JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 4, April 2007, p. 836 - 839

The Li_2O/CuO ratio influence on structure of some telluride glasses

I. ARDELEAN*, C. MARCUS, R. CICEO LUCACEL
Faculty of Physics, Babes-Bolyai University, 400084, Cluj-Napoca, Romania

The local structure of $2TeO_2 \cdot xLi_2O \cdot (1-x)CuO$ glass system with $0 \le x \le 0.5$ was investigate by means of FT-IR and Raman spectroscopies. Both techniques had provided interesting information about the structural units involved in these glasses structure. A network, mainly build by trigonal bypiramids (TeO_4), trigonal pyramids (TeO_3) and TeO_{3+1} polyhedra was propose for the investigated glasses. Moreover, the Li_2O/CuO ratio influences on the structural units detected, was analyzed. It was found that the Li_2O/CuO ratio increases implies the conversion of the TeO_4 trigonal bypiramids and TeO_{3+1} polyhedra into TeO_3 trigonal pyramids having two or three nonbridging oxygen (NBO) atoms.

(Received November 2, 2006; accepted February 28, 2007)

Keywords: Lithium-copper-tellurite glasses, FT-IR spectroscopy, Raman spectroscopy

1. Introduction

Tellurite glasses have been studied for over 150 years, however the first major systematic study was made by Stanworth [1] on the basis that tellurium has electronegativity in the range of other good glass former oxide cations (Si, B, P, Ge, As, and Sb). With the current interest in an efficient broadband, flat gain fibre optic amplification and low-loss infrared (IR) optical fibre, tellurite glasses have received considerable attention in the last 10 years. Advantages of tellurite glasses include: reasonably wide transmission range (~ 400 nm to 6 μm), good glass stability, strength and corrosion resistance, relatively low phonon energy for an oxide glass (~ 800 cm^{-1}); high refractive index, large third-order nonlinear optical susceptibility and good ionic conductors for certain composition at room temperature (~ 2) [2]. However, tellurite glasses found applications in solid state batteries, fuel cell, gas sensors and infrared filters [3].

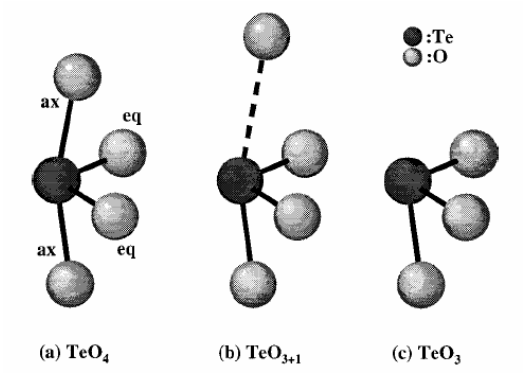

Fig. 1. Typical structural units found in tellurite glasses: TeO_4 trigonal bipyramid (a), TeO_{3+1} polyhedron (b), and TeO_3 trigonal pyramid (c).

Tellurium atoms have four neighbouring oxygen atoms and the basic structural unit is a TeO_4 disphenoid, or if we take into account the $5s^2$ lone pair of tellurium atoms, a distorted trigonal bipyramid tbp unit. In TeO_4 tbp, the two equatorial oxygen atoms are separated from Te by distances shorter than the sum of the covalent radii of O and Te, and the two axial oxygen atoms by distances longer than that value (Fig. 1). Each oxygen atom is coordinated to two tellurium atoms thus forming a highly asymmetric bridge $Te\text{-}axO_{eq}\text{-}Te$ [3 -6].

Under normal condition, tellurium oxide has no vitrification ability without a modifier. Researchers have different opinions about the fact that is difficult to form a glass of pure TeO_2. Some of theme think that TeO_2 could not form a glass by itself because of the Te-O bond is too strongly covalent to permit the requisite amount of distortion for a glass structure. Another prevalent view is that the repulsive forces between the lone pare of electrons resist to the free movement of the trigonal bipyramid in space [7-12].

Introduction of the modifier into TeO_2 network will break Te-O-Te bonds from TeO_4 tbp and at the same time will give rise to new structural units such as TeO_3 with nonbridging oxygen. The TeO_3 unit is a trigonal pyramid tp_3 in witch an electron lone pair occupies one of the Te sp^3 hybrids orbital [13, 16, 17]. The addition of transition-metal (Cu) oxide to glasses, in general, permits the possibility for the glasses to exhibit semiconducting behavior [3].

