

IR and Raman investigation of $x(\text{CuO}\cdot\text{V}_2\text{O}_5)(1-x)[\text{P}_2\text{O}_5\cdot\text{CaF}_2]$ glass system

N. VEDEANU, O. COZAR*, I. ARDELEAN, B. LENDL^a

Babes-Bolyai University, Department of Biomedical Physics, Cluj-Napoca 400084, Romania

^a*Vienna University of Technology, Institute of Chemical Technologies and Analytics, A-1060 VIENNA, Austria*

$x(\text{CuO}\cdot\text{V}_2\text{O}_5)(1-x)[\text{P}_2\text{O}_5\cdot\text{CaF}_2]$ glass system with $0 \leq x \leq 40$ mol% were investigated using IR and Raman spectroscopy in order to put in evidence the structural changes induced by the transition metal (TM) oxides (Cu^{2+} and V^{4+} ions). Both IR and Raman spectra presents the specific bands for the phosphate network. For $x \geq 7$ mol% the depolymerization of the phosphate network appears and new short units or ring structural units occur. Non-bridging oxygen atoms are involved in the V-O-P and Cu-O-P bonds. 2D correlation spectroscopy method was also used for the analysis of the structural unit formation in these glasses. Hetero-spectral correlation analysis indicates that between the IR band at 840 cm^{-1} attributed to V-O-V stretching vibration and Raman band at 710 cm^{-1} and 1175 cm^{-1} attributed to P-O-P stretching vibration and PO_2 stretching respectively exists a strong correlation. A correlation exist also between the IR band at $\sim 650\text{ cm}^{-1}$ attributed to P-O-P symmetric stretching and the Raman band at 1175 cm^{-1} due to the symmetric stretching vibration of PO_2 group.

(Received October 14, 2005; accepted January 26, 2006)

Keywords: Glass, $\text{CuO}\cdot\text{V}_2\text{O}_5\text{-P}_2\text{O}_5\text{-CaF}_2$, Infrared spectroscopy, Raman scattering

1. Introduction

Glasses containing transitional metal (TM) ions have interesting properties due to the presence several oxidation states of these ions in the glass matrix [1].

Among TM oxides vanadium pentoxide is one of the most studied because it is a network glass former [2] and its presence in other vitreous matrix determines a network modification due to the presence of V^{4+} ions. Phosphate glasses containing copper oxide have also received much attention due to the existence of copper ions in both Cu^+ and Cu^{2+} valence states [3]. Glasses containing TM ions have been studied mainly because of their interesting optical, thermal and magnetic properties and potential applications [4-6]. The technological importance of these glasses requires a detailed understanding of the molecular and structural chemistry in order to help the determination of relationships between physical properties and their structural units [3].

Phosphate glasses containing mixed TM ions are interesting because in these glasses the presence of mixed exchange pairs was detected [4,5,7]. The effects of mixed exchange $\text{Cu}^{2+}\text{-V}^{4+}$ pairs on different properties of the phosphate glasses are reported in papers [4,5].

The vibrational (IR and Raman) investigations on different glass systems were reported in the last years [8,9]. IR structural investigation on $\text{Fe}_2\text{O}_3\text{-PbO-P}_2\text{O}_5$ glass system is reported in paper [8]. This investigation revealed that the short range order of the glassy matrix is strongly affected by the addition of PbO and Fe_2O_3 to P_2O_5 . The results also showed that there are a critical concentration of Fe_2O_3 where the iron ions change their

local structure. Raman investigation of a series of calcium phosphate glasses pointed out the role of the CaO modifier on the depolymerization process of these phosphate glasses [9].

In order to put in evidence the structural changes induced by copper and vanadium ions, $x(\text{CuO}\cdot\text{V}_2\text{O}_5)(1-x)[\text{P}_2\text{O}_5\cdot\text{CaF}_2]$ glass system with $0 \leq x \leq 40$ mol% was investigated using IR and Raman spectroscopies and also 2D hetero-spectral correlation analysis. Generalized 2D correlation spectroscopy [10-12] is a flexible method that has been applied successfully to IR, Raman, UV-Vis, fluorescence or circular dichroism spectroscopy. Hetero-spectral correlation analysis was used in this paper to compares two different spectra (IR and Raman) of the same sample with the aim to establish structural correlation regarding the changes that occur in the investigated probes.

