Preparation and characterization of phosphate glasses containing titanium and vanadium

S. Kaoua a, S. Krimi a,*, A. El Jazouli b, E.K. Hlil c,*, D. de Waal d

a Laboratoire de Chimie du Solide, Faculté des Sciences Ain Chock, Casablanca, Morocco
b Laboratoire de Chimie des Matériaux Solides, Faculté des Sciences Ben M’Sik, Casablanca, Morocco
c Laboratoire de Cristallographie du CNRS, Grenoble, France
d Department of Chemistry, University of Pretoria, 0002 Pretoria, South Africa

Abstract

Na5−xTi1−xV x(PO4)3 (0 ≤ x ≤ 1) phosphates glasses have been obtained in air by direct fusion of Na2CO3, TiO2, V2O5 and (NH4)2HPO4. Vitreous Na5Ti(PO4)3 is colourless while the glasses containing vanadium are green, due to the reduction of V5+ to V4+. Glass transition and crystallization temperatures (T g, T c) decrease when the amount of vanadium increases. EPR, Raman and UV–vis spectra have been investigated. The results are consistent with the presence of V4+ ions in distorted octahedra with very strong V–O bond.

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Keywords: Glass; Vanadium; EPR; Raman; UV–vis

1. Introduction

Titanophosphate glasses have been the subject of many studies for their great importance in technological applications such as linear and non-linear optical properties, and semiconducting properties [1–4]. Previous studies have shown that Na2O–TiO2–P2O5 and Na2O–V2O5–P2O5 systems include Na5Ti(PO4)3 [5] and Na4V(PO4)3 [6] compounds, respectively. The first composition exists in both crystalline and vitreous forms. The crystalline form belongs to the Nasicon family. The present paper reports a preliminary investigation of new phosphate glasses containing vanadium and titanium: Na5−xTi1−xV x(PO4)3 (0 ≤ x ≤ 1). Elaboration process, thermal properties and Raman, EPR and diffuse reflectance spectra of these glasses will be described successively.

2. Preparation and characterization

Na5−xTi1−xV x(PO4)3 (0 ≤ x ≤ 1) phosphate glasses were obtained in air by melting mixtures of sodium carbonate Na2CO3, vanadium oxide V2O5, titanium oxide TiO2 and diamonium hydrogenophosphate (NH4)2HPO4, in suitable proportions. In a first step, powders were heated at 200°C for 12 h to decompose (NH4)2HPO4. The temperature was then progressively put to 900°C and held constant at this value for 15 min. The liquid was then poured in a metallic plate pre-heated at 150°C. Under these conditions, vitreous Na5Ti(PO4)3 is colourless while the glasses containing vanadium are green. X-ray diffraction (XRD) and transmission electronic microscopy (TEM) analysis indicated that the glasses were completely amorphous.

The densities were determined on blocks of glasses containing vanadium and titanium: Na5−xTi1−xV x(PO4)3 (0 ≤ x ≤ 1). Elaboration process, thermal properties and Raman, EPR and diffuse reflectance spectra of these glasses will be described successively.

3. Results and discussion

The values of the density, T g and T c, obtained for Na5−xTi1−xV x(PO4)3 (0 ≤ x ≤ 1) glasses, are given in Table 1.

* Corresponding authors. Tel.: +33 4 76 88 11 41; fax: +33 4 76 88 10 38.
E-mail addresses: krimisaida@yahoo.fr (S. Krimi), hlil@grenoble.cnrs.fr (E. K Hlil).
Table 1
Characteristic temperatures ($T_g$, $T_c$) and density of Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ glasses

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>Density ($\pm 0.02$)</th>
<th>$T_g$ ($\pm 5^\circ$C)</th>
<th>$T_c$ ($\pm 5^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.38</td>
<td>432</td>
<td>537</td>
</tr>
<tr>
<td>0.25</td>
<td>3.15</td>
<td>367</td>
<td>520</td>
</tr>
<tr>
<td>0.5</td>
<td>3.34</td>
<td>331</td>
<td>500</td>
</tr>
<tr>
<td>0.75</td>
<td>3.80</td>
<td>300</td>
<td>420</td>
</tr>
<tr>
<td>1</td>
<td>3.82</td>
<td>289</td>
<td>406</td>
</tr>
</tbody>
</table>

Fig. 1. DSC curve of the Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ glass; $x = 0.5$.

DSC curve for the glass with $x = 0.5$ is shown in Fig. 1 as an example. The density increases while $T_g$ and $T_c$ decrease when the amount of vanadium rises.

The crystallization of Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ ($0 \leq x \leq 1$) glasses, followed by X-ray diffraction (Fig. 2), lead to the formation of the Nasicon phase Na$_5$Ti(PO$_4$)$_3$ for $x = 0$ [7] and to a mixture of phases for the other compositions. XRD patterns of the samples containing vanadium, heated at 600$^\circ$C, reveal the existence of a Nasicon phase [7] and non-identified peaks.

