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EPR study of V_2O_5–P_2O_5–Li_2O glass system

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Abstract $xV_2O_5 \cdot (100 - x)[P_2O_5 \cdot Li_2O]$ glass system, with $0 < x \leq 50$ mol%, was prepared and investigated by EPR method. For low content of V_2O_5 all the spectra present a hyperfine structure typical for isolated V^{4+} ions. With the increasing of V_2O_5 content, the EPR absorption signal showing hyperfine structure is superposed by a broad line without hyperfine structure characteristic for clustered ions. At high V_2O_5 content, the vanadium hyperfine structure disappears and only the broad line can be observed in the spectra.

Spin Hamiltonian parameters $g\|$, $g\perp$, $A\|$, $A\perp$, dipolar hyperfine coupling parameters, P, and Fermi contact interaction parameters, K, have been calculated.The composition dependence of line widths of the first two absorptions from the parallel band and of the broad line characteristic to the cluster formations was also discussed.

1 Introduction

In recent years, the study of phosphate glasses have been of great interest due to their properties such as low melting temperature, low glass transition temperatures and high thermal expansion coefficients which makes them very important from technological point of view [1–4].

The addition of transitional metal oxides such as V_2O_5 in the phosphate glasses was investigated by several researchers [5–8]. The vanadyl ion VO^{2+} incorporated in glasses, as spectroscopic probe, is useful to characterize the glass local structure. The VO^{2+} ion like other transitional metals provide information about many specific aspects as the geometry of structural units of the glass network, the character of chemical bonds in glasses as well as the coordination polyhedra (local symmetry) of transitional metal ions [6, 7].

In this paper, $xV_2O_5 \cdot (100 - x)[P_2O_5 \cdot Li_2O]$ glass system was prepared and investigated by EPR in order to obtain further information about the local symmetry and interactions between vanadium ions with the increasing of V_2O_5 content in the $P_2O_5 \cdot Li_2O$ glass matrix.

2 Experimental

In the present work, glasses from $xV_2O_5 \cdot (100 - x)[P_2O_5 \cdot Li_2O]$ system were prepared by mixing components of reagent grade purity, $(NH_4)_2HPO_4$, Li_2CO_3 and V_2O_5, in suitable proportions to obtain the desired compositions. The mixtures were melted in sintered corundum crucibles, introduced in an electric furnace Carbolite RF 1600, directly at 1250 °C and kept for 5 min at this temperature. They were quickly cooled at room temperature by pouring onto stainless steel plates. The structure of

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these glasses was studied by means of X-ray diffraction and no crystalline phase was detected up to 50 mol % V_2O_5.

The EPR spectra were obtained at room temperature with an Adani Portable EPR Spectrometer PS8400 in X-frequency band (9.4 GHz) and a field modulation of 100 KHz. For these measurements, equal quantity of powders from the investigated samples, closed in glass tubes, were used.

3 Results and discussion

EPR spectra of $xV_2O_5(1\text{–}x)[P_2O_5\cdot Li_2O]$ glass system with 0.3 $\leq x \leq$ 50 mol% are given in Fig. 1.

For low content of V_2O_5 (x < 20 mol%) these spectra show a well resolved hyperfine structure (hfs) typical for vanadyl ions in a C_{4v} symmetry. The 16-line feature with eight parallel and eight perpendicular lines is typical of the unpaired ($3d^1$) electron of VO^{2+} ion associated with $^{51}V(I = 7/2)$ in an axially symmetric crystal field [9].

The analysis of well-resolved hyperfine structure of EPR spectra was made using an axial spin Hamiltonian appropriate for these spectra:

$$H_S = \beta_0 g B_z S_z + \beta_o g\perp(B_x S_x + B_y S_y) + A_\parallel S_z I_z + A\perp(S_x I_x + S_y I_y), \qquad (1)$$

where β_o—Bohr magneton, $g \parallel$ and $g \perp$—components of g tensor, B_x, B_y, B_z—components of the magnetic field, S_x, S_y, S_z—components of the electron spin operator, I_x, I_y, I_z—components of the nucleus spin operator, $A_\parallel$ and $A \perp$—principal components of the hyperfine coupling tensor.