2. Experimental details

2.1 Sample preparation

Glasses were prepared using a conventional melt-quenching method. As starting materials were used reagent

grade purity TeO_2, Li_2CO_3 and CuO in suitable proportion. Compositions prepared in the present study are $2TeO_2 \cdot xLi_2O \cdot (1-x)CuO$ where x is 0, 0.01, 0.03, 0.1, 0.2, 0.3, and 0.5. Since oxidation and reduction in a glass melt are known to depend on the size of the melt, on the sample geometry, whether the melt is static or stirred, on thermal history, and on quenching rate, all glass samples were prepared under similar condition to minimize these factors. There were used 2.5 g of prime materials. Those were thoroughly mixed in a crucible to obtain a homogenized mixture for each sample. The mechanically homogenized mixtures were melted for 6 minutes in an electrical furnace at 1000°C. The homogenized melt was then cast quenched between two stainless-steel plates at room temperature. For x > 0.5 we did not obtained glasses, those would be outside the region of glass formation.

2.2 FT-IR measurements

The FT-IR spectra were recorded with a Bruker EQUINOX 55 spectrometer. The EQUINOX 55 offers the highest experimental versatility available in an FT-IR spectrometer. In its base configuration, the EQUINOX 55 covers a wide range in the mid- and near-IR regions. The standard spectral resolution, better than 0.5 cm^{-1}, is suitable for most applications. The FT-IR absorption measurements were done using the KBr pellet technique. In order to obtain good quality spectra the samples were crushed in an agate mortar to obtain particles of micrometer size. This procedure was applied every time to fragments of bulk glass to avoid structural modifications due to ambient moisture.

2.3 Raman measurements

The Raman spectra of the samples were recorded with a Dilor Raman microspectrometer (Horiba-Jobin-Yvon, model LabRam) using 514.5 nm excitation line from a Spectra Physics model 2016 argon ion laser. The detection of the Raman signal was carried out with a camera Photometric model 9000 CCD camera. A laser power of 100 mW was used for the acquisition of the Raman spectra of glasses at different concentration. The Raman spectra were collected in the back-scattering geometry with a resolution of 5 cm^{-1}.

3. Results and discussion

3.1 FT-IR investigation

The FT-IR spectra of $2TeO_2 \cdot xLi_2O \cdot (1-x)CuO$ glasses with various content of lithium oxide ($0 \le x \le 0.5$) are presented in Fig. 2. The FT-IR data have been analyzed on the basis of the method given by Condrad and Tarte [18, 19] by comparing the experimental data of glasses with those of related crystalline compounds. The characteristic absorption bands for the vitreous TeO [5-10], crystalline CuO and Li_2O [9, 13 - 15] were used as a reference point in the discussion of the results.

In the glass matrix spectrum the following bands are present: a strong band at ~ 665 cm^{-1}, two weak bans at ~ 470, ~ 1032 cm^{-1} and a weak shoulders at ~ 877 cm^{-1}, all situated in the near-IR domain. The obtained bands of the IR and Raman spectra and their assignments are summarized in Table 1.

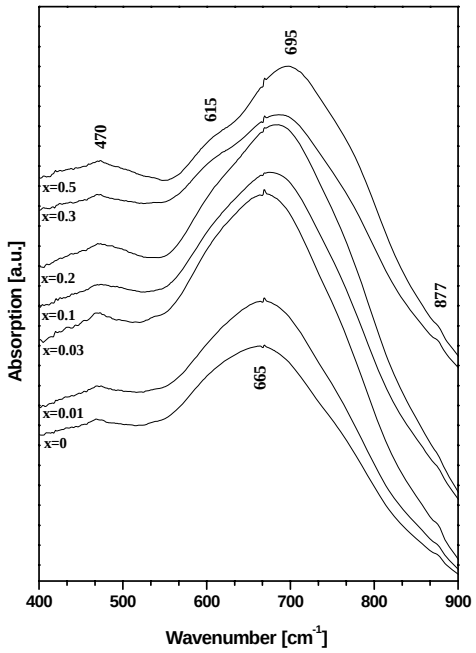

Fig. 2. FT-IR spectra of $2TeO_2 \cdot xLi_2O \cdot (1-x)CuO$.

