Glass – crystal transformation of $Na_{(5-2x)}M^{II}_xTi(PO_4)_3$ phosphates (M^{II} = Mg, Ca, Cd, Sr)

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New Nasiglass phosphates of composition $Na_{(5-2x)}M^{II}_xTi(PO_4)_3$ (M = Mg, Ca, Cd, Sr) are reported. The crystalline phases, which belong to the Nasicon-type structure, contain isolated TiO_6 octahedra whereas the corresponding glasses contain -Ti-O-Ti-O- chains. Divalent cations are located in the framework for the former and in the modifying network for the latter. Consequently the ionic conductivity is more facilitated in the crystalline materials than in the glasses.

1. Introduction

Titanium phosphates in both crystalline and glassy forms have been studied for a variety of technological applications : non linear optical and electro-optical materials, catalysts, membranes, fast ionic conductors, low expansion thermal ceramics...[1-5]. Two major types of structure can be encountered : Nasicon type structure [6] and potassium titanyl phosphate (KTP) structure [7]. The structure of these two families is based on a three-dimensional framework built of TiO_6 octahedra and PO_4 tetrahedra. The PO_4 tetrahedra are isolated from each other in both families. The TiO_6 octahedra are rather regular and isolated from each other in the Nasicon structure, while in the KTP family they are linked together by corners and form -Ti-O-Ti-O- infinite chains with alternating short (≈1.70Å) and long (≈2.30Å) Ti-O bonds. These chains are connected by PO_4 tetrahedra. Some Nasicon compounds, like $Na_5Ti(PO_4)_3$ [8], can exist also in glassy form and they are called "Nasiglass"[9]. Substitution of sodium for calcium, in $Na_5Ti(PO_4)_3$, leads to the formation of $Na_{5-2x}Ca_xTi(PO_4)_3$ compounds which exist also in crystalline and glassy forms [10]. This paper reports a summary of the results obtained for $Na_{(5-2x)}M^{II}_xTi(PO_4)_3$ (M = Mg, Ca, Cd, Sr) materials in terms of correlation between structure and electrical properties.

2. Experimental section

$Na_{(5-2x)}M^{II}_xTi(PO_4)_3$ (M = Mg, Ca, Cd, Sr) glasses have been prepared in Pt crucible by a conventional melt-quenching method as described elsewhere [11]. All the glasses are colourless. Thermal properties were investigated by DTA (SETARAM MDTA-85, 5°C/mn) and DSC (Perkin Elmer 7 series, 5°C/mn). The X-ray diffraction (XRD) data were collected at room temperature with a Philips PW1710 diffractometer (CuK_α). The Raman spectra were recorded using the microprobe on the XY Dilor Multichannel instrument. Diffuse reflectance spectra were registered at room temperature on a Cary 2415 spectrometer. The conductivity measurements were carried out on compact discs with ionically blocking gold electrodes using a frequency response analyser Solartron FRA 1255 and a broadband dielectric converter BDC Novocontrol. The frequency range was 10Hz - 3MHz and the temperature range was 373K - 673K.

3. Results and discussion

Glass transition temperature T_g increases generally with rising divalent cations content, as do the crystallisation temperature T_c (table 1). The recrystallisation of Ca ($0 \leq x \leq 1$), Cd ($0 \leq x \leq 0.5$), and Mg ($x = 1$) glasses leads to the formation of new crystalline phases of identical composition. Their structure belongs to the Nasicon type family [6]. Figure 1 presents XRD patterns of $Na_3MgTi(PO_4)_3$. The XRD spectra of the other compositions of glasses heated at T_c reveal the presence of a mixture of phases.

