JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 3, March 2007, p. 698 - 701

IR and EPR investigations of V_2O_5–P_2O_5–CaF_2 glass system

N. VEDEANU*, O. COZAR, I. ARDELEAN
Department of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania

IR and EPR investigations were performed on $xV_2O_5(100-x)[P_2O_5\cdot CaF_2]$ glass system with $0.5\leq x\leq 40$mol%. IR spectra of the studied glasses pointed out the depolymerization process induced by the addition of V_2O_5 content because for x > 20 mo% the significant reduction of the bonding force between P and O atoms leads to the appearance of more non-bridging oxygen ions that are involved in new V-O bonds. The changes observed in the EPR spectra of these glasses are explained supposing the superposition of two EPR signals, one with a well-resolved hyperfine sructure typical for isolated V^{4+} ions and the other one consisting in a broad line without hyperfine sructure characteristic for clustered ions. The dependence of the linewidth versus V_2O_5 content has shown that until x= 5mol% these ions are coupled by dipole-dipole interaction and at high content of vanadium oxide (x > 5 mol%) the superexchange interaction prevail between them.

(Received November 15, 2006; accepted December 21, 2006)

Keywords: V_2O_5-P_2O_5-CaF_2 glass, IR, ESR

1. Introduction

The interest for phosphate glasses increased because of a great variety of applications in which they are involved, like hermetic seals, in different organic or inorganic composites, as nuclear waste hosts or for medical applications [1-3]. Most of the applications are related to the molecular level structure [1] of these glasses. The addition of transition metal (TM) oxides leads to the depolymerization of the phosphate chains and to the formation of new P – O – TM which can change the electrical, optical or magnetic properties of these glasses.

V^{4+} ions incorporated in phosphate glasses as spectroscopic probe has been studied by several researcheres [4 - 14] in order to characterise the glass structure. The obtained results are related to the local structure, with the geometry of the structural units or interactions between paramagnetic ions [15].

EPR investigation of phosphate glasses containing V^{4+} ions have shown different values for $g_\parallel$ and $A_\parallel$ ($g_\parallel \leq 1.93$, $A_\parallel > 176\times10^{-4}$) comparing with other oxide glasses (borate and silicate) specific for a distorted C_{4v} symmetry [16,17].

IR investigation on various phosphate glass system were also reported. The investigation revealed that the short range order of the glass matrix is strongly affected by the addition of TM oxides and pointed out the depolymerization process of the glassy network [18, 19].

The present work is an EPR and IR study on $xV_2O_5(100-x)[P_2O_5\cdot CaF_2]$ glasses with $0.5\leq x\leq 40$ mol%, following the influence of V_2O_5 content on the local order, the interactions between vanadium ions, a possible influence of the fluorine on the EPR spectrum of VO^{2+} and the depolymerization process induced by vanadium oxide.

2. Experimental

In order to obtain the $xV_2O_5(100-x)[P_2O_5\cdot CaF_2]$ glass system($0.5\leq x\leq 40$mol%) was first prepared the matrix $[P_2O_5\cdot CaF_2]$ by mixing $(NH_4)_2HPO_4$ with CaF_2 and melting these admixtures at 1000 ºC for 12 minutes in a sintered corundum crucible using a technique previously reported [20]. The matrix was crushed and the resulting powder was mixed with appropriate amounts of V_2O_5 before final melting at 1250 ºC for 30 minutes. The melted glasses were under cooling at room temperature by quickly pouring onto stainless steel plates.

The EPR measurements were performed at 9.4 GHz(X-band) at room temperature using a JEOL-JES 3B spectrometer.

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 technique for different fragments of bulk glass to avoid structural modifications caused by the ambient moisture.

3. Results

a) IR analysis

Vitreous phosphate network is based on PO_4 tetrahedra, each of them sharing three corners [1,21]. The tetrahedra are linked to three other tetrahedra through bridging P-O-P oxygens. The fourth bond is linked to a terminal oxygen P=O and it is significantly shorter than the others [22]. In consequence, the network of phosphate glasses contains a polymeric structure; with the addition of TM oxides the phosphate structural groups passes from Q_3 to Q_2, Q_1 or even Q_0 when the TM oxide content increases. Here Q_n represents the structural unit of the tetrahedra and n is the number of bridging oxygens per tetrahedron.

