Structural investigation of V_2O_5 – P_2O_5 – K_2O glass system with antibacterial potential

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Abstract. The $xV_2O(1-x)[0.8P_2O_5 \cdot 0.2K_2O]$ glass system with $0 \leq x \leq 50$ mol% was prepared and the structural changes induced in these glasses by increasing the vanadium oxide content were investigated by IR and ESR spectroscopies. The dual behaviour role of V_2O_5 oxide, as network modifier (for $x \leq 10$ mol%) and the network former ($x \geq 20$ mol%), as a consequence of phosphate network depolymerization and P–O–V and V–O–V linkages appearance was also highlighted. The antibacterial effect of the glasses with $x \leq 20$ mol% V_2O_5 content was tested by optical density (OD) measurements. A linear correlation between the amount of vanadium and the antibacterial effect was evidenced.

Keywords. P_2O_5 ; K_2O ; V_2O_5 ; IR; ESR; antibacterial effect.

1. Introduction

In the past years, many research papers have been focussed on phosphate glasses due to their diversified applications in technology, medicine, as biomaterials and in clinical or industrial dosimetry [1–5].

Glasses containing silver have attracted considerable interest for their potential application as antibacterial materials due to silver ions release related to their biodegradability [6–9].

Novel systems allowing controlled release of components are intensely investigated and various inorganic antibacterial materials containing silver (glasses, vitroceraamics, composites) have been developed and some of them are already in the commercial use [10–13]. The vanadium oxide nanotubes (Ag/VO_x – NT_x) modified by highly dispersed Ag nanoparticles proved also to have a strong antibacterial activity [14].

Besides the materials containing silver, there are also MgO nanoparticles [15], titanium–copper alloys [16], TiO_2 nanoparticles with alpha amylase enzyme [17] or vanadium-doped, gold-capped TiO_2 nanocomposites [18] and TiO_2 photocatalysts, which manifest antibacterial effect even under room light conditions [19].

As it is shown in papers [11,16–18], *Staphylococcus aureus* (Gram positive) and *Escherichia coli* (Gram negative) bacteria are the most used to investigate the antibacterial

effect. Silver, copper and vanadium contents in the previous investigated antibacterial materials [11,16–18] were upto 20%.

Metal ions such as cobalt and vanadium and their metal-complexes derived from salicylaldehyde and its analogues are found also to be antitumoural-active, catalytic-active, antimicrobial and cytotoxic [20,21].

The antibacterial properties of the ligand and the $[CoL(NCS)OH_2]$, $[VOL(NCS)]$ complexes were also evaluated; the results have shown significant enhanced activity against the bacteria strains in comparison to the free ligand $[(H_2L = N,N'-1,2-propylene-bis(3-methylsalicylideneimine))]$. The vanadium complex was found to be the most effective against *Bacillus subtilis* [22].

In this context, the new potassium–phosphate glass system containing vanadium ions, $xV_2O(1-x)[0.8P_2O_5 \cdot 0.2K_2O]$ with $0 \leq x \leq 50$ mol% was prepared and its antibacterial effect on *S. aureus* (Gram positive) and *E. coli* (Gram negative) bacteria was tested by optical density (OD) measurements for $x \leq 20$ mol%. Besides this aspect, some structural changes induced by the increase in V_2O_5 content in the potassium–phosphate matrix were also investigated by IR and ESR spectroscopies.

We have chosen P_2O_5 – K_2O matrix for this study due to its good quality for TL (thermoluminescence) dosimetry [23], but also to the fact that K_2O oxide leads to the appearance of IR bands at low wavenumber ($<200\text{ cm}^{-1}$), which do not overlap those belonging to the phosphates, allowing the observation of the changes induced in the vibrational spectra by the other included metal oxides [24].