2. Experimental

In order to prepare $x(\text{CuO}\cdot\text{V}_2\text{O}_5)(1-x)[\text{P}_2\text{O}_5\cdot\text{CaF}_2]$ glasses with $0 \leq x \leq 40$ mol% we used $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, CuO , V_2O_5 and CaF_2 of reagent grade purity. The samples were prepared by weighting suitable amounts of these components, powder mixing and mixture melting in a sintered corundum crucibles at $1250\text{ }^\circ\text{C}$ for half an hour. The mixture was put into the furnace directly at this temperature. The melts were poured then on stainless steel plates.

Raman spectra were recorded on an Olympus BX-41 Jobin Yvon Horiba with Peltier CCD cooling, using an excitation source of 632.8 nm from a He-Ne laser.

IR measurements of the glasses were obtained in the 400-2000 cm^{-1} range with a Bruker IFS66/DSP spectrometer. The measurements were made using KBr pallet technique using different fragments of bulk glass; these fragments were immediately submit to measurements in order to avoid structural modifications caused by the ambient moisture.

3. Raman spectroscopy

Most of the papers [9, 13-15] indicate for the Raman spectra of phosphate glasses the following significant bands: 600 - 800 cm^{-1} , 950 - 1100 cm^{-1} , ~ 1175 cm^{-1} and ~ 1270 cm^{-1} which are assigned to the symmetric stretching vibration of P-O-P bonds, the vibration in the PO_2^- and PO_3^- groups, the symmetric stretching vibration in the PO_2 groups and to the vibration of the P=O bonds, respectively.

The Raman spectra of $x(\text{CuO}\cdot\text{V}_2\text{O}_5)(1-x)[\text{P}_2\text{O}_5\cdot\text{CaF}_2]$ with $0 \leq x \leq 40$ mol% obtained by us are given in Fig. 1.

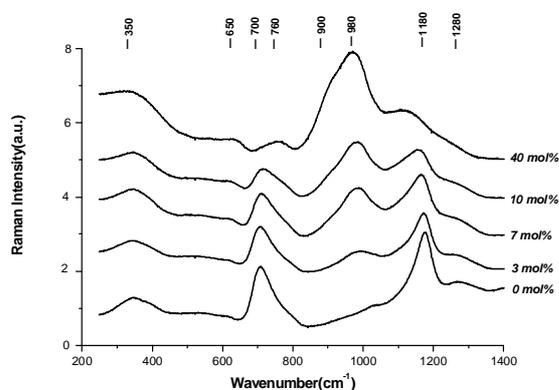


Fig. 1. Raman spectra of $x(\text{CuO}\cdot\text{V}_2\text{O}_5)(1-x)[\text{P}_2\text{O}_5\cdot\text{CaF}_2]$ glasses.

The most important bands observed in these spectra are: ~ 350 cm^{-1} assigned to the bending vibration of the phosphate polyhedra [15]; ~ 700 cm^{-1} assigned to the symmetric stretching vibration of P-O-P bonds [9, 13-15]; ~980 cm^{-1} band assigned to the vibration in the PO_2^- and PO_3^- groups [9,14,15]; ~ 1180 cm^{-1} due to the symmetric stretching vibration in the PO_2 groups [9, 15]; ~ 1280 cm^{-1} due to the vibration of the P=O bonds [14].

It is known that the TM oxides (CuO , V_2O_5) have usually a network modifier effect [16] which consist in a depolymerization of the long phosphate chains and in a local reorganization of the structural units in which only the short range phosphate units or ring structure appear.

In this context for a high content of TM oxides ($x > 7$ mol%) other bands occur in the spectra: a band at ~ 650 cm^{-1} due to the vibration of P-O-P in-chain, a band at ~ 760 cm^{-1} assigned to P-O-P asymmetric stretching vibration, a shoulder at ~ 900 cm^{-1} due to V-O stretching

vibration and a band at ~980 cm^{-1} attributed to V=O vibration in the tetragonal pyramid of V_2O_5 . These last two bands are clearly observed in the spectra of the glasses with $x \geq 10$ mol %.

