Synthesis and Electrical Conductivity of Glasses in the Li₂O·TeO₂·SiO₂ System

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ABSTRACT

The synthesis of glassy samples in the system 0.30Li₂O-0.70(1-x)TeO₂-(1-x)SiO₂ was investigated. The difference between the melting points of silica and tellurium oxide, that melts at 733°C with significant volatilization, makes this synthesis a complex one. To reduce TeO₂ losses, glassy samples were obtained by mixing appropriate amounts of glass from the binary systems 0.30Li₂O-0.70SiO₂ and 0.30Li₂O-0.70TeO₂, previously synthesized. Glass melting was carried out in an induction furnace that allows very fast temperature raising. Transparent, homogeneous glasses were obtained in the SiO₂ rich domain, until x=0.3. The content of TeO₂ and the composition of the final glasses were confirmed by wet chemical analysis and WDX microanalysis. Increasing the content of TeO₂ in the ternary system leads to the formation of opaque materials with crystalline Li₂TeO₃. Attempts of melting glasses in the Li₂O-TeO₂ rich domain (x ≥ 0.5) did not lead to homogeneous liquids up to 1200°C, since some white solids still remained at this temperature. The glass transition temperature decreases with the increasing of TeO₂ content. Carbon replica analysis shows a weak immiscibility tendency in the ternary glasses. Results of electrical conductivity are also presented.

I. INTRODUCTION

The formation of tellurium oxide glasses was predicted in the 50's by Stanworth¹, based on the electronegativity concept. Although glass of pure tellurium oxide is still not obtained, systematic investigations were carried out in binary systems, combining tellurium oxide with the classical glass formers or with the common glass modifiers. Since glassy materials containing heavy metals oxides present high refractive index, tellurite glasses have been intensely studied with respect of their optical properties.

A specific interest in lithium-tellurite glasses was first reported by Brady² who
added Li$_2$O to TeO$_2$ in order to obtain glassy samples for structural studies. More recently, Sunandana and Kumaraswamy$^3$ proposed the use of lithium tellurite glasses as solid electrolyte. This new interest had impelled the investigation on new conductor glasses containing tellurium oxide. In this way, the mixed alkali effect has already been studied$^4$ while the mixed former effect was observed in the Li$_2$O-B$_2$O$_3$-Te$_2$O$_4$$^5$ and Li$_2$O-P$_2$O$_5$-TeO$_2$$^6$ systems. In order to improve electrical conductivity of tellurite glasses, families containing considerable amounts of halides have also been proposed$^7$-$^{10}$.

Despite of this great variety in the family of tellurite glasses, samples containing TeO$_2$ and SiO$_2$ have poorly been studied. In fact, while Imaoka$^{11}$ mentioned no glass formation between TeO$_2$ and SiO$_2$ and Vogel et al$^{12}$ reported that SiO$_2$ can be added only to an Al$_2$O$_3$-TeO$_2$ based glass, Mochida et al$^{13}$ presented the glass formation range and some properties of samples from the Na$_2$O-TeO$_2$:SiO$_2$ system. The present work deals with the synthesis and characterization of glassy samples from the SiO$_2$-rich area of the 0.30Li$_2$O-0.70(1-x)TeO$_2$. The occurrence of a mixed former effect between SiO$_2$ and TeO$_2$, the electrical conductivity of the samples was measured. The 30 mol% content of Li$_2$O was chosen since it corresponds to the upper limit of glass formation in the binary Li$_2$O-TeO$_2$ system$^5$-$^{12}$. The highest possible amount of Li$_2$O were used in order to improve the electrical conductivity of glassy samples.

II. EXPERIMENTAL

The two binary compositions, x=0.0 and x=1.0 were first prepared using Li$_2$CO$_3$ and SiO$_2$ or TeO$_2$ respectively. Then, the ternary compositions were synthesized by remelting appropriate amounts of those two binary compositions. With exception to the sample with x = 1.0 (0.30Li$_2$O-0.70TeO$_2$) which was melted in a gold crucible, the other glasses were melted in a platinum crucible with a lid, using an induction furnace that enables rapid increasing of temperature and consequently short melting time. This procedure allows, also, the observation of the melt inside the crucible. Melting temperatures varied slightly with glass compositions but remained around 1100°C, while melting time varied from 5 to 20 min. Melted glasses were poured in a metal mould in order to obtain glass cylinders having 12 mm diameter and 10-20 mm height.

Glass transition temperatures were determined by DTA (heating rate of 20°C/min) with a Shimadzu DTA-50 equipment and densities were measured by pycnometry. The lithium content was determined by flame photometry (Zeiss Flapho 41), while the TeO$_2$/SiO$_2$ ratio was determined by WDX microanalysis (WDX-3PC Microspec).