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2. Experimental

To obtain the $x\text{V}_2\text{O}(1-x)[0.8\text{P}_2\text{O}_5 \cdot 0.2\text{K}_2\text{O}]$ glass system ($0 \leq x \leq 50$ mol%) the matrix ($\text{P}_2\text{O}_5 \cdot \text{K}_2\text{O}$) was first prepared by mixing $(\text{NH}_4)_2\text{HPO}_4$ with K_2CO_3 and melting them at 1250°C for 5 min in a sintered corundum crucible using the technique previously reported [23]. The matrix was crushed and the resulting powder was mixed with appropriate amounts of V_2O_5 before final melting at 1250°C . The melted glasses were cooled at room temperature by quickly pouring onto stainless steel plates.

Because of the high hygroscopicity of these glasses, the measurements were carried out immediately after preparation. The samples were also kept into exicator surrounded by silica gel.

IR spectra were obtained with a Bruker IFS66/DSP spectrometer in $400\text{--}2000\text{ cm}^{-1}$ range, using the anhydrous KBr technique to avoid structural modifications caused by the ambient moisture. The resolution of the IR spectra is of 2 cm^{-1} .

The ESR measurements were performed at 9.4 GHz (X-band) at room temperature using an ADANI Portable PS8400 (USA) spectrometer.

The structure of the samples was analysed by means of X-ray diffraction using a Bruker D8 Advanced X-ray diffractometer with a graphite monochromator for $\text{CuK}\alpha$ radiation with $\lambda = 1.54\text{ \AA}$. The obtained pattern did not show any crystalline phase for the studied glasses.

E. coli (Gram negative) and *S. aureus* (Gram positive) bacteria used in this study were provided by fermentation laboratory of University of Agriculture Science and Veterinary Medicine, Cluj-Napoca, Romania. A broth subculture was prepared by inoculating loop full from stock culture of each bacterium into a test tube containing nutrient broth (NB, Merck, Germany) and the strains were incubated for 24 h at 37°C . This incubation period allowed the bacteria to approach stationary phase of growth at a concentration of ca. 8 log CFU ml^{-1} unit. *S. aureus* was grown on Baird-Parker agar (Oxoid, UK) and *E. coli* on Levine agar in the same conditions.

Each of these overnight cultures was used to inoculate 25 ml volumes of nutrient broth (in triplicate) to a standardized optical density (OD) between 0.005 and 0.010 at a wavelength of 600 nm (OD600). A single 'glass water-extract' (3.125 ml) from 5 mg 'glass powder' in 25 ml de-ionized water, was added to each tube, and the vanadium-free glass powder ($x = 0$ mol%) was used as controls.

Growth values were obtained by measuring the turbidity at OD600 by Nanodrop ND-1000 Spectrophotometer UV/VIS (Nanodrop Technologies, USA) of the test strains over a period of 48 h. The viable counts were then determined by a serial dilution of the broth into 0.1% peptone water and plating onto nutrient agar plates. All plates were incubated overnight at 37°C for 48 h and the resulting colonies were visually counted directly from the agar plate.

3. Results

The absence of sharp peaks in the XRD spectra of all these investigated glasses shows only an amorphous character without any crystalline forms (figure 1).

3.1 IR spectra

Figure 2 shows the IR spectra of $\text{V}_2\text{O}_5\text{--P}_2\text{O}_5\text{--K}_2\text{O}$ glasses in the $400\text{--}1400\text{ cm}^{-1}$ range. To compare spectroscopic data obtained for different glass samples, the IR spectra were normalized by the technique described in paper [25]. This procedure allows us to discuss the relative intensities of the vibrational bands assigned to different atomic groups which occur in the investigated glasses.

The specific bands for phosphate-potassium ($0.8\text{P}_2\text{O}_5 \cdot 0.2\text{K}_2\text{O}$) network ($x = 0$ mol%) are found in the following

Figure 1. XRD spectra of $x\text{V}_2\text{O}(1-x)[0.8\text{P}_2\text{O}_5 \cdot 0.2\text{K}_2\text{O}]$ glass system with $0 \leq x \leq 50$ mol%.

