Synthesis of thallium silicate glasses from Tl_2O_3 and SiO_2 and their electrical properties

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Glasses with the batch composition $(\text{Tl}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ ($x = 0.20\text{--}0.40$) were synthesized by melting a mixture of Tl_2O_3 and SiO_2 , and their electrical properties were investigated. It was confirmed that the Tl in the thallium silicate glasses existed in the mono- and trivalent states. The electrical conductivity of the $(\text{Tl}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ glasses increased with an increase in the x value in the range of $x = 0.20\text{--}0.40$. The electrical conductivity of the glass with the batch composition of $(\text{Tl}_2\text{O}_3)_{0.40}(\text{SiO}_2)_{0.60}$ [analyzed composition: $(\text{Tl}^{1+}_2\text{O})_{0.332}(\text{Tl}^{3+}_2\text{O}_3)_{0.061}(\text{SiO}_2)_{0.607}$] was 5.0×10^{-6} , 2.4×10^{-5} , and $9.6 \times 10^{-5} \text{ S cm}^{-1}$ at 150, 200 and 250°C, respectively.

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We had previously investigated rare earth (RE)-doped sodium silicate ceramics, such as $\text{Na}_5\text{RESi}_4\text{O}_{12}$, which was first reported by Shannon et al.,¹⁾ and had successfully synthesized a series of mixed oxide glasses $(\text{M}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ ($\text{M}=\text{Li}$, Na , K) and studied their electrical properties.^{2)–5)} Furthermore, the electrical properties of $(\text{Na}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{GeO}_2)_{57.1}$ and $(\text{Na}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{B}_2\text{O}_3)_{57.1}$ glasses have been investigated previously.^{6,7)} In 1967, Otto and Milberg reported that, in silicate glasses, the monovalent Tl^+ ions exhibit ionic conduction similar to that of alkali-metal ions.^{8,9)} They used Tl_2CO_3 or TlNO_3 as the thallium (I) source along with SiO_2 to produce $\text{Tl}_2\text{O}\text{--}\text{SiO}_2$ glasses through melting at 1200–1650°C. Further, it has been reported that at least 97% of the thallium ions exist in the monovalent state in $\text{Tl}_2\text{O}\text{--}\text{SiO}_2$ glasses.⁸⁾ In contrast, in this study, inexpensive Tl_2O_3 was used as the source of thallium (III) to prepare thallium silicate glasses. It was found that the majority of the Tl ions in the synthesized thallium silicate glasses existed in the monovalent state (Tl^{1+} , Tl_2O), even when Tl_2O_3 (Tl^{3+}) was used as the raw material. We were interested in thallium silicate glasses in which Tl exists in the mono- and trivalent states as well as in $(\text{M}_2\text{O})_{35.7}(\text{RE}_2\text{O}_3)_{7.2}(\text{SiO}_2)_{57.1}$ glasses that contain M^{1+} and RE^{3+} . Further, the relationship between the glass composition and their electrical conductivity was also investigated.

Reagent-grade Tl_2O_3 and SiO_2 were used as the starting materials. These compounds were weighed and blended in the batch compositions shown in **Table 1**. The sample amount for each batch composition $(\text{Tl}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ ($x = 0.15\text{--}0.45$) was 10 g. Using an alumina crucible (Nikkato Inc. SSA-S) with a cover, each batch was melted at 1250°C for 1 h under atmospheric conditions in an electric furnace. The melted sample was then poured onto an iron plate and formed into a shape by pressing. X-ray powder diffraction (XRD) analyses were performed using a diffractometer (MiniFlex II, Rigaku Co.) with a $\text{Cu}\text{--K}\alpha 1$

radiation source. The Tl contents of the samples were determined using inductively coupled plasma (ICP) atomic emission spectroscopy and their Si contents were determined using ICP atomic emission spectroscopy combined with the cohesive gravimetric method (JIS R 2212-2). The concentration of elemental O in the glasses was determined using the inert gas melt/nondispersive infrared method. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 VersaProbe II system (ULVAC-PHI, Inc.) with an $\text{Al}\text{--K}\alpha$ radiation source. The electrical properties of the samples were measured at 150, 200, and 250°C for frequencies of 100 Hz to 10 MHz. An impedance analyzer (HP4194A) was used for the purpose, and Ag electrodes were placed on both sides of the test samples.

The viscosity of the melts with the batch composition $(\text{Tl}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ ($x = 0.15\text{--}0.45$) increased with a decrease in the amount of Tl_2O_3 present. When the x value was less than 0.15, the viscosity of the melt was very high, and it was possible to pour out the melt from the crucible after it had been heated to 1400°C. All the prepared glass samples were transparent. The samples with $x = 0.20\text{--}0.40$ were yellow, with the color becoming deeper with an increase in the amount of Tl_2O_3 contained. As can be seen from the XRD patterns shown in **Fig. 1**, diffraction peaks related to Tl_2O_3 [ICDD No. 33-1404, $2\theta = 29.335^\circ$ (222) and 33.993° (400)] and/or Tl_2O [ICDD No. 43-1049, $2\theta = 28.409^\circ$ (0012) and 33.821° (107)] and attributable to its crystallization were observed at $2\theta = 28.37^\circ$ and 34.31° in the case of the sample with $x = 0.45$. However, only a halo pattern was seen at $2\theta = 30^\circ$ in the case of the samples with $x = 0.20\text{--}0.40$.