The absorption band at ~ 470 cm^{-1} witch slightly increase in intensity with Li_2O/CuO ratio can be assigned to Te-O-Te bridging bond vibrations. The band from ~ 640 cm^{-1} witch is characteristic of pure TeO_2 glass is shifted to ~ 665 cm^{-1} because of the presence of cooper oxide. The band at ~ 665 cm^{-1} is attributed to symmetrical stretching vibration of Te-O bonds of TeO_4 units. Addition of a modifier to the TeO_2 glass may affect the concentration of Te-O bonds according to the type of modifier [21]. The shoulders at ~ 877 cm^{-1} is assigned to stretching vibration mode of TeO_3 tp with nonbridging oxygen.

Table 1. Frequencies and their assignments for FT-IR and Raman spectra of $2TeO_2 \cdot xLi_2O \cdot (1-x)CuO$ glasses.

Wavenumber (cm^{-1})		Assignment	
FT-IR	*Raman*	*FT-IR*	*Raman*
~470	~389	Vibrations of Te-O-Te bridging bond vibrations	Symmetric vibrations of the simple Te-O-Te bridges
~615	~460	TeO_{3+1} trigonal polyhedra units	Bending vibrations of Te-O-Te or O-Te-O linkages

Wavenumber (cm^{-1})		Assignment	
~665	~636	Symmetrical stretching vibrations of Te-O bonds of TeO_4 tbp units	Delocalised vibrations mode of the TeO_4 tbp units
~695	~754	Symmetrical stretching vibrations of Te-O-Te in TeO_4 units with bridging oxygen	Stretching vibrations of Te-O from TeO_4 tbp and TeO_3 tp with nonbridging oxygen
~877		Stretching vibration mode of TeO_3 tp with nonbridging oxygen	

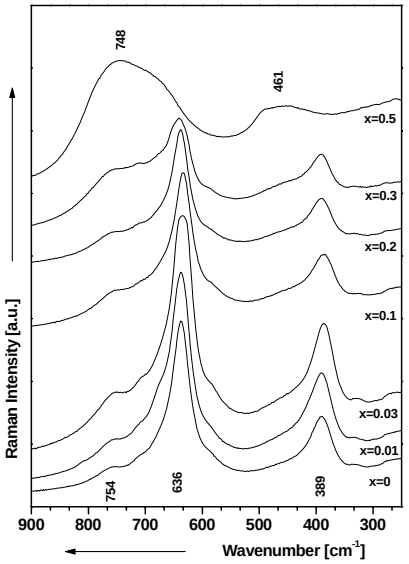

Fig. 3. Raman spectra of $2TeO_2 \cdot xLi_2O \cdot (1-x)CuO$.

With the increase of Li_2O/CuO ratio in the IR spectra of tellurite glasses appears a weak shoulder around 615 cm^{-1}, while the shoulder at ~ 877 cm^{-1} does not move substantially. The shoulder at ~ 615 cm^{-1} correspond to the so called 3+1 coordination (TeO_{3+1}), were one Te-O axial distance is elongated while the opposite is shortened [22]. Also, with increases of Li_2O/CuO ratio the strong band at ~ 665 cm^{-1} is shifted towards higher wavenumber (695 cm^{-1}) due to an enhancement of the polymerization degree of the TeO_2 network or to an increases in the formation of the TeO_{3+1} structural units [8]. The strong band at 695 cm^{-1} is assigned to symmetrical stretching vibration of Te-O-Te in TeO_4 units with bridging oxygen. IR intensity absorption bands shows a progressively disorder of the vitreous networks of TeO_2-based glasses with increasing of Li_2O/CuO ratio and tellurium polyhedra change gradually from TeO_4 trigonal bipyramid to TeO_3 trigonal pyramid [22 - 24].

3.2 Raman investigation

The experimental Raman spectra of the $2TeO_2 \cdot xLi_2O \cdot (1-x)CuO$ glass system, with various content ($0 \leq x \geq 0.5$) are shown in figure 3. In the spectrum of the glass matrix $2TeO_2 \cdot CuO$, we note the following feature: a medium band at 389 cm^{-1}, a strong band at 636 cm^{-1}, and a shoulder at 754 cm^{-1}.

