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FTIR and Raman spectroscopic studies of copper doped $2GeO_2·PbO·Ag_2O$ glasses

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

The samples from the $xCuO·(1-x)[2GeO_2·PbO·0.2Ag_2O]$ glass system ($0 \le x \le 0.05$) were prepared and studied by means of FTIR absorption and Raman scattering. Both techniques revealed that germanium is disposed in the samples structure as GeO_4 tetrahedral units. Moreover, from the Raman data has also detected the presence of the GeO_6 octahedra units in the glasses structure. With the CuO addition in the samples take place a change in the germanium atom coordination from four-fold to six-fold. The short range order of the network was found to be affected by the copper ions additions.

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1. Introduction

The glasses based on the germanium dioxide offer good possibilities for making innovations. Although the glass forming property of GeO_2 has been known for a long time, serious and systematic study of germanate glasses and the glass properties of germanium oxides has begun only in recent times [1]. A number of applications have been already made possible by developments of germanate glasses. For example, due to the large coefficient of linear expansion in germanate glasses it is possible to get glass-to-metal seals for ultra high vacuum. GeO_2 is used as one of the compounds for insulating layer, in optics as windows and for manufacturing optical waveguides [1 - 4]. Germanium dioxide has also distinguished itself in the form of the fiber optics in the infrared (IR) regions of 1.7 to 1.8 microns [1, 5].

Germanate and alkali-containing germanate glasses in particular, are known to exhibit maxima or minima in physical properties such as density, refractive index, electrical conductivity, viscosity, chemical stability and oxygen content. In alkali germanate glasses this behavior has been named “germanate anomaly” [1]. The appearance of the anomalous behavior in the properties versus composition curves was first observed by Evstropev and Ivanov [6, 7]. In many studies [1, 6 - 9] the “germanate anomaly” was interpreted as resulting from the change in the coordination state of germanium with oxygen ($4 \rightarrow 6$) up to maximum or minimum in the observed properties, followed by a conversion of GeO_6 octahedra to GeO_4 tetrahedra beyond the anomaly. The anomalous behavior of some physical properties as a function of concentrations was also evidenced in $PbO-GeO_2$ glass system [7].

It is well known that lead oxide (PbO) is unique on its influence in the structure of glasses. When PbO is added to GeO_2 network, it acts either as a network former or as a modifier, depending upon its concentration in glasses [1, 10]. From the physical properties point of view lead oxide additions into the germanate glasses enhances the resistance against devitrification, improves the chemical durability, lowers the melting temperature, increases the density and the refractive index of these glasses [1]. Interesting optical properties were also found for the lead germanate glasses [1]. It is well known that glasses containing silver oxide have a good ionic conductivity [11, 12] and also many applications such as electro-chromic display devices, chemical sensors and solid batteries [11]. Glasses containing transitional metals ions such as Cu^{2+} and Cu^{+} are of interest due their possible applications in memory switching devices [12, 13].

The structure of GeO_2-based glasses have been frequently studied by means of IR absorption and Raman scattering [1, 6, 7, 10, 13 - 16], reporting that the structure consists in tetrahedral and octahedral units of germanium connected with oxygen atoms.

We prepared and studied by means of FT-IR absorption and Raman scattering the glasses from $xCuO·(1-x)[2GeO_2·PbO·0.2Ag_2O]$ system ($0 \le x \le 0.05$), with the purpose to obtain information concerning the short range order and the coordination change of germanium atoms.

2. Experimental

2.1. Samples preparation

Samples from the glass system $xCuO·(1-x)[2GeO_2·PbO·0.2Ag_2O]$ with $0 \le x \le 0.05$ were prepared and studied. All glass samples were prepared by conventional melt quenching method from reagent grade purity CuO, GeO_2, PbO and $AgNO_3$, in suitable proportion. Mixture of these chemicals of appropriate compositions was melted in a sintered corundum crucible placed in an electrical furnace at 1150°C for 6 minutes. The mixed powders were introduced directly in the preheated furnace at this temperature to avoid losses due to the evaporation. The homogenized melts were then cast quenched between two stainless-steel plates at room temperature in air.

2.2. FTIR measurements

The FTIR measurements were performed with an Equinox 55 Bruker spectrometer using the KBr pellet technique. To interpret the spectra obtained, the spectroscopic studies of glasses were made in the range 400-1100 cm^{-1}. 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 bulk glass system were recorded with a Dilor Labram spectrometer (Horiba-Jobin-Yvon) by using 514.5 nm excitation line from a Spectra Physics argon ion laser. The spectra were collected in the back-scattering geometry with a spectral resolution of 2 cm^{-1}. The detection of the Raman signal was carried out with a CCD camera (Photometric 9000 model). Raman spectra were recorded at room temperature using a laser power of 100 mW.