Another important remark regarding the changes in the spectra of the glasses with high TM oxides content is the decrease in intensity of the 700 cm^{-1} band due to the breaking of the P-O-P phosphate chains [14] and to the appearance of short phosphate units or ring structures [9,16]. The increase in intensity of the band at ~ 650 cm^{-1} is related with the shorter chains or ring structures of phosphate units [9]. In the same time a second P-O-P symmetric stretching vibration band due to the PO_4 isolated polyhedra appears at 760 cm^{-1} as the content of PO_4 groups increases when the phosphate chains are breaking [16].

The intensity of the 1180 cm^{-1} band due to the PO_2 groups decreases in intensity and becomes broader with the increase of TM oxides content because of the depolymerization of the phosphate matrix and the increase of the disorder degree in these glasses.

The 1275 cm^{-1} band due to the P=O stretching vibration decrease also in intensity with the increasing of TM oxides content because of the formation of $\text{M} - \text{O} \equiv \text{P}$ bonds which makes weaker the initial P=O bond. The appearance of $\text{M}(\text{Cu}, \text{V}) - \text{O} - \text{P}$ bonds ($\text{Cu}-\text{O}$ at ~380 cm^{-1}) leads in the same time to the broadening of the 350 cm^{-1} band [15, 17].

4. IR spectroscopy

The same tendency of strong depolymerization of the glass network by introducing TM oxides (CuO , V_2O_5) is confirmed by the IR spectra (Fig. 2).

The important bands and their assignments are the followings: ~ 620 cm^{-1} due to the bending vibration of the P-O-P bonds; ~ 750 cm^{-1} a symmetric vibration due the P-O-P chains; ~ 940 cm^{-1} a possible superposition of the asymmetric stretching vibration of P-O-P bonds and stretching vibration in VO_2 groups; ~ 1100 cm^{-1} a symmetric stretching vibration of PO_2 groups and V=O stretching vibration; ~ 1280 cm^{-1} for P=O double stretching vibration [17-23].

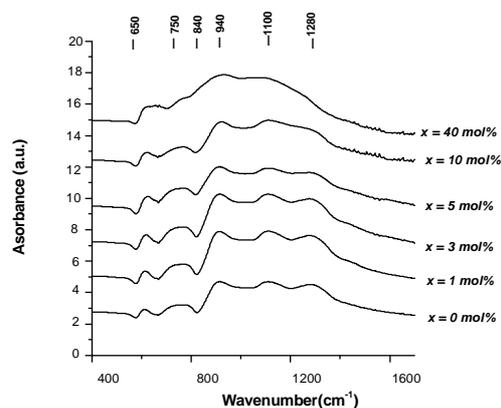


Fig. 2. IR spectra of $x(\text{CuO}\cdot\text{V}_2\text{O}_5)(1-x)[\text{P}_2\text{O}_5\cdot\text{CaF}_2]$ glasses.

The shape of the spectra is changing with the increase of the TM oxides content. The band at $\sim 650 \text{ cm}^{-1}$ becomes broader because of the phosphate chains breaking induced by the presence of TM ions. For the band at $\sim 750 \text{ cm}^{-1}$ a shift of $\sim 30 \text{ cm}^{-1}$ and a strong attenuation is observed probably due to the increase of disorder degree and the appearance of Cu-O-P bonds [17-19]. For high content of vanadium ions ($x > 20 \text{ mol\%}$) a shoulder at $\sim 840 \text{ cm}^{-1}$ appear in the spectra attributed to V-O-V stretching vibration. The band at $\sim 1100 \text{ cm}^{-1}$ increases in intensity with the increase of TM oxides because of the increase of the number of ionic (PO_2^-) groups and $\text{V}=\text{O}$ bonds. The shape of the spectra in this region has a cover form, like a large band that contains the unresolved superposed bands belonging to both phosphate and vanadate bonds of the new structural units.

The same tendency occurs for the 1280 cm^{-1} band due to the breaking of the $\text{P}=\text{O}$ bonds and to a reduction of the bonding force between P and O atoms that leads to the appearance of more non-bridging oxygen ions which are involved in the new TM-Oxygen bonds. There is also a shift to lower wavenumber of this band for the same reasons [17].

5. 2D correlation spectroscopy

Hetero-spectral correlation analysis [11,24,25] compares two different spectra of the same probe obtained by different spectroscopic methods. The aim of this comparison in our study is to establish the structural changes that appear in the investigated samples. Raman and IR spectra of $x(\text{CuO}\cdot\text{V}_2\text{O}_5)(1-x)[\text{P}_2\text{O}_5\text{-CaF}_2]$ glasses were compared in this respect and the synchronous and asynchronous spectra are given in Fig. 3.