IR absorption spectra for phosphate glasses usually give significant bands in the frequency region 400 – 1100 cm^{-1} [23]. According to the previous data [24,25] V_2O_5 gives in the IR spectra an important band at ~828 cm^{-1} due to V-O vibration in V-O-V chains and at ~1018 cm^{-1} for V=O vibration.

For the studied $xV_2O_5(100-x)[P_2O_5{\cdot}CaF_2]$ glasses the absorption bands characteristic for both P_2O_5 and V_2O_5 oxides were also found (Fig. 1).

IR bands and their assignments are the followings: ~ 610 cm^{-1} a band due to the O-P-O and O=P-O bending vibrations; ~ 700 cm^{-1} band due to the symmetric vibrations of P-O-P chains; at ~ 900 cm^{-1} a possible superposition of the stretching vibration in VO_2 groups and P-O-P bonds; ~ 1100 cm^{-1} a superposition of PO_4^{3-} groups and V=O stretching vibration; ~ 1280 cm^{-1} due to P=O stretghing vibration [24, 26-29].

The shape of the spectra is changing with the increase of the V_2O_5 oxide content. The band at ~ 700 cm^{-1} due to P-O-P bonds in Q_1 phosphate structures shifts with ~ 50 cm^{-1} at high concentration of V_2O_5 oxide because of the breaking of these bonds and formation of PO_4 isolated tetrahedra corresponding to Q_0 phosphate groups; a strong attenuation is also observed probably due to the increase of disorder degree in the network [21, 29,30].

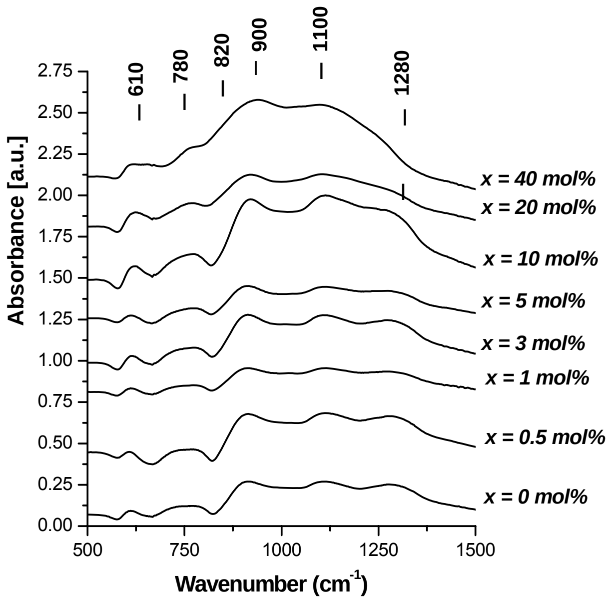
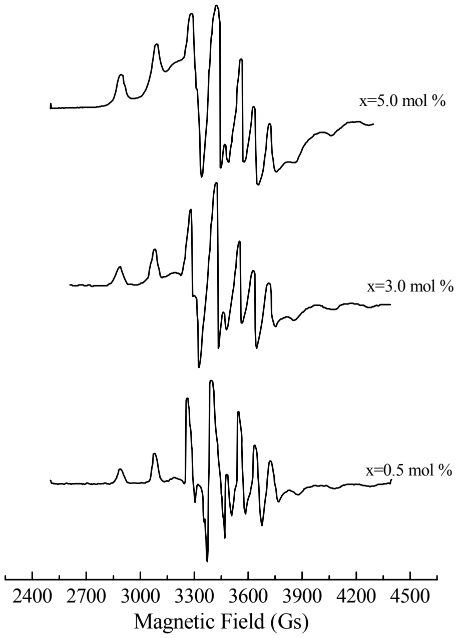


Fig. 1. IR spectra of $xV_2O_5(100-x)[P_2O_5{\cdot}CaF_2]$ glasses.