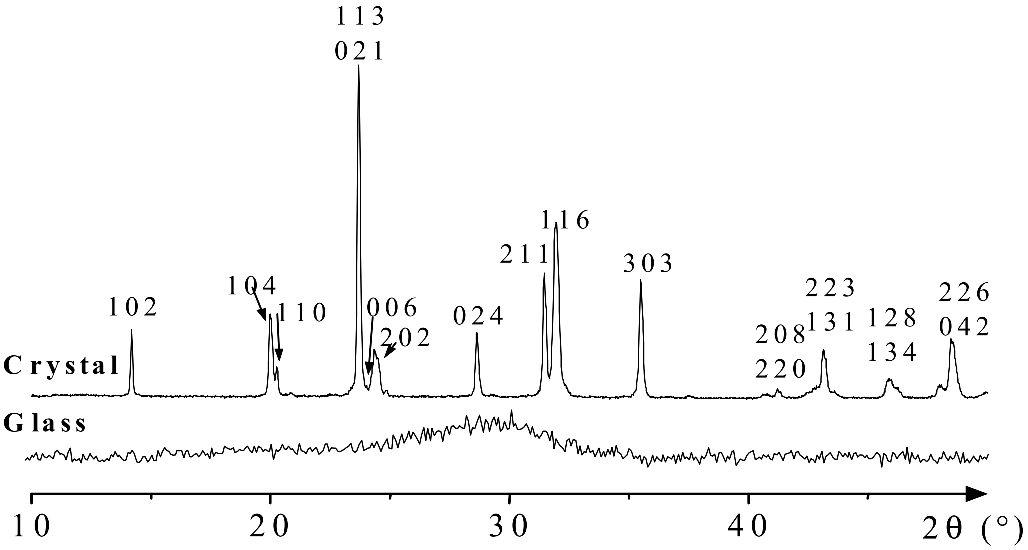

Figure 1. XRD patterns of $Na_3MgTi(PO_4)_3$

Table 1. Compositions and some properties of the $Na_{(5-2x)}M^{II}_x(PO_4)_3$ glasses

Composition	(Tg± 5)°C	(Tc± 5)°C	Density ± 0.03	Ea(eV) Glass	Ea(eV) Crystal
$Na_5Ti(PO_4)_3$	370/432	465/537	2.73	0.60	0.85
$Na_{4.5}Ca_{0.25}Ti(PO_4)_3$	427	460	2.71	0.80	0.80
$Na_4Ca_{0.5}Ti(PO_4)_3$	462	532	2.79	0.94	0.74
$Na_{3.5}Ca_{0.75}Ti(PO_4)_3$	483	512	2.80	0.98	0.72
$Na_3CaTi(PO_4)_3$	506	577	2.86	1.0	0.70
$Na_4Cd_{0.5}Ti(PO_4)_3$	441	487	3.03	0.92	0.66
$Na_3MgTi(PO_4)_3$	499	522	2.81	0.84	0.70
$Na_4Sr_{0.5}Ti(PO_4)_3$	465	539/551	2.89	1.0	No hay

The crystalline structure of $Na_5Ti(PO_4)_3$ [12] consists of a three-dimensional framework built of PO_4 tetrahedra and AO_6 (A = Ti, Na) octahedra. The cavities, usually labelled M1 and M2, are totally occupied by sodium atoms. The cationic distribution is $[Na_3]_{M2}[Na]_{M1}[NaTi]_A(PO_4)_3$. In $Na_{5-2x}Ca_x\square_xTi(PO_4)_3$ phases (□ : vacancy) the calcium atoms occupy the A sites of the framework while the vacancies are in the M2 sites :
$[Na_{3-x}\square_x]_{M2}[Na]_{M1}[Na_{1-x}Ca_xTi]_A(PO_4)_3$ [10,13]. Similar cationic distributions are found for Mg and Cd phases [14].

Raman study has been taken in order to have information on the structure of the glasses. Details of this study will be published elsewhere. Figure 2 compares Raman spectra of $Na_{5-2x}Cd_xTi(PO_4)_3$ in both crystalline and vitreous forms to that of the oxyphosphate $Ni_{0.5}TiOPO_4$ [13]. The structure of the latter belongs to the KTP family. The band observed between 700 and 800 cm^{-1} in all the $Na_{(5-2x)}M^{II}_xTi(PO_4)_3$ glasses and absent in the Nasicon titanium phosphates is likely due to oxyphosphate titanium structure indicating the formation of -Ti-O-Ti-O- chains in these glasses.