The synchronus map indicates for the most important peaks that IR peak at 970 cm^{-1} is synchronous with the Raman peak at 925 cm^{-1} , IR peak at 830 cm^{-1} is synchronous with Raman peaks at 1175 cm^{-1} , 925 cm^{-1} , 708 cm^{-1} and 640 cm^{-1} . The IR peak is also synchronous with Raman peak at 1175 cm^{-1} . In addition to this the synchronus map also indicates that the IR and Raman bands corresponding to $(830,1175) \text{ cm}^{-1}$, $(830,708) \text{ cm}^{-1}$ and $(650,1175)$ develop in the same way, increasing in intensity with the increasing of the TM ions content. This result is in agreement with the depolymerization of the phosphate network and with the formation of short chains or ring structural units, fact underlined in the IR and Raman spectral analysis. In the synchronus maps also occur cross-peaks at $(1325,1230) \text{ cm}^{-1}$, $(1325,1175) \text{ cm}^{-1}$, $(1325,925) \text{ cm}^{-1}$, $(1325,708) \text{ cm}^{-1}$, but we could not identify and assign the 1325 cm^{-1} band in our IR spectra.

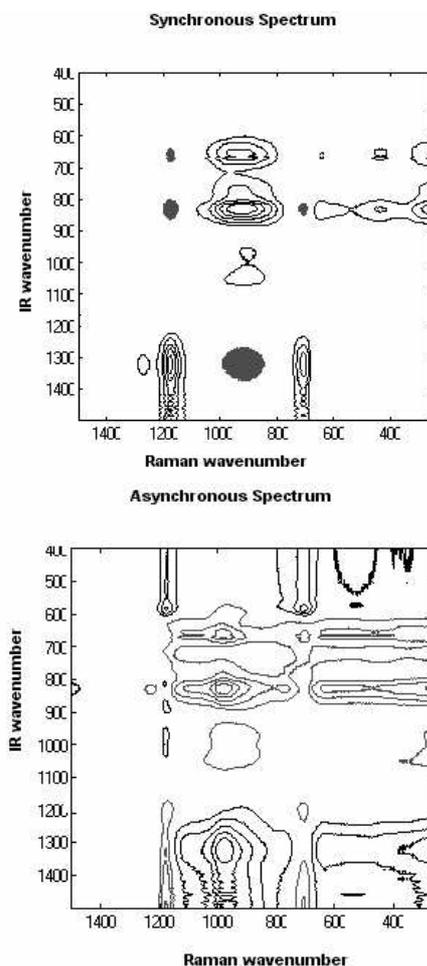


Fig. 3. 2D hetero-spectral correlation spectrum of $x(\text{CuO}\cdot\text{V}_2\text{O}_5)(1-x)[\text{P}_2\text{O}_5\text{-CaF}_2]$ glasses.

The asynchronous map indicates that the peak at 960 cm^{-1} from IR spectra is asynchronous with those at 1180 cm^{-1} and 975 cm^{-1} from Raman spectra. Also the peak at 830 cm^{-1} from IR spectra is asynchronous with the peaks at 1250 cm^{-1} , 975 cm^{-1} and 780 cm^{-1} from Raman spectra. This information show that these peaks (bands) belong to the structural units which develop independently with the increase of TM oxide content.

Hetero-spectral correlation analysis [9,24] indicates that exist a very good correlation between the IR band at 840 cm^{-1} attributed to V-O-V stretching vibration and Raman bands at 710 cm^{-1} and 1175 cm^{-1} attributed to P-O-P stretching vibration and PO_2 stretching respectively. A good correlation exist also between the IR band at $\sim 650 \text{ cm}^{-1}$ attributed to P-O-P symmetric stretching and the Raman band at 1175 cm^{-1} due to the symmetric stretching vibration of PO_2 groups. This correlation indicates once again the process of depolymerization of the phosphate network by breaking the P-O-P bonds and replacing them with V-O-P and Cu-O-P bond. Concurrently with this

bond breaking, new PO_2 short structures occur in the glasses.

6. Conclusions

The shape of the Raman and IR spectra of the studied glasses are influenced by the content of TM oxides (CuO , V_2O_5).

