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R. C. Lucacel, I. C. Marcus, I. Ardelean, O. Hulpus. Structural studies of copper doped 2TeO-PbO-AgO glass by FT-IR and Raman spectroscopies. European Physical Journal: Applied Physics, 2010, 51 (3), pp.30901. 10.1051/epjap/2010120 . hal-00618498

HAL Id: hal-00618498

<https://hal.science/hal-00618498>

Submitted on 2 Sep 2011

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STRUCTURAL STUDIES OF COPPER DOPED 2TeO_2 - PbO - Ag_2O GLASS BY FT-IR AND RAMAN SPECTROSCOPIES

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Abstract

The FT-IR absorption and Raman scattering were used in order to obtain information concerning the short range order in $x\text{CuO} \cdot (100-x)[2\text{TeO}_2 \cdot \text{PbO} \cdot 0.2\text{Ag}_2\text{O}]$ ($0 \leq x \leq 5$ mol %) glasses. Moreover, the changes in tellurium atoms coordination that occurs with copper oxide addition were followed. Both techniques reveal that tellurium is disposed in the network structure as trigonal bipyramids (TeO_4), trigonal pyramids (TeO_3) along with TeO_{3+1} polyhedra units. Increasing the CuO content in the glasses changes the coordination of tellurium atoms from 4 to 3 through the so-called 3+1 intermediate units, simultaneously with the increase of the non-bridging oxygen (NBOs) causing a depolymerization process in the glass structure.

PACS: 61.43.Fs, 78.30.-j

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1. Introduction

Tellurium oxide glasses are the subject of intense current research because of their interesting electrical and optical properties. TeO_2 -based multi-component glasses have good glass stability, strength and corrosion resistance [1], high density [2] and low melting temperature ($\approx 800^\circ\text{C}$) [3]. Tellurite glasses are well known to have the highest refractive index among oxide glasses in the visible and IR region [4] along with a wide band infrared transmittance [5]. Beside these tellurite glasses have also a high dielectric constant [6], high thermal-expansion coefficient [7] and thermochromic properties [2]. Based on the above properties tellurite glasses can be utilized as photonic devices [8], in optical filters, modulators, memories, laser window, in solid state batteries, fuel cells and gas sensors [9].

Different infrared [10, 11] and Raman [9, 12-13] spectroscopic studies have showed that tellurite based network is formed from several asymmetric structural units, such as TeO_4 trigonal bipyramids (TBP), TeO_{3+1} polyhedra and TeO_3 trigonal pyramids (TP). It is well known that tellurium oxide belongs to the intermediate class of glass-forming oxides and does not readily form glass because the octahedral Te-O polyhedron is highly rigid to get the required distortion of Te-O bonds necessary for forming a stable random network. However, it does form glass when mixed with modifiers such as PbO. Introducing a network modifier into the glass matrix changes the Te coordination polyhedron from TeO_4 to TeO_3 by breaking Te-O-Te bonds, along with the formation of non-bridging oxygen (NBOs) atoms. It is well known that lead oxide acts in the glass structure as both network modifier and/or former depending upon its concentration in the composition. Beside its interesting behavior lead oxide was chosen also because it gives resistance against devitrification [11]. A recent study has showed that tellurite glasses containing silver nanoparticles possess optical birefringence [14] and good ionic conductivity [15] while those containing copper oxide present semiconducting and magnetic properties [16].

Therefore, in this work we report the melting synthesis of glasses from CuO- TeO_2 -PbO-Ag₂O system and their structural characterization through spectroscopic methods with a goal to optimize the composition of the glasses for some possible future application.

2. Experimental details

The samples from the $x\text{CuO} \cdot (100-x)[2\text{TeO}_2 \cdot \text{PbO} \cdot 0.2\text{Ag}_2\text{O}]$ where x values vary from 0 to 5 mol% were prepared using the conventional melt quenching technique. The starting materials used were of analytical grade, i.e. CuO, TeO₂, PbO and AgNO₃. The appropriate amounts of chemicals were manually mixed in an agate pellet. The mixtures corresponding to the desired compositions were melted in air, in sintered corundum crucibles, in an electric furnace at 1150°C for 6 minutes. The melts were quickly cooled at room temperature by pouring and stamp them between two stainless-steel plates to avoid any undesired crystallization process. For FT-IR measurements same amount of glasses were powdered and mixed with KBr in order to obtain thin pellets with a thickness of about 3 mm. The FT-IR absorption spectra were recorded in the range 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹ using an Equinox 55 Bruker spectrometer. The Raman spectra were performed using a Dilor Labram spectrometer (Horiba-Jobin-Yvon, model LabRam) with 785 nm excitation line from a Spectra Physics model 2016 argon ion laser. The detection of the Raman signal was carried out with a CCD camera (Photometric 9000 model). The spectra were collected in the back-scattering geometry with a resolution of 2 cm⁻¹.

