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# Mixed former effect between $\text{TeO}_2$ and $\text{SiO}_2$ in the $\text{Li}_2\text{O} \cdot \text{TeO}_2 \cdot \text{SiO}_2$ system

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## Abstract

Glass samples of the  $0.30\text{Li}_2\text{O} \cdot 0.70(x\text{TeO}_2 \cdot (1-x)\text{SiO}_2)$  system were synthesized. The difference between the melting points of silica and tellurium oxide, which melts at  $733^\circ\text{C}$  with further volatilization, makes this synthesis a complex one. However, transparent and homogeneous glasses were obtained in the  $\text{SiO}_2$ -rich domain up to  $x = 0.30$  by mixing appropriate amounts of the two binary systems,  $0.30\text{Li}_2\text{O} \cdot 0.70\text{SiO}_2$  and  $0.30\text{Li}_2\text{O} \cdot 0.70\text{TeO}_2$ , in an induction furnace. With the increase of the  $\text{TeO}_2$  content in the samples investigated a decrease of  $T_g$  and an increase in the samples' densities were measured. The results of electrical measurements, carried out by impedance spectroscopy, show an increase in electrical conductivity when  $\text{TeO}_2$  is added to the  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  glass, which we attribute to a mixed former effect between  $\text{TeO}_2$  and  $\text{SiO}_2$ . Both the activation energy and the  $\sigma_0$  parameter of the Arrhenius equation increase with increased  $\text{TeO}_2$  content in the samples. A carbon replica analysis of the samples shows a phase separation in the ternary glasses. © 2000 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

The formation of tellurium oxide glasses was predicted in the 50s by Stanworth [1], based on the electronegativity concept. Although pure tellurium oxide glass has not yet been obtained ( $\text{TeO}_2$  is classified as an intermediate oxide according to Dietzel's field strength concept [2]), systematic investigations have been carried out in binary systems, combining tellurium oxide with the classical glass formers or with the common glass modifiers. Since glasses containing  $\text{TeO}_2$  have large refractive indices ( $n_d$ ) (e.g.,  $n_d = 2.1$  to  $2.3$ ) [2], the optical

properties of tellurite glasses have been studied intensely [2].

Specific interest in lithium–tellurite glasses was first reported by Brady [3], who added  $\text{Li}_2\text{O}$  to  $\text{TeO}_2$  to obtain glass samples for structural studies. More recently, Sunandana and Kumaraswani [4] proposed the use of lithium–tellurite glass as a solid electrolyte. This new interest added an impetus to the investigation on new conductor glasses containing tellurium oxide. Thus, the mixed alkali effect has already been studied [5] while the mixed former effect has also been observed in the  $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{Te}_2\text{O}_4$  [6] system. To improve the electrical conductivity of tellurite glasses, families containing considerable amounts of halides have also been proposed [7–10].

Despite this variety in the family of tellurite glasses, samples containing  $\text{TeO}_2$  and  $\text{SiO}_2$  have so

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far been the subject of little study. Indeed, while Imaoka [11] mentioned no glass formation between  $\text{TeO}_2$  and  $\text{SiO}_2$  and Vogel et al. [12] reported that  $\text{SiO}_2$  can be added only to an  $\text{Al}_2\text{O}_3$ – $\text{TeO}_2$  based glass, Mochida et al. [13] presented the glass formation range and some properties of samples from the  $\text{Na}_2\text{O} \cdot \text{TeO}_2 \cdot \text{SiO}_2$  system.

This work deals with the synthesis and electrical measurements of glass samples from the  $\text{SiO}_2$ -rich area of the  $0.30\text{Li}_2\text{O} \cdot 0.70(x\text{TeO}_2 - (1-x)\text{SiO}_2)$  system. The electrical conductivity of the samples was measured to verify the occurrence of a mixed former effect between  $\text{SiO}_2$  and  $\text{TeO}_2$ . The 30 mol% content of  $\text{Li}_2\text{O}$  was chosen because it corresponds to the upper limit of glass formation in the binary  $\text{Li}_2\text{O} \cdot \text{TeO}_2$  system [6,12]. The largest possible amount of  $\text{Li}_2\text{O}$  was used to increase the electrical conductivities of the glass samples.