Both Raman and IR spectra show that at high concentration of copper and vanadium ions a depolymerization of the phosphate glass network appears by breaking the P-O-P bonds and creating new and more durable P-O-V or P-O-Cu bonds.

The effect of vanadium ions seems to be larger than the effect of copper ions due to the fact that vanadium ions are in a higher number in the chemical composition of the investigated glasses.

2D correlation spectroscopy was also successfully used in this case in order to confirm the IR and Raman analysis and to establish the type of structural units, whose number increases with the increasing of the TM content.

References

- [1] C. Mercier, G. Palavit, L. Montagne, C. Follet, *C. R. Acad. Sci. Paris* **5**, 693 (2003).
- [2] G. Tricot, L. Montagne, L. Delevoye, G. Palavit, V. Kostoj, *J. Non-Cryst. Solids* **345**, 56 (2004).
- [3] A. Chahine, M. Et-Tabirou, *Ann. Chim. Sci. Mat.* **28**, 25 (2003).
- [4] L. D. Bogomolova, *J. Non-Cryst. Solids* **30**, 379 (1979).
- [5] L. D. Bogomolova, M. P. Glassova, *J. Non-Cryst. Solids* **37**, 423 (1980).
- [6] R. K. Brow, *J. Non-Cryst. Solids* **263**, 1 (2000).
- [7] O. Cozar, I. Ardelean, V. Simon, L. David, N. Vedeanu, V. Mih, *Appl. Magn. Reson.* **16**, 473 (1999).
- [8] H. Doweidar, Y. M. Moustafa, K. El-Egili, I. Abbas, *Vibrational Spectroscopy* **37**, 91(2005).
- [9] J. E. Pemberton, L. Latifzadeh, J. Fletcher, S. H. Risbud, *Chem. Mater.* **3**, 195 (1991).
- [10] I. Noda, A. E. Dowrey, C. Marcott, G. M. Story, Procter and Gamble Company, Miami Valley Lab. **54**(7), 236 (2000).
- [11] I. Noda, *Appl. Spectrosc.* **47**(9), 1329 (1993).
- [12] Y. Ozaki, S. Sasik, T. Tanaka, I. Noda, *Bull. Chem. Soc. Jpn.* **74**, 1 (2001).
- [13] J. E. Garbarczyk, P. Machowski, M. Wasiucionek, L. Tykarski, R. Bacewicz, A. Aleksiejuk, *Sol. State Ionics* **136**, 1077 (2000).
- [14] J. Koo, B. S. Bae, H. K. Na, *J. Non-Cryst. Solids* **212**, 173 (1997).
- [15] M. A. Karakassides, A. Saranti, I. Koutselas, *J. Non-Cryst. Solids* **347**, 69 (2004).
- [16] O. Cozar, A. Magdas, L. Nasdala, I. Ardelean, G. Damian, *J. Non-Cryst. Solids*, in press.
- [17] I. Ardelean, C. Andronache, C. Campean, P. Pascuta, *Mod. Phys. Lett.* **B18**, 45 (2004).
- [18] B. N. Nelson, G. J. Exarhos, *J. Chem. Phys.* **71**, 2739 (1979).
- [19] G. B. Rouse Jr., P. J. Miller, W. M. Risen, *J. Non-Cryst. Solids* **28**, 193 (1978).
- [20] M. A. Salim, G. D. Khattak, M. Sakhawat Hussain, *J. Non-Cryst. Solids* **185**, 101 (1995).
- [21] D. Ilieva, B. Jivov, D. Kovacheva, T. Tsacheva, Y. Dimitriev, G. Bogachev, Ch. Petkov, *J. Non-Cryst. Solids* **293**, 562 (2001).
- [22] N. Vedeanu, O. Cozar, I. Ardelean, *Studia Univ. Babeş-Bolyai, Physica XLIX*, 3(2004).
- [23] G. Le Saout, P. Simon, F. Fayon, A. Blin, Y. Vaills, *J. Raman Spectrosc.* **33**, 740 (2002).
- [24] B. Chae, Y. M. Jung, X. Wu, S. B. Kim, *J. Raman Spectrosc.* **34**, 451 (2003).
- [25] I. Noda, *Chemtracts-Macromol. Chem.* **1**, 89 (1990).

* Corresponding author: cozar@phys.ubbcluj.ro