For high content of vanadium ions (x > 20 mol%) a shoulder at ~ 840 cm^{-1} appear in the spectra attributed to V-O-V stretching vibration. The band at ~ 1100 cm^{-1} increases in intensity with the increase of V_2O_5 oxide because the number of Q_2 groups and the number of V = O bonds increase with the depolymerization of the phosphate network. The shape of the spectra in this region has the form of a large band that contains the unresolved superposed bands belonging to both phosphate and vanadate bonds of the new structural units. The 1275 cm^{-1} band due to the P=O stretching vibration decrease in intensity with the increasing of V_2O_5 oxide content because of the formation of $M - O = P$ bonds which makes weaker the initial P=O bond. The reduction of the bonding force between P and O atoms leads to the appearance of more non-bridging oxygen ions which are involved in the new V-O bonds and a shift to lower wavenumber also appears[24].

b) EPR analysis

The EPR spectra obtained for the studied glasses with a small content of V_2O_5 ($x \leq 5$ mol%) show a well-resolved hfs typical for isolated vanadium ions in a C_{4v} symmetry, present as vanadyl ions (Fig. 1).



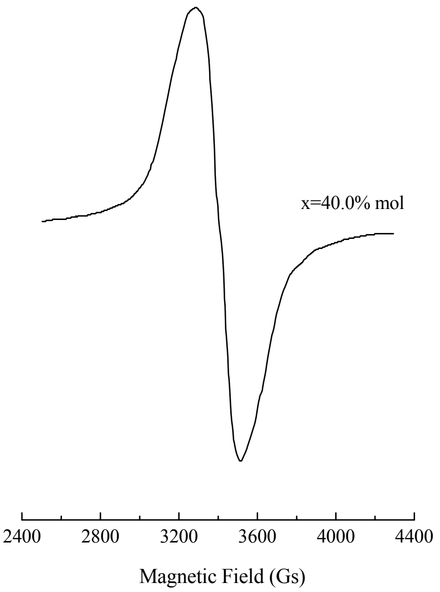


Fig. 2. EPR spectra of the $xV_2O_5(100-x)[P_2O_5{\cdot}CaF_2]$ glasses.

The apropriate spin Hamiltonian for these spectra is:

$$H_S = \beta_0 g\, B_zS_z + \beta_o g_\perp(B_xS_x+B_yS_y) + A_{||}S_zI_z + A_\perp(S_xI_x+S_yI_y) \quad (1)$$

where: β_o is the Bohr magneton; $g_\|$ and $g_\perp$ are the components of g tensor; B_x, B_y, B_z are the components of the magnetic field; S_x, S_y, S_z are the components of the electron spin operator; I_x, I_y, I_z are the components of the nucleus spin operator; $A_\|$ and $A_\perp$ are the main components of the hyperfine coupling tensor.

The values of the magnetic field for the hfs peaks from the parallel and perpendicular absorbtions are given by the following eqs [13]:

$$B_\| (m) = B_\| (0) - A_{||}\, m - [(63/4) - m^2]\, A_\perp^2/2B_{||}(0) \quad (2)$$

$$B_\perp(m) = B_\perp(0) - A_\perp\, m - [(63/4) - m^2](A^2 + A_\perp^2)/4B_\perp(0) \quad (3)$$

where: m = magnetic nuclear quantum number for vanadium nucleus having the following values: ±7/2, ±5/2,±3/2 and ±1/2;

$$B_\| (0) = h\nu/g_\|\, \beta_o \quad (4)$$

$$B_\perp(0) = h\nu/g_\perp \beta_o \quad (5)$$

where ν is the microwave frequency.

Spin- Hamiltonian parameters of VO^{2+} ions determined from the observed positions of hfs lines and eqs. (2-5) are given in Table 1.

Table 1. EPR parameters of VO^{2+} ions in $xV_2O_5(100-x)[P_2O_5{\cdot}CaF_2]$ glasses.

x(mol%)	$g_\|$	$g_\perp$	$A_\|$ [10^{-4} cm^{-1}]	$A_\perp$ [10^{-4} cm^{-1}]
0.5	1.945	1.986	152.6	58.9
1	1.932	1.981	157.9	59.2
3	1.948	1.989	152.4	60.3
5	1.950	1.987	154.5	60.4

The values of of these parameters confirm that the vanadium ions exist in the studied glasses as VO^{2+} ions in octahedral coordination with a tetragonal compression, particularly of C_{4v} symmetry.