## 2. Experimental

The two binary compositions,  $x = 0.0$  and  $x = 1.0$ , were first prepared using  $\text{Li}_2\text{CO}_3$  and  $\text{SiO}_2$  or  $\text{TeO}_2$ , respectively. The ternary compositions were then synthesized by re-melting appropriate amounts of the two binary compositions. With the exception of the sample with  $x = 1.0(0.30\text{Li}_2\text{O} \cdot 0.70\text{TeO}_2)$  which was melted in a gold crucible, the other glasses were melted in a platinum crucible with a cover, using an induction furnace in which increases in temperature of  $9 \text{ K s}^{-1}$  and, consequently, short melting times are achieved. This procedure also allowed observation of the liquid inside the crucible. The melting temperatures varied slightly according to the glass compositions, but remained around  $1100^\circ\text{C}$ , while the melting time varied from 5 to 20 min. The melted glasses were poured into a metal mould to form 12-mm diameter and 10–20-mm tall glass cylinders.

Glass transition temperatures were determined by differential thermal analysis (DTA) (heating rate of  $20^\circ\text{C}/\text{min}$  – Shimadzu DTA-50 equipment) and densities were measured by pycnometry. The lithium content was determined by flame photometry (Zeiss Flapho 41), while the  $\text{TeO}_2/\text{SiO}_2$  ratio was determined by wavelength-dispersive

spectrometry (WDS) microanalysis (WDS-3PC Microspec).

Electrical conductivity measurements were made in 2-mm thick samples cut from the initial glass cylinder, with gold electrodes deposited on both faces. Measurements were carried out by impedance spectroscopy using an impedance analyzer (HP 4192A), in the 5 Hz–13 MHz frequency range, from  $100^\circ\text{C}$  to  $240^\circ\text{C}$ .

To verify whether the glasses were phase separated, carbon replicas of samples were made, as described by Vogel [14].

## 3. Results

### 3.1. Glass formation

Glass samples were obtained for  $0 < x < 0.30$ . The  $x = 0.30$  corresponds to a  $\text{TeO}_2$  molar ratio of 0.21 and to 46.6 wt% of  $\text{TeO}_2$ . The melting and quenching of the composition with  $x = 0.35$  produced opaque materials with  $\text{LiTeO}_3$  (lithium tellurate) as the crystalline phase. Attempts to melt glasses in the  $\text{Li}_2\text{O}$ – $\text{TeO}_2$ -rich domain ( $x > 0.5$ ) produced inhomogeneous liquids, up to  $1200^\circ\text{C}$ . Hence, it was possible to add  $\text{TeO}_2$  to the  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  glass melt and obtain glass samples up to  $x = 0.30$ , but it was impossible to add any  $\text{SiO}_2$  to the  $\text{Li}_2\text{O} \cdot \text{TeO}_2$  glass melt. Based on observation of the liquid during synthesis we suggest either a liquid–liquid immiscibility or that some crystals in the  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  system are not soluble in the  $\text{Li}_2\text{O} \cdot \text{TeO}_2$  liquid.

### 3.2. Chemical analysis, density and $T_g$

Since  $\text{TeO}_2$  has a low melting point ( $733^\circ\text{C}$ ) and may volatilize during melting, a chemical analysis was necessary to determine the glass composition. Table 1 shows the results of this analysis. Some loss in lithium content was observed while the  $\text{TeO}_2/\text{SiO}_2$  ratio in the melted glasses remained close to the batch ratio. No loss of tellurium oxide was observed and the glasses obtained had compositions close to the batches nominal formulas. Alumina and potassium oxide were detected in the silica used as starting material. The molar content

Table 1

Chemical analyses of samples from the  $0.30\text{Li}_2\text{O} \cdot 0.70(x\text{TeO}_2 \cdot (1-x)\text{SiO}_2)$  glass system, in wt%<sup>a</sup>

x	%Li <sub>2</sub> O		%TeO <sub>2</sub>		%SiO <sub>2</sub>		Others	
	Expected	Experimental	Expected	Experimental	Expected	Experimental	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O
0.00	17.6	19.0	–	–	82.4	78.7	0.23	–
0.10	15.5	14.0	19.3	19.9	65.3	65.1	0.96	–
0.20	13.8	12.7	34.4	34.2	51.8	52.3	0.76	–
0.25	13.1	12.0	40.8	41.7	46.1	45.9	0.73	0.52
0.30	12.5	11.7	46.6	46.7	40.9	40.5	0.65	0.47
1.00	7.4	6.9	92.6	92.0	–	–	–	–

<sup>a</sup>The experimental data precision is  $\pm 2\%$ .

of alumina and K<sub>2</sub>O was, in all cases,  $< 0.01$  and, in most cases,  $< 0.005$ .