The band in the 350-600 cm^{-1} compositional range (~ 389 cm^{-1}), can be conventionally associated with the symmetric vibration of the simple Te-O-Te bridges. The high-frequency side of this band is assigned to vibration of the double Te-O_2-Te bridges. We can assume the existence of simple asymmetric Te-axO_{eq}-Te linkages as formed in α-TeO_2, and the existence of simple symmetric and asymmetric bridging bonds existing in γ-TeO_2 polymorph [11,13].

As can bee seen the strongest band at ~ 636 cm^{-1} can be assigned to the delocalized vibrational mode of the TeO_4 tbp units. The band at ~ 636 cm^{-1} witch dominates the Raman spectrum of the glasses mainly originates from the symmetric pulsation of the largely covalent Te-O_{eq} bonds [8]. The existence of the shoulder (754 cm^{-1}) can be related to the presence of a small amount of TeO_3 tp units containing terminal Te-O bonds such as Te=O and Te-O^- [25, 26]. The shoulder at 754 cm^{-1} correspond also to the symmetric stretching vibration of Te-O from TeO_4 with nonbridging oxygen (NBO) and of some deformed TeO_{3+1} polyhedra units [12, 25, 26].

In $TeO_2 \cdot Li_2O$ glass system [27], Raman bands due to TeO_4 tbp and TeO_3 tp were found at ~ 770 and 670 cm^{-1} respectively, at higher wavenumber than that observed in our work (~ 754 and ~ 636 cm^{-1}). We attribute this difference to the influence of Cu^{2+} ion, which, apart from breaking up the network and converting the TeO_4 tbp units to TeO_3 tp units, also lengthens the Te-O bonds and hence lower the vibrational wavenumber of the corresponding bands [27]. In our glass system the concentration of CuO is higher for all samples. The relative intensity of the ~ 754 cm^{-1} band increases with Li_2O/CuO ratio, in relation to that of the ~ 636 cm^{-1} band.

The Raman mode intensity at ~ 636 cm^{-1} decreases, whiles the shoulder at ~ 754 cm^{-1} increase. This evolution indicates the changes among the basic units. The perturbation of the telluride network consists in the conversion of a part of the TeO_4 units (~ 636 cm^{-1}) into TeO_3 units via the intermediate coordination TeO_{3+1} (~ 754 cm^{-1}) [28]. The shoulder at ~ 754 cm^{-1} would come from a redistribution of the Raman intensities due to the spatial rearrangement of TeO_4 units with low symmetry [29].

When the concentration of Li_2O reaches at 0.5 values the strong band at 636 cm^{-1} is shifted to higher frequency (~ 748 cm^{-1}) while the shoulder at ~ 754 cm^{-1} is hided by this new band. The band at ~ 389 cm^{-1} that indicates the presence of at least two kinds of Te-O-Te bridging bonds [9], is shifted to ~ 461 cm^{-1}, whose intensity is much lower. This new band corresponds to bending vibration of Te-O-Te or O-Te-O linkages, as encountered in α-TeO_2 structure [11,15].

4. Conclusion

FT-IR and Raman spectroscopies have been used in order to approach the structure of TeO_2-Li_2O-CuO glasses. The two intense bands dominating the Raman spectrum of TeO_2 glasses, and lying in the range 300-400 and 600-800 cm^{-1}, indicate that the Te-O-Te bridges and Te-O terminal bonds are the independent structural fragments of the glass.

Tellurium in those glasses is present as TeO_4 trigonal bipyramids, TeO_3 pyramids and TeO_{3+1} polyhedra. The increase of Li_2O/CuO content modified the coordination of tellurium atoms from 4 to 3, simultaneously with the apparition of nonbridging oxygen atoms, denoting the depolymerization of the structure. Li_2O oxide induced structural modifications of the telluride glasses network and thus it is assumed to play the role of glass modifier. The relative properties of each entity depend on the glass concentration. No characteristic bands for Li-O or Cu-O links vibrations were found.

References

[1] J.E. Stanworth, J. Soc. Glass Technol. **38**, 425T (1954)

[2] M. D. O'Donnell, C. A. Miller, D. Furniss, V. K. Tikhomirov, A. B. Seddon, J. Non-Cryst. Solids **331,** 48 (2003).