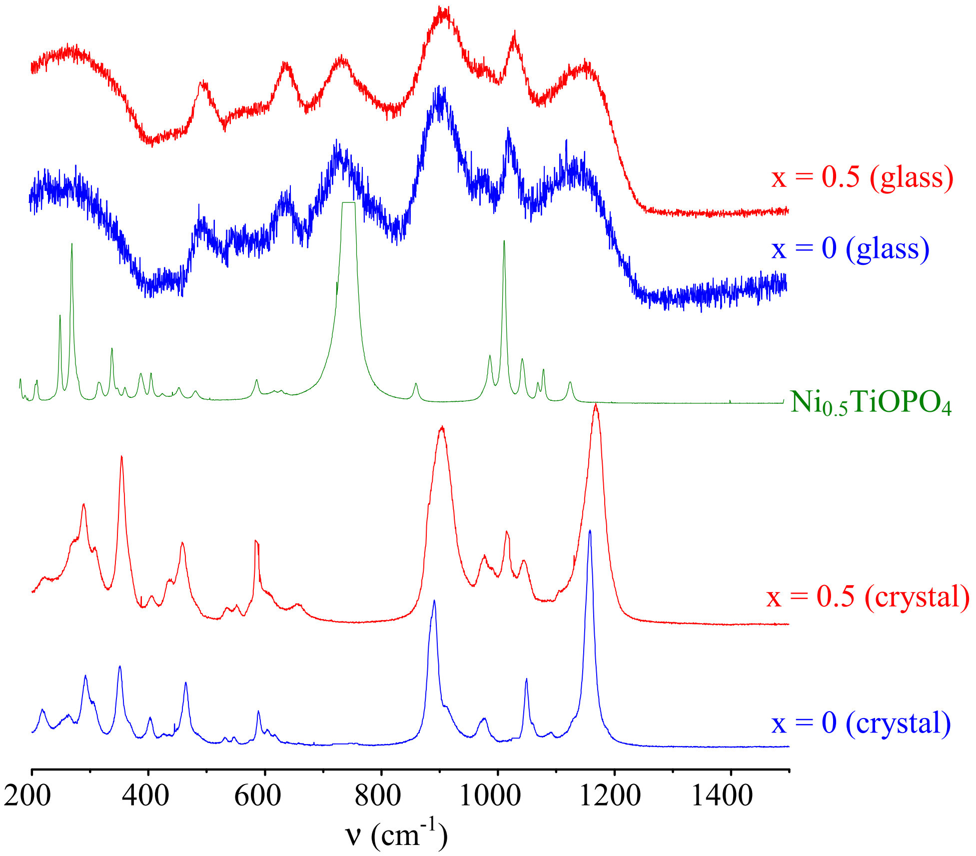

Figure 2 Raman spectra of $Na_{(5-2x)}Cd_x(PO_4)_3$ and $Ni_{0.5}TiOPO_4$

Figure 3 shows diffuse reflectance spectra of $Na_3MgTi(PO_4)_3$ in both glassy and crystalline forms. The strong absorption is due to the electronic transfer :

$O^{2-}\ (2p^6) + Ti^{4+}\ (3d^0) \longrightarrow O^{-}\ (2p^5) + Ti^{3+}\ (3d^1)$….

The values of the absorption threshold (Eg/eV) are 3.35 for the glass and 3.54 for the crystalline phase. Those of TiO_2 and the oxyphosphate $Mg_{0.5}TiO(PO_4)$ are respectively 3.00eV and 3.37eV [15]. The evolution of Eg observed for the three crystalline phases is related to the environment of the TiO_6 octahedron which is linked to six other TiO_6 in TiO_2, to two TiO_6 and four PO_4 in $Mg_{0.5}TiOP_4$ and to six PO_4 in $Na_3MgTi(PO_4)_3$ (Fig. 4). The marked covalence of the P-O bond makes the electronic transfer from oxygen to titanium difficult and explains the high values obtained for the phosphates. For vitreous $Na_3MgTi(PO_4)_3$ the value of Eg (3.35eV) is close to that obtained for $Mg_{0.5}TiOP_4$ (3.37eV) indicating that the glass contains distorted TiO_6 octahedra which are linked to other TiO_6 octahedra and to PO_4

tetrahedra. In other words, the structure of $Na_{(5-2x)}M^{II}_xTi(PO_4)_3$ Nasiglass phosphates is based on -Ti-O-P- and -Ti-O-Ti- linkages.