Figure 2. IR spectra of $x\text{V}_2\text{O}(1-x)[0.8\text{P}_2\text{O}_5 \cdot 0.2\text{K}_2\text{O}]$ glass system with $0 \leq x \leq 50$ mol%.

regions: 490, 720–780, 905–1160 and 1290 cm⁻¹. The band from 490 cm⁻¹ is assigned to the bending vibrations of O–P–O units, $\delta(\text{PO})_2$ modes of $(\text{PO}_2^-)_n$ chain groups [26,27]. The weak bands from 720 to 780 cm⁻¹ may be attributed to the symmetric and asymmetric stretching vibrations of the P–O–P linkages [28,29]. The absorption band situated at 905 cm⁻¹ is assigned, according to the literature data, to the asymmetric stretching modes of the P–O–P linkages $(\text{P–O–P})_{\text{as}}$ in linear metaphosphate chain [26,30]. The bands near 1080 and 1160 cm⁻¹ may be attributed to PO_3^{2-} end groups [28] and P–O⁻ groups (chain ending) [28], respectively. The band near 1290 cm⁻¹ is attributed to the asymmetric stretching mode of the double-bonded oxygen vibrations, $\nu_{\text{as}}(\text{P=O})$ [26–28].

For $x \geq 20$ mol%, new bands characteristic for V–O bonds prevail in the IR spectra (figure 2). The bands from 490 to 655 cm⁻¹ range are produced by the lattice vibrations in vanadium oxide network [31,32]. The band at 890 cm⁻¹ may be assigned to the symmetric vibration of the V–O bonds of the VO_4 tetrahedra in glass structure [32]. The other bands from 910 to 1006 cm⁻¹ may be attributed to V–O bonds and also to the polyvanadate (clustered) ions formation [33]. The absorption bands from 1080 to 1110 cm⁻¹ region are due to the vibrations of the isolated V=O vanadyl groups in VO_5 trigonal bipyramids [32,34].

Figure 3. Representative ESR spectra of $x\text{V}_2\text{O}_5(1-x)[0.8 \text{P}_2\text{O}_5 \cdot 0.2 \text{K}_2\text{O}]$ glass system.

3.2 ESR spectra

Representative ESR spectra of $x\text{V}_2\text{O}_5(1-x)[0.8 \text{P}_2\text{O}_5 \cdot 0.2 \text{K}_2\text{O}]$ glass system are given in figure 3. For low content of V_2O_5 ($x \leq 5$ 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 isotope ($I = 7/2$) in an axially symmetric crystal field [35,36].

The ESR spectrum for $x = 1$ mol% does not follow the trend of V_2O_5 content because its amplifier mode (degree) is not adjusted as that for the other spectra ($x = 0.3, 5, 10$, etc.). This spectrum was left as a typical vanadium (V^{4+}) ESR spectrum for the reader.

The following axial spin Hamiltonian is appropriate for these ESR spectra [35,37]:

$$H_s = \beta_0 g_{\parallel} B_z S_z + \beta_0 g_{\perp} (B_x S_x + B_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y), \quad (1)$$

where β_0 , 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.

ESR 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 [35,36,38].

3.3 Antibacterial effect

The vanadium containing system has been tested against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria to assess its antibacterial activity by plotting the optical density (OD) as a function of V_2O_5 content below 20 mol%.

As shown in figure 4, the control medium possessed weaker antimicrobial activity than the rest of the samples for both investigated strains. The efficiency of the antimicrobial effect of vanadium incorporated into the vitreous system is dependent by its doping content. The plot between the experimental points is only a guide for the eyes.

Table 1. ESR parameters for V^{4+} ions in $x\text{V}_2\text{O}_5(1-x)[0.8 \text{P}_2\text{O}_5 \cdot 0.2 \text{K}_2\text{O}]$ glass system.*

$X(\text{mol}\%)$	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} (10^{-4} \text{cm}^{-1})$	$A_{\perp} (10^{-4} \text{cm}^{-1})$	K	$P (10^{-4} \text{cm}^{-1})$	β_2^2	ε_{π}^2
0.3	1.92	2.00	193	79	0.88	133	1.12	0.90
0.5	1.93	1.99	193	77	0.86	135	1.08	0.91
1	1.93	2.00	195	78	0.85	137	1.10	0.90
3	1.93	1.99	197	78	0.84	139	1.08	0.92
5	1.92	2.00	198	77	0.83	140	1.12	0.91

*The error on g values is 0.01 and $1 \cdot 10^{-4} \text{cm}^{-1}$ on A values.