Fig. 1 shows the variation of  $T_g$  and the density as a function of the tellurium content,  $x$ . The two binary glasses have different  $T_g$ s and densities. The  $T_g$  of the binary lithium–tellurium oxide glasses ( $x = 1$ ) is as low as  $253^\circ\text{C}$ , while its density is  $4.614 \text{ g cm}^{-3}$ . In the ternary glasses,  $T_g$  decreases if TeO<sub>2</sub> is introduced into the lithium–silica glass, while the density increases. Both variations are monotonic, showing no interruption.

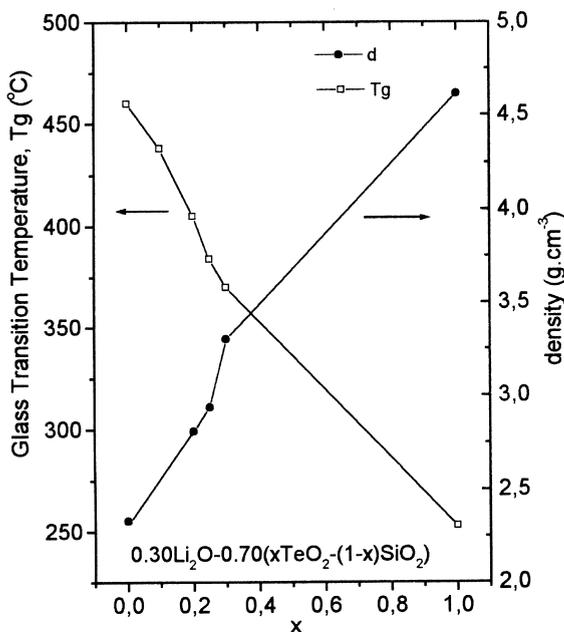


Fig. 1. Density and  $T_g$  as a function of the tellurium content,  $x$ . Solid lines are drawn as guides to the eye. Estimated errors:  $T_g$ :  $\pm 2^\circ\text{C}$ , density:  $\pm 0.004 \text{ g cm}^{-3}$ .

### 3.3. Electrical conductivity, activation energy and $\sigma_0$

The plot of electrical conductivity for each composition studied is shown in Fig. 2. The linear functions fitted to the data had correlation coefficients  $> 0.9995$ . Fig. 3 illustrates the electrical conductivity at different temperatures, calculated from the linear regression shown in Fig. 2. At a

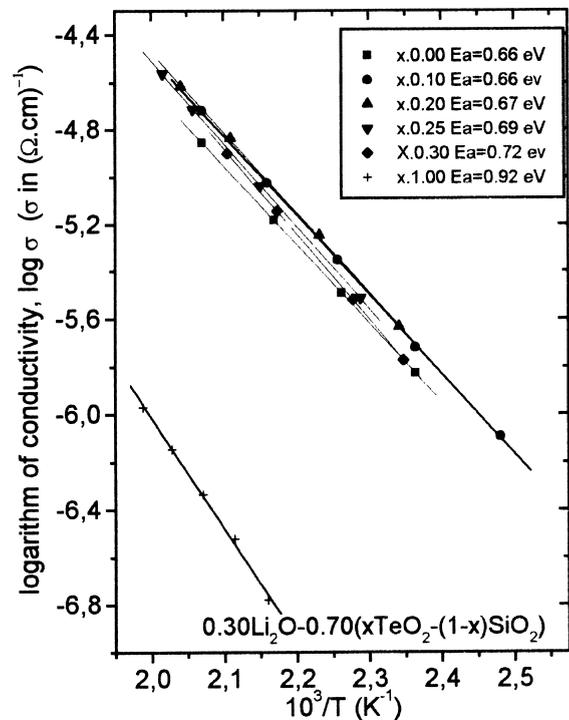


Fig. 2. Arrhenius plots of electrical conductivity. Solid lines represent a linear regression analysis of the experimental data points. All correlation coefficients are above 0.9995. Conductivity measurements have a precision of 3%.