3. Results and discussion

3.1. FTIR and Raman investigation

Fig. 1 shows the FTIR spectra of the Cu-2GeO$_2$-PbO-Ag$_2$O glass samples. The bands evidenced in the FT-IR spectra and their assignments are summarized in Table 1. The assignments were made comparing the experimental data of glasses with those of related crystalline and vitreous compounds [1 - 3,5,15,17]. The FT-IR glass matrix spectrum is dominated by two wide, intense absorption bands placed around 566 cm^{-1} and 775 cm^{-1}. Moreover, four shoulders positioned at 430 cm^{-1}, 515 cm^{-1}, 710 cm^{-1} and 990 cm^{-1} were detected in the spectrum. As the assignments of the detected FT-IR absorption bands (see Table 1) have revealed, the germanium atoms were disposed in the glass matrix only in tetrahedral sites.

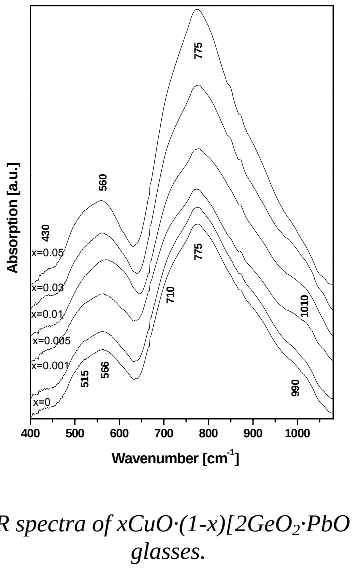


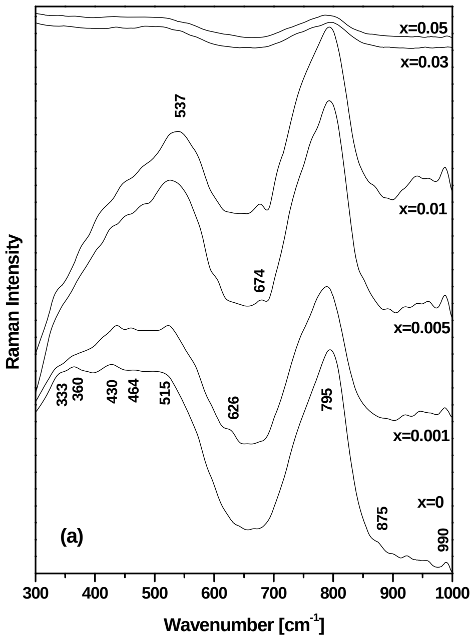
Fig. 1. FTIR spectra of xCuO·(1-x)[2GeO$_2$·PbO·0.2Ag$_2$O] glasses.

The addition of the copper oxide in the glass matrix composition and then rising this content implies an increasing in the intensity of almost all absorption bands and shoulders (515, 566, 710, 775 cm^{-1}), indicating that the number of nonbridgin oxygens (NBOs) in the tetrahedral network increases. Moreover, no supplementary absorption bands were detected with the CuO addition. Furthermore, since all above mentioned bands are coming from vibrations of different kind of linkages in GeO$_4$ units, it's seems that the copper addition leads to a numerical increase of these structural units. In the case of the shoulders placed at 430 cm^{-1} and 990 cm^{-1}, their intensities reached the maximum value for samples with x = 0.05 and 0.001, respectively. The minor shift evidenced in the case of 566 cm^{-1} absorption band to a lower wavenumber (560 cm^{-1}) can be attributed to a distribution of the mean intertetrahedral Ge-O-Ge angle (α) and an increase in tetrahedral distortion because of small ring formation [18, 19]. The shift of the shoulder around 990 cm^{-1} to a higher wavenumber (1010 cm^{-1}) with CuO addition is due to an augmentation of the average Ge-O bond strength.

Table 1. Assignments of the FTIR and Raman bands in the spectra of xCuO·(1-x)[2GeO$_2$·PbO·0.2Ag$_2$O] glasses.

Peak positions (cm^{-1})		**Assignment**	
FTIR	*Raman*	*FTIR*	*Raman*
~ 430	~ 333 ~ 360	Symmetric stretching vibrations of Ge-O-Ge from GeO$_4$ units	Ge-O-Ge bending modes
~ 515 ~ 566	~ 430 ~ 464	Symmetric stretching vibrations of Ge-O-Ge bonds	Symmetric stretching vibrations of Ge-O-Ge bonds
~ 710	~ 515	Vibrations of GeO$_4$ units	Symmetric stretching vibrations along the Ge-O-Ge chain
~ 775	~ 626 ~ 674	Asymmetric stretching vibrations of Ge-O-Ge in GeO$_4$ units	Vibrations of Ge-O bonds in GeO$_6$ octahedral units
~ 990 ~ 1010	~ 795	Asymmetric stretching vibrations of Ge-O-Ge bridges involving both O and Ge motions	Ge-O$^-$ and Ge-O-Ge symmetric stretching vibrations in GeO$_4$ tetrahedral units
	~ 875 ~ 990		Asymmetric stretching vibrations of Ge-O-Ge bonds