Figure 4. Optical density vs. vanadium content in $x\text{V}_2\text{O}_5(1-x)[0.8\text{P}_2\text{O}_5 \cdot 0.2\text{K}_2\text{O}]$ glasses containing *S. aureus* and *E. coli* bacteria (the error bars are provided with 5% error limits).

4. Discussion

4.1 IR spectra

The decreasing intensity of all phosphate bands can be observed with the increase in V_2O_5 content until $x = 10$ mol% (figure 2). This fact may be attributed to V_2O_5 network modifier role; it produces the depolymerization of the phosphate–potassium network leading to the breaking of P–O–P chains in Q_1 groups and thus to the increase in the disorder degree in the phosphate network [39,40].

Relevant changes like the shift of certain bands to lower wavenumber (720–710, 780–765 and 1160–1110 cm^{-1}) and the appearance of other new bands can be observed in the IR spectra for $x \geq 20$ mol%.

Thus, in the lower wavenumber region, new bands appear at 550, 565 and 655 cm^{-1} , while the bands at 890, 910, 1006, 1080 and 1110 cm^{-1} prevail in the IR spectrum in the higher wavenumber region.

The shift of the mentioned vibrational bands to lower wavenumbers and the appearance of new bands in the IR spectra of glasses with high V_2O_5 content ($x \geq 20$ mol%) may be ascribed to the reduction of the bonding force between P and O atoms and to the implication of non-bridging oxygen ions in new vanadate structural groups formation at glass matrix level [32,33].

The 1290 cm^{-1} band also decreases in amplitude due to the decrease in P_2O_5 content and the shortening of the phosphate chain length. This fact suggests that V_2O_5 acts in this concentration range as a network former which converts P=O bonds to bridging oxygen upon formation of P–O–V bonds analogue with P–O–Fe and P–O–Cu bonds reported in papers [26,28].

The evidence of P–O–V linkages is the appearance of the bands from 910 to 1006 cm^{-1} assigned to V–O bonds and also to the polyvanadate (clustered) ions formation [33] for $x = 20$ mol%. For $x \geq 20$ mol%, the appearance of the new bands at 890 and 1080–110 cm^{-1} assigned to V–O bonds in the VO_4 tetrahedra [32] and isolated V=O vanadyl groups in

VO_5 trigonal bipyramids [32,34] is the proof of the imposed vanadate structural groups (network former role of V_2O_5) in the glass matrix.

We may finally conclude that vanadium atoms bridge with non-bridging oxygen of PO_4 units and V_2O_5 oxide act as a network former. 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. Thus, the phosphate groups are isolated in the vanadate network and in consequence, V_2O_5 acts for $x \geq 20$ mol% as a network former instead of a network modifier.

4.2 ESR spectra

ESR parameters given in table 1 show that $g_{\parallel} < g_{\perp} < g_e$ and $A_{\parallel} > A_{\perp}$ relations that correspond to vanadyl ions in a square-pyramidal site as C_{4v} symmetry [35,36]. The vanadyl oxygen is attached axially above the V^{4+} site along the z -axis (V=O bond), while the sixth oxygen forming the $\text{O}-\text{VO}_4-\text{O}$ unit lies axially below the V^{4+} site in opposition with vanadyl ‘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 glass samples [35,41].

Fermi contact interaction term K , dipolar hyperfine coupling parameter P and MO (molecular orbital) coefficients are evaluated by using the expressions developed by Kivelson and Lee [42].

$$K = \frac{A_{\parallel} + 2A_{\perp}}{A_{\parallel} - A_{\perp}}, \quad (2)$$

$$P = \frac{A_{\parallel} + 2A_{\perp}}{3K}, \quad (3)$$

$$\beta_2^2 = \frac{7}{6} \left[\left(\frac{A_{\parallel} - A_{\perp}}{P} \right) - (g_e - g_{\parallel}) + (g_e - g_{\perp}) \right], \quad (4)$$

$$\varepsilon_{\pi}^2 = \frac{\Delta_{\perp}(g_e - g_{\perp})}{2\lambda\beta_2^2}, \quad (5)$$

where $\Delta_{\perp} = 15100 \text{ cm}^{-1}$, $\lambda = 170 \text{ cm}^{-1}$ and $g_e = 2.002$.