The shape of the spectra are modified with the increasing of vanadium ions content. This modification consists in the partial dissapearance of the vanadyl hfs and the appearance of a broad line due to the clustered ions coupled by dipole-dipole interaction. At high content of vanadium ions (x > 8 %) the superexchange interaction prevails between clustered ions.

The EPR spectra may be regarded as the superposition of two EPR signals: one with a well resolved hfs typical for isolated VO^{2+} ions and another one consisting in a broad line typical for associated (clustered) vanadium ions.

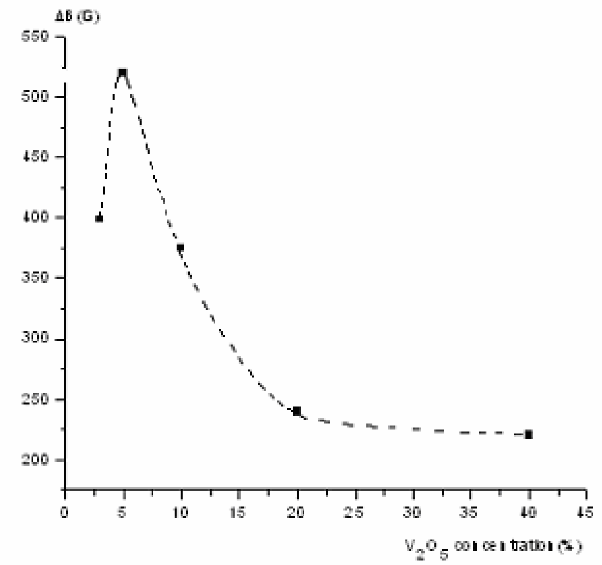


Fig. 3. The V_2O_5 concentration dependence of the EPR linewidth.

The composition dependence of the linewidths of the broad line ΔB characteristic for clustered ions is given in Fig. 3. It increases with V_2O_5 content until x ≈ 5 mol% suggesting that the dipole – dipole interaction prevail among V^{4+} ions and decreases for the V_2O_5 content over x > 5 mol% showing that in this range the superexchange interaction prevails between resonance centers [14].

In order to give attention to the effect of fluorine on the VO^{2+} complex, it is possible that one fluorine atom to coordinate at V^{4+} ion in the transposition with respect to the „yl" oxygen. This fact leads to the weakness of the V=O bond and consequently to the decrease in the tetragonal character of the vanadium coordination polyhedra. The most probable is that the fluorine atom substitutes the sixth oxygen. According to the literature data [9,14, 32] this fact leads to the increase of $g_{||}$ and to the decrease of $A_{||}$ values. The $g_{||}$ and $A_{||}$ values obtained for these glasses are in good agreement with the octahedral distortion of vanadium coordination polyhedra. Similar results were reported also for some VO^{2+} compounds [32]. The possible superhyperfine coupling with the fluorine nucleus leads to the broadening of the vanadium hfs lines [33].

4. Conclusions

IR spectra of the studied glasses pointed out the depolymerization process induced by the addition of V_2O_5 content because for x > 20 mo% the significant reduction of the bonding force between P and O atoms leads to the appearance of more non-bridging oxygen ions that are involved in new V-O bonds.

EPR spectra of these glasses are considered as the superposition of two EPR signals: one with a well resolved hfs typical for isolated VO^{2+} ions and another one consisting in a broad line typical for associated vanadium ions. For x >5 mol% the superexchange interactions between the paramagnetic centers.prevails

A careful analysis on EPR spectra gives also information about the glass network which contains fluorine ions. They can substitute the sixth oxygen atom from the transposition with respect to the „yl"oxygen (V=O) with the appearance of VO_5F chromofore.