Table 1 lists the Tl, Si, and O contents of the samples along with their batch and analyzed compositions. When the synthesized glasses consisted of only Tl_2O_3 and SiO_2 , the O content was very low. Therefore, it was concluded that the Tl ions existed in not only the trivalent state (Tl^{3+} , Tl_2O_3) but also the monovalent state (Tl^{1+} , Tl_2O) in the synthesized glasses. It was concluded that 80–90% of the Tl existed as Tl^{1+} ; this value is lower than that (approximately 97%) for a thallium silicate ($\text{Tl}_2\text{O}\text{--}\text{SiO}_2$)

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Table 1. Results of chemical analysis of the various synthesized glasses

Batch composition	wt %			Analyzed composition
	Tl	Si	O	
(Ti ₂ O ₃) _{0.20} (SiO ₂) _{0.80}	60.60	16.80	21.71	(Ti ₂ O) _{0.190} (Ti ₂ O ₃) _{0.008} (SiO ₂) _{0.801}
(Ti ₂ O ₃) _{0.25} (SiO ₂) _{0.75}	65.53	14.23	19.31	(Ti ₂ O) _{0.215} (Ti ₂ O ₃) _{0.025} (SiO ₂) _{0.760}
(Ti ₂ O ₃) _{0.30} (SiO ₂) _{0.70}	70.24	11.85	17.01	(Ti ₂ O) _{0.249} (Ti ₂ O ₃) _{0.040} (SiO ₂) _{0.711}
(Ti ₂ O ₃) _{0.35} (SiO ₂) _{0.65}	74.28	9.83	14.94	(Ti ₂ O) _{0.293} (Ti ₂ O ₃) _{0.049} (SiO ₂) _{0.658}
(Ti ₂ O ₃) _{0.40} (SiO ₂) _{0.60}	77.51	8.22	13.35	(Ti ₂ O) _{0.332} (Ti ₂ O ₃) _{0.061} (SiO ₂) _{0.607}

Fig. 1. XRD patterns of the glasses with the batch compositions of (Ti₂O₃)_x(SiO₂)_{1-x}: (a) $x = 0.20$, (b) $x = 0.25$, (c) $x = 0.30$, (d) $x = 0.35$, (e) $x = 0.40$, and (f) $x = 0.45$.

glass prepared from Ti₂CO₃ or TiNO₃ and SiO₂ by Otto and Milberg.⁷⁾ A large amount of Ti₂O was formed owing to the “inert pair effect”^{10,11)} when Ti₂O₃ was used as the raw material.

The XPS Ti4f spectrum for the glass with the batch composition of (Ti₂O₃)_{0.30}(SiO₂)_{0.70} was determined, in order to investigate the valence state of Ti in the glass. As shown in Fig. 2, a peak corresponding to the Ti4f_{7/2} state was observed between 116 and 122 eV. Further, a high-intensity peak was seen at 118.6 eV. However, the binding energies corresponding to the Ti4f_{7/2} state in the Ti₂O phase (Ti¹⁺) and the Ti4f_{7/2} state in the Ti₂O₃ phase (Ti³⁺) are known to be 118.7¹²⁾ and 117.4 eV,¹³⁾ respectively. Thus, the broad band observed at 118.6 eV could not be assigned solely to either the Ti¹⁺ valence state or the Ti³⁺ valence state and was regarded as being related to a combination of the two states. This result suggested that the Ti incorporated into the glass with the batch composition of (Ti₂O₃)_{0.30}(SiO₂)_{0.70} exhibited two valence states, namely, Ti¹⁺ and Ti³⁺. The atomic ratio of the Ti₂O phase (Ti¹⁺) to the Ti₂O₃ phase (Ti³⁺) was estimated to be 89.7/10.3, based on the areas of the corresponding peaks, as

Fig. 2. XPS Ti4f spectrum of the glass with the batch composition of (Ti₂O₃)_{0.30}(SiO₂)_{0.70}. Fig. 3. Relationship between the x value and electrical conductivity (σ) of the glasses with the batch composition of (Ti₂O₃)_x(SiO₂)_{1-x} ($x = 0.20, 0.25, 0.30, 0.35$, and 0.40) at different temperatures. Inset is the complex impedance plot of the glass with the batch composition of (Ti₂O₃)_{0.30}(SiO₂)_{0.70} at 250 °C.

determined by the separation of the peaks of the XPS Ti4f_{7/2} spectrum.