The value estimated for K (~ 0.85) indicates a poor contribution of the vanadium 4s orbital to the vanadyl bond in these glasses.

The dipolar hyperfine coupling parameter value P ($\sim 137 \cdot 10^{-4} \text{ cm}^{-1}$) is similar with that reported for other phosphate glasses containing vanadium ions [29,35].

The MO coefficients (table 1) show an ionic character for both π bonds in $x\text{Oy}$ base-pyramidal plane ($\beta_2^2 \cong 1$) and with vanadyl oxygen ($\varepsilon_{\pi}^2 \cong 0.91$) [35,42].

For very low content of V_2O_5 oxide ($x \leq 1$ mol%), the network is dominated by P_2O_5 oxide which has a polymeric structure (organized at long range) and fixes metallic ions in some specific positions, finally determining isolated distribution species without interaction between paramagnetic ions (V^{4+}).

By increasing the V_2O_5 content ($x \leq 10$ mol%), this leads to the depolymerization of phosphate network which affects (destroys) the isolated distribution mode of the metallic

ions, allowing the appearance of dipole-dipole interactions between them and increasing hfs-lines (peaks) linewidth. The dependences ΔB_1 and ΔB_2 linewidths for the first (1) and second (2) peaks in the parallel absorption band vs. vanadium content (figure 5) confirm this fact. For this reason, ESR spectra shape suggest the network modifier role of V₂O₅ with the depolymerization of the phosphate network.

At high content of vanadium oxide ($x \geq 10$ mol%), the ESR spectra may be regarded as a superposition of two ESR signals, one with a well-resolved hfs typical for isolated VO²⁺ ions and another one consisting a broad line typical for associated (clustered) V⁴⁺-V⁴⁺ ions. The number of associated ions increases with the increasing of V₂O₅ content and the presence of super-exchange interaction in V⁴⁺-O²⁻-V⁴⁺ chains prevails. This is suggested by the dependence of the broad line ΔB characteristic to the cluster formation in function of V₂O₅ content (figure 6). The presence of vanadate structures which isolate the phosphate groups at high V₂O₅

content in good agreement with the network former role of vanadium oxide.

4.3 Antibacterial effect

A stronger inhibitory effect on *S. aureus* than *E. coli* bacteria is observed in figure 4. The strongest effect occurs at low concentrations of V₂O₅ ($x \leq 5$ mol%) and it decreases with the increasing of vanadium content in a linear correlation form (dependence).

Taking into consideration IR and ESR results for the studied glass system, the highest antimicrobial effect can be related with the atomic dispersion (isolation) of vanadium ions ($x < 5$ mol%) as in the case of other reported antibacterial materials [11,16,18]. This effect decreases with the increasing of vanadium ions content due to the depolymerization process. In consequence, vanadium ions do not remain atomic dispersed, the distance between them is reduced and the dipole-dipole and super-exchange interactions increase, leading to the formation of clustered (associated) species.

5. Conclusions

The IR bands, characteristic for phosphate structural groups, decrease in intensity and are shifted at different wavenumbers due to the phosphate network depolymerization and thus showing the network modifier role of V₂O₅ for $x \leq 10$ mol%.

The new bands characteristic for P-O-V and V-O-V groups appearing in the IR spectra for $x \geq 20$ mol% suggest the network former role of vanadium oxide.

The same dual role of vanadium oxide is also proved by the line shape modifications of the ESR spectra.

The antibacterial test of the studied glasses ($x \leq 20$ mol%) shows an inhibition in growth and a linear correlation between this effect and the amount of V₂O₅, for both *E. coli* and *S. aureus* bacteria.

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Figure 5. ΔB_1 and ΔB_2 linewidths dependences vs. V₂O₅ content (the error bars are provided with 5% error limits).

Figure 6. The dependence of the cluster line (ΔB) with V₂O₅ content (the error bars are provided with 5% error limits).

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