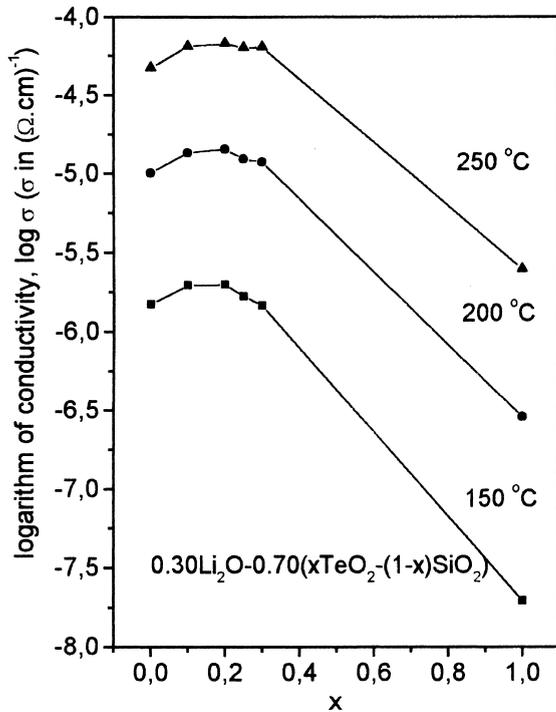


Fig. 3. Electrical conductivity at different temperatures as a function of  $x$ . Solid lines are guides to the eye. Conductivity measurements have a precision of 3%.

given temperature, the electrical conductivity of the binary lithium–tellurium oxide glass is more than two orders of magnitude less than those of the binary lithium–silica glass. The increase in the tellurium oxide content to  $x = 0.25$  in the samples in the ternary system increased the electrical conductivity. Fig. 4 shows, also as a function of  $x$ , the activation energy ( $E_a$ ) and the pre-exponential factor  $\sigma_0$ . The logarithms of the pre-exponential factor ( $\sigma_0$ ) of the Arrhenius expression ( $\sigma = \sigma_0 \exp(-E_a/kT)$ ) (with  $\sigma$  in  $(\Omega \text{ cm})^{-1}$ ) increased from 2.0 to 3.3 as  $x$  increased from 0 to 1. There is a difference between the activation energies for conduction of binary samples, with the  $0.30\text{Li}_2\text{O} \cdot 0.70\text{TeO}_2$  glass having the largest.

### 3.4. Carbon replica

Glass immiscibility analyses were made by carbon replica for all the samples studied. Fig. 5 shows the micrographs corresponding to samples

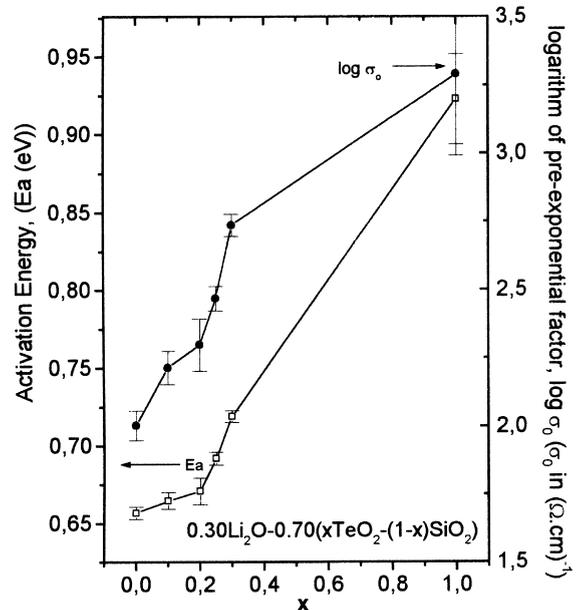


Fig. 4. Activation energy and pre-exponential factor,  $\sigma_0$ , as a function of  $x$ . Solid lines are guides to the eye.

with  $x = 0.25$  and  $0.30$ , in which we observe a tendency toward phase separation, indicated by a difference between the surface reliefs of a sample and the  $\text{MoO}_3$  crystal test plane.