The values of the magnetic field for the hfs peaks from the parallel and perpendicular absorption bands are given by Eq. (2) and (3) [10]:

$$B_\parallel(m) = B(0) - A_\parallel m - [(63/4) - m^2]A\perp^2/2B_\parallel(0) \qquad (2)$$

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

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

$$B_\parallel(0) = hv/g_\parallel \beta_o, \qquad (4)$$

$$B_\perp(0) = hv/g_\perp \beta_o, \qquad (5)$$

where v is the microwave frequency.

EPR parameters for vanadium ions in the studied glasses are given in Table 1. The values obtained by us are in good agreement with other results reported in literature [8, 9, 11, 12].

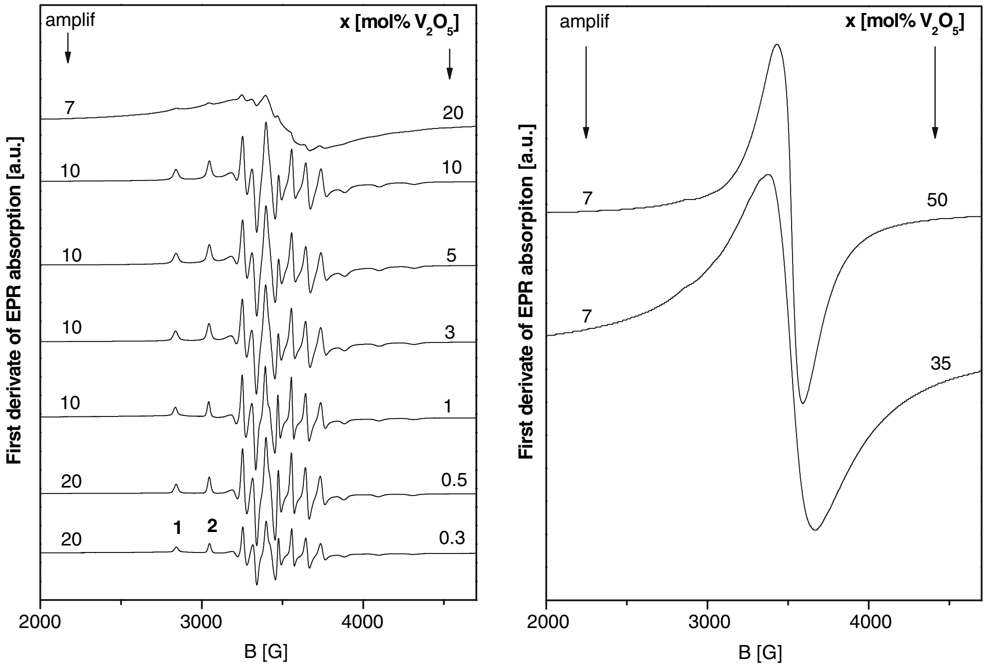

Fig. 1 EPR spectra of $xV_2O_5 \cdot (1-x)[P_2O_5Li_2O]$ glass system with 0.3 $\leq x \leq$ 50 mol%

Table 1 EPR parameters for V^{4+} ions in $xV_2O_5 \cdot (1-x)[P_2O_5 \cdot Li_2O]$ glass system

x mol%	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} 10^{-4}$ cm^{-1}	$A_{\perp} 10^{-4}$ cm^{-1}	K	P 10^{-4} cm^{-1}
0.3	1.93	1.98	166	56.7	0.73	127.5
0.5	1.92	1.97	165	56.7	0.73	126.4
1	1.92	1.99	165	61.0	0.78	121.4
3	1.92	1.98	165	58.3	0.75	124.5
5	1.92	1.98	165	58.3	0.75	124.5
10	1.92	1.98	165	55.2	0.71	128.2

The data obtained show that $g_{\parallel} < g_{\perp} < g_e$ and $A_{\parallel} > A_{\perp}$, relation that corresponds to vanadyl ions in square pyramidal site as C_{4v} symmetry. The vanadyl oxygen is attached axially above the V^{4+} site along the z-axis (V = O bond), while the sixth oxygen forming the O–VO_4–O unit lies axially bellow the V^{4+} site in opposition with “yl” oxygen. The predominant axial distortion of the VO^{2+} octahedral oxygen complex along V = O direction may be the reason for nearly equal g and A values for all the glass samples [10].