The Raman spectra of Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ glasses are given in Fig. 3. The bands observed between 1200 and 900 cm$^{-1}$ are attributed to the symmetrical and asymmetrical vibrations of the PO$_4$ and VO$_4$ groups. The band at 930 cm$^{-1}$, observed clearly in the spectrum of the composition $x = 0.75$, may be assigned to the very short V–O bonds (V=O) in the VO$_{2+}$ vanadyl groups [8–10]. This band could also be attributed to TiO$_5$ polyhedra [11]. The intensity of the band around 740 cm$^{-1}$ and 1022 cm$^{-1}$ decreases with the substitution of titanium by vanadium. The first one is attributed to the Ti–O vibrations in the TiO$_5$–TiO$_5$–TiO$_5$–TiO$_5$– chains formed by linked corner TiO$_6$ octahedra [12]. The band at 1022 cm$^{-1}$, observed in the pyrophosphates [13], is due to P$_2$O$_7^{4-}$ ions.

Figs. 4 and 5 show the EPR spectra of Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ glasses with $x = 0.25, 0.50, 0.75, 1$. No signal was observed for $x = 0$. The spectra of the compositions $x = 0.25$ and $x = 0.50$ exhibit an anisotropic structure, which is attributed to the vanadium (+IV) ion [14]. The hyperfine structure, resulting from the interaction between the unpaired 3$d^1$ electron and the vanadium nucleus spin ($I = 7/2$), shows two groups of eight lines, leading to the following EPR parameters: $g_{//} = 1.945, g_{\perp} = 1.985$; $A_{//} = 185$ G; $A_{\perp} = 69$ G. The values of $g_{//}$ and $g_{\perp}$ ($g_{//} < g_{\perp} < 2$)

Fig. 2. XRD patterns of Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ glasses heated at 600$^\circ$C.

Fig. 3. Raman spectra of Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ glasses.

Fig. 4. EPR spectra of Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ glasses with $x = 0.25$ and $x = 0.50$. 

Fig. 5. EPR spectra of Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ glasses with $x = 0.75$. 

* Non Identified Phases
are consistent with the presence of the V$^{4+}$ ion in a compressed octahedron. The EPR spectra of the vanadium rich glass samples showed broad signal centred at $g = 1.964$ for $x = 0.75$ and at $g = 1.957$ for $x = 1$. They are characteristic of V$^{4+}$ ions in distorted octahedra [14]. The absence of hyperfine structure in these EPR spectra is related to the high rate of V$^{4+}$ in the corresponding samples.

Fig. 6 gives the diffuse reflectance spectra of Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ glasses. The strong absorption observed at high energy ($I$) results from the formal electronic transfers [15,16]:

\[ O^2-(2p^6) + Ti^{4+}(3d^0) \rightarrow O^- (2p^5) + Ti^{3+}(3d^1) \]

\[ O^2-(2p^6) + V^{5+}(3d^0) \rightarrow O^- (2p^5) + V^{4+}(3d^1) \]

\[ O^2-(2p^6) + V^{4+}(3d^1) \rightarrow O^- (2p^5) + V^{3+}(3d^2) \]

The absorption bands (II) observed in the visible and infrared ranges correspond to the crystal field transitions of V$^{4+}$. The increase of the intensity of these bands when the amount of vanadium rises indicates that the concentration of V$^{4+}$ increases with the vanadium content. The EPR study reported previously showed that V$^{4+}$ ion (3$d^1$) is located in a compressed octahedron. For such geometry, the energy levels are given in Fig. 7. The unpaired 3$d^1$ electron occupy the $d_{xy}$ orbital. The EPR parameters $g_//$ and $g_\perp$ are related to the spin–orbit coupling $\lambda$ and to the energies of the $d$–$d$ transitions ($\Delta_1 : d_{xy} \rightarrow d_x^2 - d_y^2$; $\Delta_2 : d_{xz}, d_{yz}$) by the expressions [17]:

\[ g_// = g_e - \left( \frac{8\lambda k^2_{//}}{\Delta_1} \right) = 2 - \left( \frac{8\lambda k^2_{//}}{\Delta_1} \right) \]  

(1)

\[ g_\perp = g_e - \left( \frac{2\lambda k^2_{\perp}}{\Delta_2} \right) = 2 - \left( \frac{2\lambda k^2_{\perp}}{\Delta_2} \right) \]  

(2)

The $g$ and $\Delta$ parameters, obtained respectively from EPR and diffuse reflectance spectra, allow us to calculate the orbital reduction factors $k_{//}$ and $k_\perp$. For $x = 0.5$ ($g_// = 1.945$, $g_\perp = 1.985$, $\Delta_1 = 16484$ cm$^{-1}$ and $\Delta_2 = 10653$ cm$^{-1}$), we obtained $k_{//} = 0.727$ and $k_\perp = 0.625$. These low values of $k_{//}$ and $k_\perp$ suggest the existence of a very strong V–O bond, in good agreement with Raman study which showed the presence of VO$^{2+}$ vanadyl groups in these glasses.

4. Conclusion

In this work, we presented the preliminary results obtained for Na$_{5-x}$Ti$_{1-x}$V$_x$(PO$_4$)$_3$ (0 $\leq x \leq 1$) glasses investigated by Raman, EPR and UV–vis spectroscopies. These glasses contain V$^{5+}$ and V$^{4+}$ ions. V$^{4+}$ ions are located in compressed octahedra with very short V–O bond.

Acknowledgement

The authors wish to thank F. Guillen (ICMCB) for the record of the UV–vis spectra.

References