## 4. Discussion

The mixed former effect is the increase in electrical conductivity observed in a ternary glass, when a glass former is partially substituted by another at a constant modifier concentration [6,15,16]. This effect has been observed mainly in glasses containing  $\text{B}_2\text{O}_3$  or  $\text{P}_2\text{O}_5$  [17] as the glass former and increased conductivity may be detected by the presence of one or two maxima in the conductivity plotted as a function of composition. Accordingly, sodium [17] and silver [18,19] borophosphate glasses, as well as lithium borotellurate [6] and silver phosphotellurate [20], have two maxima in conductivity while lithium borophosphate [17] shows only one. In the case of borophosphate glasses, these maxima were related to the formation of some  $\text{BPO}_4$  units [17]. In lithium

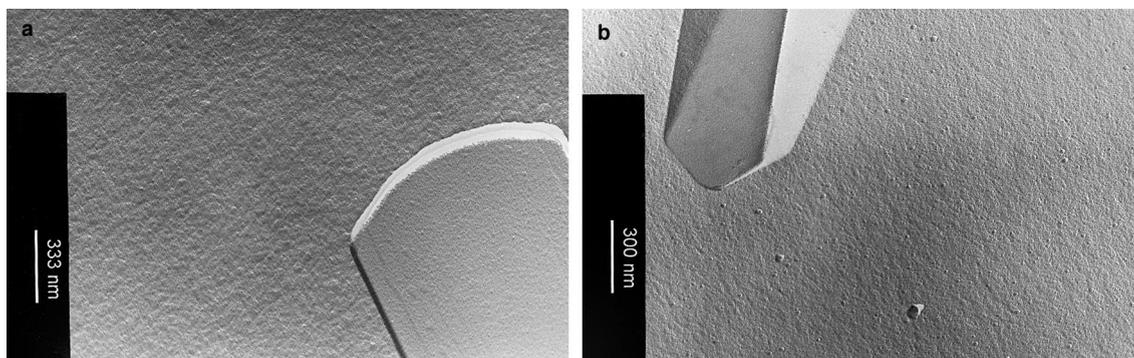


Fig. 5. Micrograph after carbon replica of sample with: (a)  $x = 0.25$  and (b)  $x = 0.30$ . Comparison with  $\text{MoO}_3$  crystal test plane indicates a phase separation.

borosilicate glasses, the mixed former effect appears only at the larger concentrations of modifier [21]. Such an increase in conductivity has also been observed in lithium sulfide glasses [15,16] with only one maximum. In the latter case [16], the increased conductivity is attributed to a phase separation leading to a modifier-rich phase.

Although the entire system could not be synthesized, the results presented in Fig. 3 show an increase in the electrical conductivity, which suggests a mixed former effect in the silica-rich region of the  $0.30\text{Li}_2\text{O} \cdot 0.70(x\text{TeO}_2 \cdot (1-x)\text{SiO}_2)$  system. This increase in conductivity, however, is not followed by the same variation in  $T_g$  or in density, as observed in other systems [16].

It can be observed, from Fig. 4, that the activation energy increases with increase in tellurium content. Although this increase is small up to  $x = 0.20$ , it is quite an unusual change since increased electrical conductivity ( $\sigma$ )  $\sigma = \sigma_0 \exp(-E_a/kT)$  is usually the result of decreased activation energy for conduction ( $E_a$ ) [6,16,20], with the  $\sigma_0$  parameter being assumed constant [15,16,20]. In the case of the present work, since activation energy for conduction does not vary within errors of measurement with changes in  $x$  (until  $x = 0.20$ ), the changes in conductivity must be due to changes in  $\sigma_0$  (Fig. 4). The mixed former effect observed in Fig. 3 may be related to the phase separation detected by the carbon replica technique (Fig. 5), similarly to the case of the  $0.3\text{Li}_2\text{S} \cdot 0.7[(1-x)\text{SiS}_2 \cdot x\text{GeS}_2]$  system [16].

## 5. Conclusion

Glass samples were obtained in the  $0.30\text{Li}_2\text{O} \cdot 0.70(x\text{TeO}_2 \cdot (1-x)\text{SiO}_2)$  system for  $0 < x < 0.3$  and  $x = 1$ . Samples with  $x \geq 0.35$  crystallized during cooling. No homogeneous liquid was observed at temperatures up to  $1200^\circ\text{C}$  in the  $\text{TeO}_2$ -rich domain. Properties such as  $T_g$ , and density varied monotonically with increasing  $\text{TeO}_2$  content. The electrical conductivity increased with the increase of  $\text{TeO}_2$  content in the ternary system, indicating a mixed former effect between  $\text{SiO}_2$  and  $\text{TeO}_2$  in the glass system investigated. As the activation energy increased only slightly (for the smaller of  $x$ ) with the  $\text{TeO}_2$  content, the increase of electrical conductivity is mathematically ascribed to the increase of the  $\sigma_0$  pre-exponential factor. Carbon replicas show that the ternary samples are phase separated, which could be the cause of the observed mixed former effect.

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