3. Results and discussion

The FT-IR spectra obtained for studied glasses are given in figure 1 (a). The spectra were analyzed based on the method given by Condrate and Tarte [17, 18] by comparing the experimental data of glasses with those of related crystalline or vitreous compounds. In other words as reference point were used the characteristic absorption bands from vitreous TeO₂ and PbO [19] along with the crystalline compounds Ag₂O and CuO [15, 20].

Fig. 1. FT-IR spectra of $x\text{CuO}(100-x)[2\text{TeO}_2\cdot\text{PbO}\cdot 0.2\text{Ag}_2\text{O}]$ glasses (a)

Due to the fact that the infrared spectra consist on a relatively wide envelope centered at $\sim 667\text{ cm}^{-1}$, along with minor contribution at ~ 425 and 875 cm^{-1} a curve-fitting procedure (PeakFit v4.12) has been use to deconvolute the spectra using the same number of peaks at approximately the same frequency.

The analysis of the deconvoluted spectrum of the glass matrix (figure 1 (b)) shows the existence of four weak bands at ~ 425 , ~ 509 , ~ 817 and $\sim 875\text{ cm}^{-1}$, two medium bands at ~ 565 and $\sim 747\text{ cm}^{-1}$ and a strong band at $\sim 667\text{ cm}^{-1}$. Their assignments are summarized in table 1.

Fig. 1. FT-IR deconvoluted bands of the glass matrix $2\text{TeO}_2\cdot\text{PbO}\cdot 0.2\text{Ag}_2\text{O}$ (b)

Table 1. Assignments of the FT-IR and Raman bands in the spectra of $x\text{CuO}(100-x)[2\text{TeO}_2\cdot\text{PbO}\cdot 0.2\text{Ag}_2\text{O}]$ glasses

Peak positions (cm^{-1})		Assignments	
FT-IR	Raman	FT-IR	Raman
	~ 335		Bending vibrations of TeO_3 tp units with NBOs [24], Te-O-Pb linkages [12]
~ 425	~ 465	Vibrations of Te-O-Te bridging bond in TeO_4 tbp units [3, 10-11, 24]	Bending vibrations of Te-O-Te or O-Te-O linkages in TeO_4 tbp units [9, 20]
~ 509		Symmetric Te-O-Te linkage vibrations [3]	
~ 565		Te-O vibrations, where the O anions were considered as NBO [3]	
~ 667	~ 645	Symmetric stretching vibrations of Te-O-Te in TeO_4 tbp units [3, 11, 24]	Stretching vibrations of Te-O-Te linkages from TeO_4 tbp [2, 9, 24]

~ 747	~ 725	Stretching vibrations of TeO_3 tp or TeO_{3+1} polyhedra with NBOs [11, 24]	Stretching vibrations mode of TeO_{3+1} polyhedra and TeO_3 tp with NBOs [2, 9, 20, 23]
~ 817 ~ 875		Stretching vibrations mode of TeO_3 tp with NBOs [3, 13]	

Since we have used in description of these glasses structure the term of TeOn polyhedra, it is necessary to define the terms tbp and the tp units with respect to configuration and bond lengths. Trigonal pyramid units (tp) (TeO_3^{2-} , $\text{O}_{2/2}\text{Te}-\text{O}$ and $\text{O}_{1/2}\text{Te}(=\text{O})\text{O}^-$) have shorter bonds (app. 0.188nm) [21] while TeO_4 trigonal bipyramid units (TBP) have longer bonds though the length depends on crystals. Suzuki [22] propose as ones constituent for TeO_2 glasses, the TeO_{3+1} units where three oxygen atoms are at 0.195 nm and the fourth one at 0.218 nm.

According to the assignments of the infrared absorption bands the glass matrix show that tellurium ions are both 4^- and 3^- coordinated, the network being mainly build by TeO_4 (TBP). The existence of the TeO_3 trigonal pyramid and TeO_{3+1} polyhedra unit was also detected in the local structure of vitreous matrix.

Adding gradually small quantities of copper oxide into the glass matrix composition induces some changes in terms of FT-IR line shape. The weak band centered at $\sim 425 \text{ cm}^{-1}$ disappears proving that the Te-O-Te bridging are broken leading to an increase of the amount of the nonbridging oxygen atoms (NBO). Another proof of this aspect is the lack of the band from $\sim 509 \text{ cm}^{-1}$ in the FT-IR spectra of samples containing even and more than 1 mol% copper oxide. When the amount of copper oxide reaches the 5 mol% value, the band at $\sim 565 \text{ cm}^{-1}$ shifts to a lower wavenumber ($\sim 548 \text{ cm}^{-1}$) revealing the increase of the Te-O- bond and more over, the gradually depolymerisation of the glass network.

The absorption band centered at $\sim 667 \text{ cm}^{-1}$ dominates the spectra through all compositional range showing the predominance of TeO_4 tbp units in the local

structure of these glasses. On the other hand no major changes undergo with the bands from ~ 747 , ~ 817 and ~ 875 cm^{-1} with the copper oxide addition.