Fermi contact interaction term, *K* and dipolar hyperfine coupling parameter, *P*, are evaluated by using the expressions developed by Kivelson and Lee [13]:

$$A_{\parallel} = -P[K - 4/7 - \Delta g_{\parallel} - 3/7\,\Delta g_{\perp}], \tag{6}$$

$$A_{\perp} = -P[\mathrm{K} - 2/7 - 11/14\,\Delta g_{\perp}], \tag{7}$$

where $\Delta g_{\parallel} = g_{\parallel} - g_e$, $\Delta g_{\perp} = g_{\perp} - g_e$ and $g_e = 2.0023$.

The low value estimated for *K* (~ 0.75) indicates a poor contribution of the vanadium 4s orbital to the vanadyl bond in these glasses [9].

For high content of vanadium oxide ($x = 20$ mol%), the EPR spectra may be regarded as a 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 V^{4+}–V^{4+} ions [6]. The number of associated ions increases with the increasing of V_2O_5 content. The formation of associated V^{4+} ions in the composition range of $x < 20$ mol% is due to the dipole–dipole interaction between vanadium ions. This fact is suggested by the composition dependence (Fig. 2a) of the line-width of first ΔB_1 and second ΔB_2 hfs-peaks from the parallel absorption (Fig. 1). These line-widths increase with V_2O_5 content up to $x = 10$ mol% and prove the associated formation of vanadium ions.

For $x \geq 20$ mol% ΔB of the broad line decreases with the increasing of V_2O_5 content due to the presence of superexchange interactions in V^{4+}–O^{2-}–V^{4+} chains.

Analyzing the shape of EPR spectra, from Fig. 1, it can be noticed that up to 20 mol% V_2O_5 the number of V^{4+} ions which are forming in the $P_2O_5 \cdot LiO$ vitreous matrix is relatively small. The proportion of these ions is considerable higher for high content of V_2O_5, which determines the appearance of the superexchange magnetic interactions between V^{4+} ions.

4 Conclusions

The EPR measurements evidenced the presence in the studied glasses of the vanadium ions as vanadyl ions. The shape of the spectra is modified with the increasing of vanadium content.

The vanadyl ions appear in the studied glasses as isolated species for $0.3 \leq x < 20$ mol%. In addition to the isolated species in the samples with $x < 20$ mol% is also evidenced the presence of associated ions coupled by means of dipol–dipol interaction. For $x > 20$ mol% the prevalent interaction between V^{4+} ions which form magnetic clusters is of the superexchange type.

The values of EPR parameters ($g_{\parallel} \sim 1.92$, $g_{\perp} \sim 1.98$ and $A_{\parallel} = 165 \times 10^{-4}$ cm^{-1}) are in good agreement with those reported in previous papers and

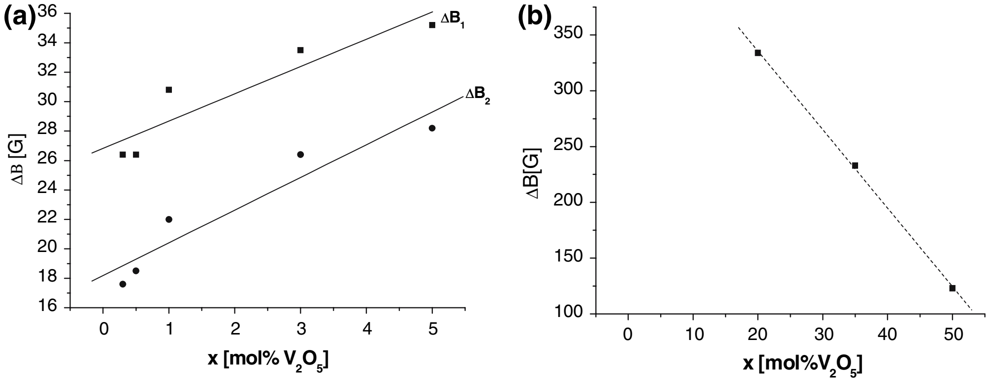

Fig. 2 Composition dependence of the line-width of first ΔB_1 and second ΔB_2 hfs-peaks from the parallel absorption (**a**) and of the broad line ΔB characteristic to the cluster formation (**b**)

the low values estimated for K (~ 0.75) indicate a poor contribution of the vanadium 4s orbital to the vanadyl bond in these glasses.

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