses $(\text{R}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ (R=Li, Na, K) treated at 1000°C shown in Fig. 3. The arrhenius plots of conductivity data for the $\text{K}_5\text{YSi}_4\text{O}_{12}$ ceramics are also shown in Fig. 5, together with the plots for the $\text{R}_5\text{YSi}_4\text{O}_{12}$ ceramics (R=Li, Na).^{12,13} We previously found that the conductivity of $(\text{Na}_2\text{O})_{35.7}$

Fig. 6. Temperature dependence of conductivity.

○ $(\text{Li}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$, △ $(\text{Na}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ and □ $(\text{K}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glasses.^{12,13}

Fig. 7. Relationship between the ionic radius of R^+ and the electrical conductivity of $(\text{R}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glasses at 400°C.

$(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass is about 2 orders lower than that of $\text{Na}_5\text{YSi}_4\text{O}_{12}$ ceramic and that the conductivity of $(\text{Li}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass is about 2.5 orders higher than that of the $\text{Li}_5\text{YSi}_4\text{O}_{12}$ ceramic.^{12,13} On the other hand, the present work revealed that there is little difference between the conductivities of $(\text{K}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass ($1.3 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 400°C) and $\text{K}_5\text{YSi}_4\text{O}_{12}$ ceramics ($5.9 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 400°C).

Relationships between the conductivities (σ) of $(\text{R}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glasses at 400°C and the ionic radii of alkali metals are plotted in Fig. 7. The conductivity was decreased with increasing the ionic radius of alkali metal. The potassium system glass showed the relatively steep decrease of conductivity by the 0.4–0.8 order lower than that of Li and Na system glasses.

4. Conclusion

Potassium rare earth silicate glasses, $(\text{K}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ (RE = Sm, Gd, Dy, Ho, Y, Er, Yb) were prepared by melting the mixture of K_2CO_3 , RE_2O_3 and SiO_2 . Their some properties including electrical conductivity were examined and compared with those of the lithium and sodium system glasses previously reported.

(1) The density, which was increased with increasing the atomic weight of RE, was lower than those of the Li and Na system glasses.

(2) An exothermic DTA peak due to the crystallization was observed in the range of 720 to 800°C. The powder X-ray diffraction analysis for the glasses prepared by heating above this crystallization temperature showed the formation of two KREO_2 and K_2SiO_3 phases. The crystallization temperature was increased linearly with decreasing the ionic radius of rare earth.

(3) The conductivity of $(\text{K}_2\text{O})_{35.7}(\text{Y}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glass was similar to that of $(\text{K}_2\text{O})_{36}(\text{SiO}_2)_{64}$ glass, with little effect of the conductivity enhancement by the addition of Y_2O_3 to $(\text{K}_2\text{O})_{36}(\text{SiO}_2)_{64}$ glass. The conductivity was also close to that of $\text{K}_5\text{YSi}_4\text{O}_{12}$ ceramics (a mixture of KYO_2 and K_2SiO_3).

(4) The conductivities of $(\text{K}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glasses were lower by 0.4–0.8 order of magnitude than those of the Li and Na system glasses.

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