The integrated absorptions of the characteristic bands between 645-1100 cm^{-1} and 430-645 cm^{-1} were calculated using a computer program (PeakFit v4.12). For all compositional range the calculated area under the absorption bands corresponding to the *asymmetric* Ge-O-Ge linkage vibrations (645-1100 cm^{-1}) is higher than that corresponding to the area coming from the *symmetric* vibrations of the same bond (430-645 cm^{-1}). Moreover, the CuO content increases the ratio between these areas rises from 2.9 to 3.2. denoting modification in the short range order of the glass network structure.



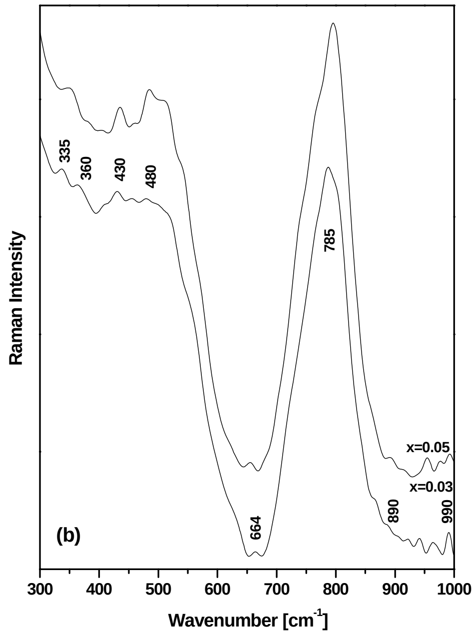


Fig. 2. Raman spectra of $xCuO \cdot (1-x)[2GeO_2 \cdot PbO \cdot 0.2Ag_2O]$ glasses.

The Raman spectra of the investigated glasses are illustrated in Fig. 2 (a) and the assignments of the detected bands are summarized in Table 1. For a better view of the changes that occur in glasses network with the cooper oxide addition the Raman spectra of samples with x = 0.03 and 0.05 are presented in Fig. 2 (b). The Raman spectrum of the glass matrix reveals five weak bands positioned at 333 cm^{-1}, 360 cm^{-1}, 430 cm^{-1}, 464 cm^{-1} and 515 cm^{-1}, a strong band at 795 cm^{-1}, a shoulder at 875 cm^{-1} and another weak band at 990 cm^{-1}. The glass matrix structure is based on GeO_4 tetrahedral units according with the assignments of the detected bands (see Table 1).

With copper oxide addition the intensity of the bands positioned at 333 cm^{-1} and 360 cm^{-1}, assigned to the Ge-O-Ge bending modes vibrations decreases but are still present as an individual contribution even in samples with x = 0.03; 0.05 (see Fig. 2 (b)). Increasing the CuO concentration over 0.001 value, the weak band from 430 cm^{-1} decrease in intensity and become a shoulder (446 cm^{-1}), with a concomitant increase in the intensity of the 515 cm^{-1} band. This trend has been previously described by Henderson et al [20], as indicating a transition from four- (or larger) membered GeO_4 rings to predominantly three-membered GeO_4 rings [15, 21]. There is also a shift of the band at 515 cm^{-1} to a higher wavenumber (537 cm^{-1}) followed by a shift back toward its original position [18, 20]. The shift to a higher wavenumber with increasing CuO content could be associated with a decrease in the main intertatrahedral bond angle (α). An increase in the number of nonbridging oxygen (NBO) per germanium tetrahedra would reduce the number of Ge-O-Ge bridges in the glasses and this correlates well with the observed decrease in intensity of the band at 537 cm^{-1}. The weak band from 626 cm^{-1} observed just for samples with x = 0.001, 0.005 and 0.01 is the proof that GeO_6 octaedral units are present in our glasses but in a small fraction [22, 23]. The band at 674 cm^{-1} (0.005 and 0.01) assigned to the GeO_6 octahedral units evidenced in the Raman spectra is shifted for x = 0.03 to a smaller wavenumber (664 cm^{-1}). At higher copper oxide content (0.03 and 0.05), the number of six-coordinated germanium atoms decreases in favor of the tetrahedral arrangements with NBOs. As cooper oxide content increases to x = 0.03 the band centered at 795 cm^{-1} is shifted to a lower wavenumber (785 cm^{-1}), denoting a decrease in the Ge-O force constant which occur as the Ge-O bond length increases. The shoulder at 875 cm^{-1} assigned to the asymmetric stretching vibrations of Ge-O-Ge bonds within the network, decrease in intensity an shifts to a higher wavenumber (890 cm^{-1}) indicating bonding changes within the tetrahedral environment [21]. For all the bands from the Raman spectra a pronounced decreases in intensity was observed when copper oxide quantity is higher than 0.03, denoting a progressively disorder of the glass network. No characteristic bands for PbO or AgO links vibrations were found.