Figure 3 shows the complex impedance plot of the glass with the batch composition of (Ti₂O₃)_{0.30}(SiO₂)_{0.70} at 250 °C. An arc that passes through the origin can be seen in the high-frequency region, while a spike can be seen in the low-frequency region. The arc was related to the resistance of the glass, while the spike was attributable to the resistance of the interface between the sample and the Ag electrode. The component of the glass resistance corresponding to the location indicated by the arrow was estimated which were a section of the extrapolated line from the arc on real axis. The electrical conductivities (σ) of the glasses

Fig. 4. (a) Input waveform of AC power and (b) output current waveform obtained for a standard resistance, as observed with an oscilloscope using the shown measurement circuit, for the glass with the batch composition of $(\text{Tl}_2\text{O}_3)_{0.30}(\text{SiO}_2)_{0.70}$ at 250°C .

with the batch compositions of $(\text{Tl}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ ($x = 0.2\text{--}0.4$) at 150, 200, and 250°C are also shown in Fig. 3. The electrical conductivity increased with an increase in the Tl_2O_3 concentration (x), with the curves for the electrical conductivities as functions of x being smooth and having relatively large curvatures. The electrical conductivity of the glass with the batch composition of $(\text{Tl}_2\text{O}_3)_{0.30}(\text{SiO}_2)_{0.70}$ [analyzed composition: $(\text{Tl}_2\text{O})_{0.249}(\text{Tl}_2\text{O}_3)_{0.040}(\text{SiO}_2)_{0.711}$] was 3.5×10^{-6} , 1.7×10^{-5} , and $6.0 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 150, 200, and 250°C , respectively. The conductivity of this glass at 250°C was approximately six and three times as high as those of the $(\text{Tl}_2\text{O})_{0.205}(\text{SiO}_2)_{0.795}$ ($2.8 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 250°C) and $(\text{Tl}_2\text{O})_{0.301}(\text{SiO}_2)_{0.699}$ ($6.0 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 250°C) glasses, respectively, reported by Otto and Milberg.⁹⁾ On the other hand, in the case where the compositional and ionic radii were similar [$\text{Tl}^{1+}(\text{VI}) = 0.150 \text{ nm}$, $\text{K}^{1+}(\text{VI}) = 0.138 \text{ nm}$, $\text{Ti}^{3+}(\text{VI}) = 0.0880 \text{ nm}$, and $\text{Er}^{3+}(\text{VI}) = 0.0881 \text{ nm}$], the electrical conductivity ($2.4 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 200°C) of the $(\text{Tl}_2\text{O}_3)_{0.40}(\text{SiO}_2)_{0.60}$ glass [analyzed composition: $(\text{Ti}^{1+}_2\text{O})_{0.332}(\text{Ti}^{3+}_2\text{O}_3)_{0.061}(\text{SiO}_2)_{0.607}$] was almost similar to that of the $(\text{K}^{1+}_2\text{O})_{0.357}(\text{Er}^{3+}_2\text{O}_3)_{0.072}(\text{SiO}_2)_{0.571}$ glass ($3.2 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 200°C).³⁾

Since it is known that Tl_2O_3 shows good electronic conduction,^{14),15)} it was assumed that the conduction exhibited by the glasses was not only ion-based but also electron-based. The output current waveform for a standard resistance in response to a square-wave input waveform (AC power) was observed using an oscilloscope, as shown in Fig. 4. The circuit shown in the figure was employed for the measurement. The input waveform and the

output current waveform are shown in Figs. 4(a) and 4(b), respectively. The amplitude of the current waveform decreased gradually owing to the transients generated because of the switching between the positive and negative amplitudes, which, in turn, resulted in polarization because of the presence of ionic charge carriers. Therefore, it was concluded that the conduction in the glasses was primarily ionic in nature.

In this study, thallium silicate glasses were synthesized by mixing Tl_2O_3 and SiO_2 , and their electrical properties were investigated. The primary results of the study can be summarized as follows: Thallium silicate glasses with the batch composition $(\text{Tl}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ ($x = 0.20\text{--}0.40$) could be synthesized successfully. The glasses with $x = 0.20\text{--}0.40$ were yellow, with the color becoming deeper with an increase in the Tl_2O_3 concentration (x). The XRD diffraction peaks observed in the case of the sample with $x = 0.45$ were assignable to the crystallization of Tl_2O_3 and/or Tl_2O . Based on the results of chemical analyses and XPS measurements, it was concluded that the Tl in the thallium silicate glasses existed in the mono- and trivalent states. The electrical conductivity of the glass with the batch composition of $(\text{Tl}_2\text{O}_3)_{0.30}(\text{SiO}_2)_{0.70}$ [analyzed composition: $(\text{Tl}_2\text{O})_{0.249}(\text{Tl}_2\text{O}_3)_{0.040}(\text{SiO}_2)_{0.711}$] was $6.0 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 250°C . Further, it was concluded that the conduction in the glass was owing to Ti^+ ions.

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