Based on the way in which the infrared spectra of these glasses has changed at the copper oxide addition we may assume a minor rearrangement tendency of the local structure which relates mostly to changes in the relative amount of TeO_3 and TeO_4 units. A better understanding of the changes that occur in the local order of these glasses can be obtained by calculating the relative area under the infrared absorption bands that are responsible for $\nu(\text{TeO}_3)$ and $\nu(\text{TeO}_4)$, keeping in view that the main contributions of those appear around 747, 817, 875 cm^{-1} for TeO_3 units and 425, 667 cm^{-1} for TeO_4 units. So that, we have calculated the relative areas corresponding to these peaks individually, then we have found the relative area corresponding to the peaks coming from all TeO_3 units (A_{TeO_3}) and all TeO_4 units (A_{TeO_4}). We assume that the calculated ratio between these two geometrical relative areas ($A_r = A_{\text{TeO}_3} / A_{\text{TeO}_4}$) reflect the ration between the relative amount of TeO_3 (N_{TeO_3}) and TeO_4 (N_{TeO_4}) units ($A_r \sim N_{\text{TeO}_3} / N_{\text{TeO}_4}$). The evolution of the ratio between the relative amount of TeO_3 and TeO_4 units A_r as function of copper oxide mol% concentration is shown in figure 2 (a).

Fig. 2. A_r ratio vs. x mol% (a)

All the values of A_r ratio are powerfully sub unitary signifying as we suspect that in all compositional range the amount of the units where tellurium is 4⁻ coordinated is higher than the one in which is 3⁻ coordinated. The trend of A_r ratio with the copper oxide confirms the gradual depolymerization of the vitreous network at CuO addition. The transition between TeO_4 and TeO_3 structural units is made by shortening of one of the axial bond while one equatorial bond gets longer (TeO_{3+1} polyhedra).

Fig. 2. Raman spectra of $x\text{CuO}(100-x)[2\text{TeO}_2\cdot\text{PbO}\cdot 0.2\text{Ag}_2\text{O}]$ glasses (b)

Figure 2 (b) shows the Raman spectra of the investigated glasses. The assignments of the bands detected in the Raman spectra are also listed in table 1. Raman spectrum of the glass matrix is dominated by two bands centered at $\sim 335\text{ cm}^{-1}$

and $\sim 725\text{ cm}^{-1}$. Raman measurements seem to be more sensitive to the direct effect of the lead oxide as modifier into the glass matrix network rather than the infrared measurements. Noticeable effects are as follows: first the appearance of the band at $\sim 335\text{ cm}^{-1}$ which can be either assigned to the bending vibrations of TeO_3 tp units with NBOs or to the Te-O-Pb bond and second the fact that the band from 725 cm^{-1} (responsible for vibrations mode of TeO_{3+1} polyhedra and TeO_3 tp with NBOs) it is already present – usually it appears when the network is already depolymerised. This happens because PbO enters into the glass lattice network by breaking up the Te-O-Te bonds (the oxygen atoms of lead oxide break the local symmetry while Pb^{2+} ions occupy interstitial positions) inducing coordinated rearrangements. Along these two above bands, Raman spectrum of the matrix presents also two shoulders centered at $\sim 465\text{ cm}^{-1}$ and $\sim 645\text{ cm}^{-1}$ proving the existence of the three structural units detected also through the FT-IR measurements is confirmed by the Raman scattering. Therefore, the structure of the glass matrix network is a mixture of TeO_4 , TeO_{3+1} and TeO_3 units. A very confusing aspect is regarding to the fact that the Raman spectra present a dominant band centered at $\sim 725\text{ cm}^{-1}$ revealing a structure mainly build by TeO_{3+1} and trigonal pyramid units-contrary with that proposed by FT-IR data. So that, we assume that the contribution of TP units at this band is minor related to that of TeO_{3+1} units.

With copper oxide addition the Raman intensity of all bands decreases slowly up to 0.5 mol% and then rapidly for the rest of compositional domain. This evolution indicates that the change in coordination of Te atoms depends strongly on the cation. Thus, while the band from 645 cm^{-1} is exclusively due to the TeO_4 units and band from 725 cm^{-1} is due to both TeO_3 and TeO_4 it is quite difficult to predict the exact amount of each TBP and TP units. Still it is obvious that copper oxide addition induces a continuously depolymerisation of these glasses local structure given by the increases of TP units and probably NBO atoms numbers.

4. Conclusion

The glasses from $x\text{CuO} \cdot (100-x)[2\text{TeO}_2 \cdot \text{PbO} \cdot 0.2\text{Ag}_2\text{O}]$ ($0 \leq x \leq 5$ mol%) system were prepared and investigated through FT-IR absorption and Raman scattering. The presence of the TeO_4 , TeO_{3+1} and TeO_3 structural units in these glasses local structure was detected by both techniques used. Moreover, we assume that TeO_4 and TeO_{3+1} structural units dominate the vitreous network of these samples. A gradually depolymerization of the glass network with CuO addition was evidenced. The increase of the disorder at short range order is given by the transformation of TeO_4 and TeO_{3+1} units to TeO_3 ones along with the increase of NBO atoms number. All these sustained that the CuO behaves as a network modifying oxide in these tellurite based glasses.

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