4. Conclusion

The structure of the glass system $xCuO \cdot (1-x)[2GeO_2 \cdot PbO \cdot 0.2Ag_2O]$ ($0 \leq x \leq 0.05$) consists in tetrahedral GeO_4 units, information supported by both kinds of measurements, FTIR and Raman, while the presence of the octahedral GeO_6 structural units is confirmed only by Raman scattering. The spectroscopic analysis of the studied glasses suggested that CuO acts as a modifier and facilitate the germanium coordination changes from 4 to 6 in the compositional range 0 - 0.01 CuO. The GeO_6 units reach their maximum concentrations at ca 0.005 - 0.01 modifier level, over these values follows a conversion from GeO_6 octahedral to GeO_4 tetrahedral units. With the copper additions was observed a decrease in the polymerization degree of the structure.

References

[1] A. Margaryan, M. A. Piliavin, “Germanate glasses: Structure, Spectroscopy and Properties”, Artech House, Boston, London, 1993.

[2] L. Baia, T. Iliescu, S. Simon, W. Kiefer, J. Molec. Struct. **599,** 9 (2001).

[3] L. Baia, R. Stefan, W. Kiefer, S. Simon, Studia Univ. Babes-Bolyai, Physica, Special Issue **2**, XLVIII, 476 (2003).

[4] P. Beneventi, D. Bersani, P. P. Lottici, L. Kovacs, F. Cordioli, A. Montenero, G. Gnappi, J. Non-Cryst. Solids **192&193,** 258 (1995).

[5] K. Blaszczak, A. Adamczyk, J. Molec. Struct. **596,** 61 (2001).

[6] K. S. Estropev, A. O. Ivanov, Optomechan. Promishlinost **9,** 1 (1959).

[7] A. O. Ivanov, K. S. Evstropev, Dolk. Akad. Nauk, SSSR **145,** 797 (1962).

[8] T. Furukawa, W. B. White, J. Chem. Phys. **95(2),** 776 (1991).

[9] P. Pernice, A. Aronne, A. Marotta, M. Catauro, J. Non-Cryst. Solids **210,** 23 (1997).

[10] H. Doweidar, K. El-Igili, Abd El-Maksoud, Appl. Phys **33**, 2532 (2000).

[11] A. A. Ahmed, M. R. El-Thomy, Glass Technol **38(3),** 97 (1997).

[12] E. I. Kamitsos, J. A. Kapoutsis, G. D. Chryssikos, G. Taillades, A. Pradel, M. Ribes, J. Solid State Chem. **112,** 255 (1994).

[13] O. K. Geokchyan, K. A. Kostanyan, A. M. Sheviakov, I. V. Tarlakov, Arm. Chem. **27,** 643 (1974).

[14] D. Di Martino, L. F. Santos, A. C. Marques, R. M. Almeida, J. Non-Cryst. Solids **293-295,** 394 (2001).

[15] Y. Kim, J. Saienga, S. W. Martin, J. Non-Cryst. Solids **351,** 3716 (2005).

[16] V. N. Sigaev, I. Gregora, P. Pernice, B. Champagnon, E. N. Smelyanskaya, A. Aronne, P. D. Sarkisov, J. Non-Cryst. Solids **279,** 136 (2001).

[17] T. Yano, T. Kobayashi, S. Shibata, M. Yamane, Proc. Int. Congr. Glass **2,** 261 (2001).

[18] G. S. Henderson, R. T. Amos, J. Non-Cryst. Solids **328,** 1 (2003).

[19] G. S. Henderson, H. M. Wang, Eur. J. Mineral. **14**, 733 (2002).

[20] G. S. Henderson, H. Wang, Euro. J. Min., J. Non-Cryst. Solids **14,** 733 (2002).

[21] D. A. McKeown, C. I. Merzbacher, J. Non-Cryst. Solids **183,** 61 (1995).

[22] H. Verweij, J. H. J. M. Buster, J. Non-Cryst. Solids **34**, 81 (1979).

[23] E. I. Kamitsos, Y. D. Yainnopoulos, M. A. Karakassides, G. D. Chryssikos, H. Jain, J. Phys. Chem. **100**, 11755 (1996).

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[*] Corresponding author: arde@phys.ubbcluj.ro