References

[1] R. K. Brow, J. Non-Cryst. Solids **263**, 1 (2000).
[2] R. K. Brow, L. Kovacic, R. E. Loehman, Ceram. Trans. **70**, 177 (1996).
[3] J. Vogel, P. Wange, P. Hartman, Glastech. Ber. **70**, 23 (1997).
[4] G. Hochstrasser, Phys. Chem. Glasses **7**, 178 (1966).
[5] H. Toyuki, S. Akagi, Phys. Chem. Glasses **13**, 15 (1972).
[6] A. Paul, F. Assabghy, J. Mater. Sci **10**, 613 (1975).
[7] L. D. Bogomolova, V. N. Jackin, V. N. Lazukin, T. K. Pavlushkina., V. A. Shmuckler, J. NonCryst. Solids **28**, 375 (1978).
[8] H. Hosono, H. Kawazoe, T. Kanazawa, J. NonCryst. Solids **33**, 125 (1978).
[9] H. Hosono, H. Kawazoe, T. Kanazawa, J. NonCryst. Solids **37**, 427 (1980).
[10] V. P. Seth, S. Gupta, A. Jindal, S. K. Gupta, J. NonCryst.Solids **162**, 263 (1993).
[11] D. Prakash, V. P. Seth, I. Chand, P. Chand, J. NonCryst. Solids **204**, 46 (1996).
[12] A. Shames, O. Lev, B. Iosefzon-Kuyavskaya, J. NonCryst. Solids **163**, 105 (1993).
[13] V. R. Kumar, R. P. S. Chakradhar, A. Murali, N. O. Gopal, J. L. Rao, Int. J. Modern Physics B, **17**, 3033 (2003).
[14] O. Cozar, I. Ardelean, V. Simon, L. David, V. Mih, N. Vedeanu, Appl. Magn. Reson. **16**, 529 (1999).
[15] H. Doweidar, Y. M. Moustafa, K. El-Egili, I. Abbas, Vibrational Spectroscopy **37**, 91 (2005).
[16] N. Vedeanu, O. Cozar, I. Ardelean, S. Filip, J. Optoelectron. Adv. Mater. **8**(3), 1135 (2006).
[17] H. Hosono, H. Kawazoe, K. Kanazawa, J. Non-Cryst. Solids **37**, 427 (1980).
[18] S. Gupta, N. Khanijo, A. Mansingh, J. Non-Cryst. Solids **181**, 58 (1995).
[19] C. Mercier, G. Palavit, L. Montagne, C. Follet, C. R. Chimie **5**, 693 (2002).
[20] I. Ardelean, O. Cozar, Gh. Ilonca, V. Simon, V. Mih, C. Craciun, S. Simon, J. Mat. Science **11**, 401 (2000).
[21] Y. M. Moustafa, K. El-Egily, J. Non-Cryst. Solids **240**, 144 (1998).
[22] T. Uchino, Y. Ogata, J. Non-Cryst. Solids **181**, 175 (1995).
[23] C. Dayannand, G. Bhikshamaiah, V. J. Tyagaraju, M. Salagran, A. S. R. Krishna Murthy, J. Mat. Science **31**, 1945 (1996).
[24] I. Ardelean, C. Andronache, C. Campean, P. Pascuta, Mod. Phys. Lett. B **18**, 45 (2004).
[25] L. Stanescu, E. Indrea, I. Ardelean, M. Coldea, I. Bratu, D. Stanescu, Rev. Roum. Phys. **21**/9, 939 (1976).
[26] G. Le Saout, P. Simon, F. Fayon, A. Blin, Y. Vaills, J. Raman Spectrosc. **33**, 740 (2002).
[27] M. Sayer, A. Mansingh, Phys. Rev. B**6**, 4629 (1972).
[28] D. Ilieva, B. Jivov, D. Kovacheva, T. Tsacheva, Y. Dimitriev, G. Bogachev, Ch. Petkov, J. Non-Cryst. Sol. **293**, 562 (2001).
[29] E. Metwalli, M. Karabulut, D. L. Sidebottom, M. M. Morsi, R. K. Brow, J. Non-Cryst. Sol. **344**, 128 (2004).
[30] O. Cozar, A. Magdas, L. Nasdala, I. Ardelean, G. Damian, J. Non-Cryst. Solids **352**, 3121 (2006).
[31] N. Vedeanu, O. Cozar, I. Ardelean, B. Lendl, J. Optoelectron. Adv. Mater. **8**(1), 78 (2006).
[32] O. Cozar, V. Grecu, V. Znamirovski, Rezonanta electronica de spin pe complecsi metalici, Ed. Academiei, Bucuresti (2001), p. 163, 171.
[33] G. Scholz, R. Stosser, S. Sebastian, T. Grande, S. Aasland, M. Nofz, Ber. Bunsenges. Phys. Chem. **100**, 1617 (1996).

---

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