Synthesis and Electrical Conductivity of Glasses in the $Li_2O.TeO_2.SiO_2$ System

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ABSTRACT

The synthesis of glassy samples in the system $0.30Li_2O\text{-}0.70(xTeO_2\text{-}(1\text{-}x)SiO_2)$ 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 TeO_2 losses, glassy samples were obtained by mixing appropriate amounts of glass from the binary systems $0.30Li_2O\text{-}0.70SiO_2$ and $0.30Li_2O\text{-}0.70TeO_2$, previously synthesized. Glass melting was carried out in an induction furnace that allows very fast temperature raising. Transparent, homogeneous glasses were obtained in the SiO_2 rich domain, until x=0.3. The content of TeO_2 and the composition of the final glasses were confirmed by wet chemical analysis and WDX microanalysis. Increasing the content of TeO_2 in the ternary system leads to the formation of opaque materials with crystalline Li_2TeO_3. Attempts of melting glasses in the $Li_2O\text{-}TeO_2$ rich domain ($x \geq 0.5$) 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 TeO_2 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 Stanworth[1], 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 Brady[2] who

added Li_2O to TeO_2 in order to obtain glassy samples for structural studies. More recently, Sunandana and Kumaraswani[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 $Li_2O.B_2O_3.Te_2O_4$[5] and $Li_2O.P_2O_5.TeO_2$[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_2O_3-TeO_2 based glass, Mochida et al[13] presented the glass formation range and some properties of samples from the $Na_2O.TeO_2.SiO_2$ system.

The present work deals with the synthesis and characterization of glassy samples from the SiO_2-rich area of the $0.30Li_2O.0.70(xTeO_2.(1-x)SiO_2)$ system. In order to verify 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_2O was chosen since it corresponds to the upper limit of glass formation in the binary $Li_2O.TeO_2$ system[5,12]. The highest possible amount of Li_2O 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_2CO_3 and SiO_2 or TeO_2 respectively. Then, the ternary compositions were synthesized by re-melting appropriate amounts of those two binary compositions. With exception to the sample with x = 1.0 ($0.30Li_2O.0.70TeO_2$) which was melted in a gold crucible, the other glasses were melted in a platinum crucible with a cover, 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[14].

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_2O-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 $Li_2O.SiO_2$ glass melt and to obtain glassy samples until $x = 0.30$, but it was not possible to add any SiO_2 to the $Li_2O.TeO_2$ glass melt. The observation of the melt during synthesis suggested either a liquid-liquid immiscibility or that some crystals in the $Li_2O.SiO_2$ system are not soluble in the $Li_2O.TeO_2$ 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_2O are in all cases lower than 0.01 and in most cases lower than 0.005

Table 1: Chemical analyses of samples from the $0.30Li_2O$-$0.70(xTeO_2$ $(1-x)SiO_2)$ glass system, in weight % (experim. = experimental)

x	%Li_2O		%TeO_2		%SiO_2		others	
	expected	experim.	expected	experim.	expected	experim.	Al_2O_3	K_2O
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	--	--	--	--

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 σ_0. The values found for the pre-exponential factor of the Arrhenius expression, $\log\sigma_0$, (with σ in $(\Omega.cm)^{-1}$) were around 2.0 which is a typical value for glassy lithium ionic conductors[15]. Both activation energy and σ_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 $Li_2O.SiO_2$ glass do not increase significantly the electrical conductivity.

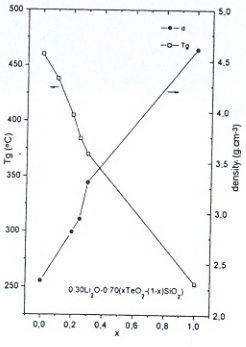

Figure 1: Density and Tg as a function of the tellurium content, x.

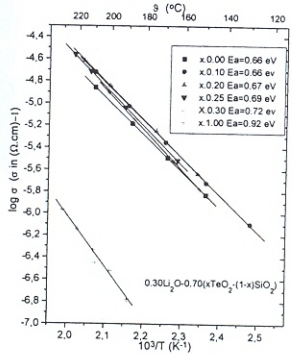

Figure 2: Arrhenius plot of electrical conductivity.

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).