[3] G. D. Khattak, A.Mekki, L. E. Wegner, J. Non-Cryst. Solids **337,** 174 (2004).

[4] A. P. Mirgorodsky, T. Merle-Mejean, J.-C. Champarnaud, P. Thomas, B. Frit, J. of Phys. Chem. of Solids, **61,** 501 (2000).

[5] S. Suehara, S. Hishita, S. Inoue, A. Nukai, Phys. Rev. B, **58**(21), 14 124 (1998).

[6] J. C. Champarnaud-Mesjard, S. Blanchandin, P. Thomas, A. Mirgorodsky, T. Merle- Mejean, B. Frit,J. of Phys. Chem. of Solids, **61,** 1499 (2000).

[7] M. A. Salim, G. D. Khattak, N. Tabet, L. E. Wenger, J. of Elect. Spec., **128,** 75 (2003).

[8] L. Baia, M. Bolboaca, W. Kiefer, E. S. Yousef, C. Rüssel, F. W. Breitbarth, T. G. Mayerhöfer, J. Popp, Phys. Chem. Glasses, **45**(3), 178 (2004).

[9] K. Muruganandam, M. Seshasayee, J. Non-Cryst. Solids**, 222,** 131 (1997).

[10] T. Sekiya, N. Mochida, S. Ogawa, J. Non-Cryst. Solids, **185,** 135 (1995).

[11] T. Sekiya, N. Mochida, A. Soejima, J. Non-Cryst. Solids, **191,** 115 (1995).

[12] I. Shaltout, YI Tang, R. Braunstein, A. M. Abu-Elazm, J. Phys. Chem. Solids, **56(1),** 141 (1995).

[13] B. V. R. Chowardi, K. L. Tan, Fang Ling, J. of Mat. Sci., **35,** 2015 (2000).

[14] F. Bentley, L. D. Smithson and A. L. Rozek, Infrared Spectra and Characteristic Frequencies 700-300 cm^{-1}, Interscience, New York, (1986) p. 103.

[15] R. F. Cuevas, L. C. Barbosa, A. M. de Paula, Y. Liu, V. C. S. Reynoso, O. L. Alves, N. Aranha, C. L. Cesar, J. Non-Cryst. Solids, **191,** 107 (1995).

[16] L. C. Sabadel, P. Armand, D. Cachau-Herreillat, P. Baldeck, O. Doclot, A. Ibanez, E. Philippot, J. of Solid State Chem., **132,** 411 (1997).

[17] M. A. Salim, G. D. Khattak, N. Tabet, L. E. Wenger, J. of Elect. Spec., **128,** 75 (2003).

[18] P. Tarte, Physics of Non Crystalline Solids, Ed. by I. A. Prins, Elsevier, Amsterdam, (1964) p. 549.

[19] R. A. Condrate, J. Non-Cryst. Solids, **84**, 26 (1986).

[20] A. Abd El-Moneim, Mat. Chem. Phys. **73,** 318 (2002).

[21] P. Charton, P. Armand, J. Non-Cryst. Solids **333,** 307 (2004).

[22] Y. Dimitriv, V. Dimitrov, M. Armandov, D. Topolov, J. Non-Cryst. Solids, **57,** 147 (1983).

[23] V. Ravi Kumar, N. Veeraiah, J.of Mat. Sci. Lett. **16,** 1816 (1997).

[24] B. V. R. Chowardi, K. L. Tan, Fang Ling, Solid State Ionic **113-115,** 711 (1998).

[25] Y. Iwadate, M. Suzuki, T. Hattori, K. Fukushima, S. Nishiyama, M. Misawa, T. Fukunaga, K. Itoh, J. of Alloys and Compounds **389,** 229 (2005).

[26] R. Ciceo Lucacel, I. Ardelean, Phys. Chem. Glasses, **45**(4), 295 (2004).

[27] J. Zhang, J. Qui, Y. Kawamoto, Mat. Lett**. 55,** 77 (2002).

[28] Y. B. Dimitriev, M. A. Bursukova, E. P. Kashchieva G. P. Gotchev, J. Mater. Sci. Lett. **16,** 1622 (1997).

[29] T. Sekiya, N. Mochida, A. Ohtsuka, M. Tonokawa, J. Non-Cryst. Solids **144,** 128 (1992).

*Corresponding author: arde@phys.ubbcluj.ro