For electrical conductivity measurements, 2 mm thick samples were cut from the
initial glass cylinder, and gold electrodes were deposited on both faces. Measurements were carried out by impedance spectroscopy using a HP 4192A impedance analyzer, in the 5Hz-13MHz frequency range, from 100 to 240°C.

In order to verify if the glasses show phase separation, carbon replica of samples were carried out as described by Vogel.

III. RESULTS AND DISCUSSION

a) glass formation

Glassy samples were obtained for $0 < x < 0.3$. The value of $x = 0.30$ corresponds to a TeO$_2$ molar ratio of 0.21 and to 46.6 weight % of TeO$_2$. The melting and quenching of the composition with $x = 0.35$ led to opaque materials with LiTeO$_3$ (lithium tellurate) as crystalline phase. Attempts to melt glasses in the Li$_2$O-TeO$_2$ rich domain ($x > 0.5$) did not lead to homogeneous liquids, up to 1200°C. In this way, it was possible to add TeO$_2$ to the Li$_2$O:SiO$_2$ glass melt and to obtain glassy samples until $x = 0.30$, but it was not possible to add any SiO$_2$ to the Li$_2$O:TeO$_2$ glass melt. The observation of the melt during synthesis suggested either a liquid-liquid immiscibility or that some crystals in the Li$_2$O:SiO$_2$ system are not soluble in the Li$_2$O:TeO$_2$ melt.

b) chemical analysis, density and Tg

Since TeO$_2$ has a low melting point (730°C) and may volatilize during melting, chemical analysis was necessary to control glass composition. Results are shown in Table I. A low loss in the lithium content is observed while the ratio TeO$_2$/SiO$_2$ in the melted glasses remained very close to the expected one. No loss of tellurium oxide was observed and the obtained glasses correspond to their nominal formulas. Alumina and potassium oxide were found as impurity in the silica used as starting material. The molar content of alumina and K$_2$O are in all cases lower than 0.01 and in most cases lower than 0.005

<table>
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<th>x</th>
<th>%Li$_2$O</th>
<th>%TeO$_2$</th>
<th>%SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>K$_2$O</th>
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<td>expected</td>
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<tr>
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<td>6.9</td>
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</table>
Figure 1 shows the variation of Tg and the density as a function of the tellurium content, x. The two binary glasses present very different values of Tg and density. The Tg of the binary lithium-tellurium oxide glasses is as low as 253°C, while its density is 2.331 g.cm\(^{-3}\). In the ternary glasses, Tg decreases if TeO\(_2\) is introduced to the lithium-silica glass, while the density increases. Both variations are continuous with no significant interruption.

c) electrical conductivity and activation energy

The Arrhenius plot of electrical conductivity for each composition studied is shown in Figure 2. All straight lines had correlation coefficients higher than 0.9995. The electrical conductivities at different temperatures are shown at Figure 3. At a given temperature, the electrical conductivity of the binary lithium-tellurium oxide glass is two orders of magnitude lower than those presented by the binary lithium-silica glass. The increase in the tellurium oxide content of samples in the ternary system slightly increases the electrical conductivity until x = 0.25. Figure 4 shows, also as a function of x, the activation energy and the pre-exponential factor \(\sigma_0\). The values found for the pre-exponential factor of the Arrhenius expression, \(\log\sigma_0\), (with \(\sigma\) in \(\Omega\cdot\text{cm}\)) were around 2.0 which is a typical value for glassy lithium ionic conductors\(^{15}\). Both activation energy and \(\sigma_0\) parameter increase monotonically with x. Hence, no strong evidence of a mixed former effect between SiO\(_2\) and TeO\(_2\) was found, since the introduction of TeO\(_2\) to the Li\(_2\)O.SiO\(_2\) glass do not increase significantly the electrical conductivity.
d) carbon replica

Analysis of glass immiscibility were made by carbon replica for all studied samples. All compositions show only a weak tendency toward immiscibility. This tendency is slightly more pronounced in the lithium-tellurium oxide glass (x=1.0).

![Figure 3: Electrical conductivity at different temperatures as a function of x.](image1)

![Figure 4: Activation energy and pre-exponential factor, $\sigma_0$, as a function of x.](image2)

IV. CONCLUSION

It was possible to obtain glassy samples in the system 0.30Li$_2$O-0.70(xTeO$_2$ (1-x)SiO$_2$) for 0 < x < 0.3 and x = 1. Samples with x ≥ 0.35 crystallized during cooling. In the TeO$_2$ rich domain, no homogeneous liquid was observed at temperatures up to 1200°C. Properties such as Tg, and density varied monotonically with increasing TeO$_2$ content. The electrical conductivity increases only slightly with the increasing of TeO$_2$ in the ternary system. These results indicate no strong evidence of a mixed former effect between SiO$_2$ and TeO$_2$ in the glass system investigated. Carbon replicas show that the samples studied present only a weak tendency toward immiscibility.

V. ACKNOWLEDGEMENTS

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VI. REFERENCES