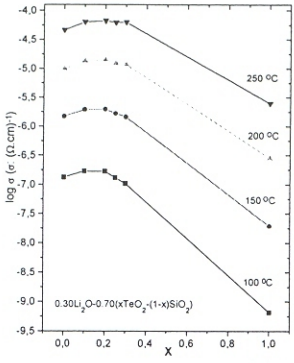

Figure 3: Electrical conductivity at different temperatures as a function of x.

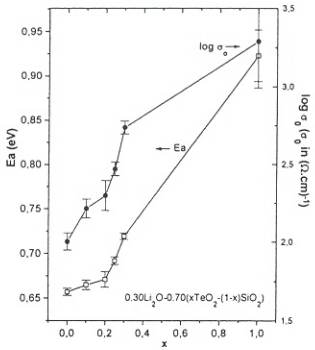

Figure 4: Activation energy and pre-exponential factor, σ_0, as a function of x .

IV. CONCLUSION

It was possible to obtain glassy samples in the system $0.30Li_2O$-$0.70(xTeO_2$ $(1-x)SiO_2)$ for $0 < x < 0.3$ and $x = 1$. Samples with $x \geq 0.35$ 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

1. Stanworth, J.E.: Tellurite Glasses, Nature **169** (1952) p. 581-582.

2. Brady, G.W.: Structure of tellurium oxide glass, J. Chem. Phys. **27** (1957), p.300-303 .

3. Sunandana, C.S.; Kumaraswani, T.: Li_4TeO_4: new glassy Li^+ ion conductor, J. Non-Cryst. Solids. **85** (1986) p.247-250.

4. Balaya, P.; Sunandana, C.S.: Mixed alkali effect in the $30[(1-x)Li_2O\ xNa_2O]:TeO_2$ glass system, J. Non-Cryst. Solids **175** (1994) p.51-58.

5. Martins Rodrigues, A.C.; Duclot, M.J.: Lithium conducting glasses: the $Li_20.B_2O_3.TeO_2$ system, Solid State Ionics **28-30** (1988) p. 729-731.

6. Jayasinghe, G.D.L.K.; Bandaranayake, P.W.S.K.; Dissanayake, M.A.K.L.; Gunawardane,R.P.: Ionic conductivity of glasses in the system Li_2O-P_2O_5-TeO_2, Solid State Ionics **78** (1995) p.199-202.

7. Tanaka, K.; Yoko, T.; Yamada, H.; Kamiya, K.: Structure and ionic conductivity of LiCl-Li_2O-TeO_2 glasses, J. Non-Cryst. Solids **103** (1988) p. 250-256.

8. Rojo, J.M.; Sanz, J.; Reau, J.M.; Tanguy, B.: Influence of ion distribution on the ionic conductivity of lithium tellurite glasses (Li_2O-TeO_2 and LiF-TeO_2), J. Non-Cryst. Solids **116** (1990) p. 167-174.

9. Tanaka, K.; Yoko, T.; Kamiya, K..; Yamada, H.; Sakka, S.: Properties of oxybromide tellurite glasses in the system LiBr-Li_2O-TeO_2, J. Non-Cryst. Solids **135** (1991) p. 211-218.

10. Rojo, J.M.; Herrero, P.; Rojas, R.M.; Sanz, J.; Réau, J.M.; Rossignol, S.; Tanguy, B.; Portier, J.: Influence of chlorine-oxygen substitution on the electrical properties of some oxychloride tellurite glasses, J. Mater. Chem. **4** (1994) p. 1433-1436.

11. Imaoka, M.: Glass-formation range and glass structure, Advances in Glass Technology Part I, PlenumPress, New York (1962), p. 149-164.

12. Vogel, W.; Bürger, H.; Müller, B.; Zerge, G.: Untersuchungen an Telluritgläsern, Silikattechnik **25** (1974) p.205-209.

13. Mochida, N.; Takahashi, K.; Shibusawa, S.: The behavior of Te^{4+} ion in Na_2O-TeO_2-SiO_2 glasses, J. Ceram. Soc. Jpn **88** (1980) p 583-588.

14. Vogel, W.: Glass Chemistry - 2nd edition, Spring Berlin (1992) p.75.

15. Jayasinghe, G.D.L.K., Dissanayake, M.A.K.L., Careem, M.A., Souquet, J.L.: Electronic to ionic conductivity of glasses in the Na_2O-V_2O_5-TeO_2 system, Solid State Ionics **93** (1997) p.291-295.