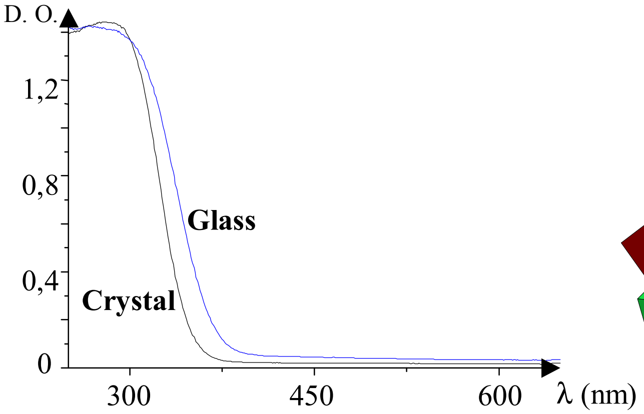

Figure 3 Diffuse reflectance spectra of $Na_3MgTi(PO_4)_3$

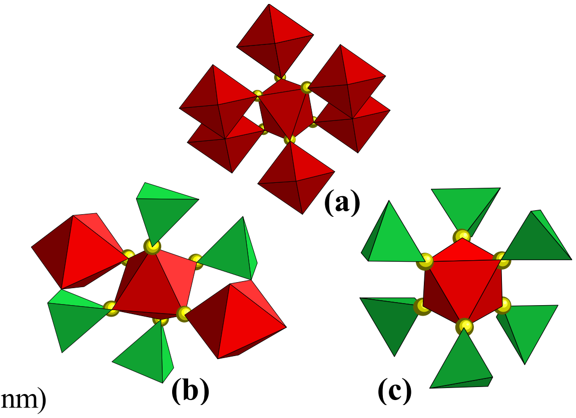

Figure 4 Titanium environment in TiO_2 **(a)**, $Mg_{0,5}TiO(PO_4)$ **(b)** and Nasicon $Na_3MgTi(PO_4)_3$ **(c)**

Ionic conductivity measurements have been done for all $Na_{(5-2x)}M^{II}_xTi(PO_4)_3$ (M = Mg, Ca, Cd, Sr) compounds in both crystalline and glassy forms. Variation of conductivity versus reciprocal temperature is linear (figure 5). The values of the activation energies Ea, deduced from Arrhenius plots, are given in table 1. Ea increases for the glasses and decreases for the crystalline phases when the amount of divalent cations rises. As previously pointed out for the crystalline phases $Na_{(5-2x)}M^{II}_xTi(PO_4)_3$, the divalent ions are located in the framework whereas the vacancies occupied the interstitial sites and their number increases with x. Consequently the diffusion of Na^+ ions is facilitated. The high values of activation energie obtained for the vitreous phosphates imply that the divalent cations act as glass modifiers and occupy sites similar to that of sodium in $Na_5Ti(PO_4)_3$ base glass.

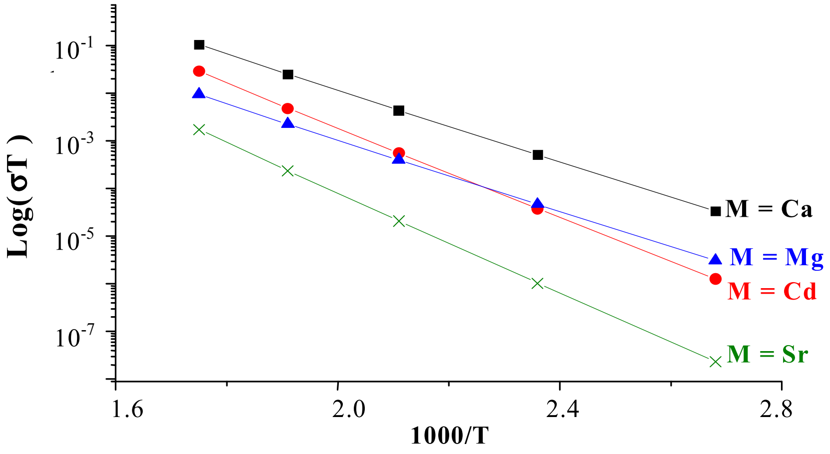

Figure 5 Arrhenius plots for $Na_4M^{II}_{0.5}Ti(PO_4)_3$ glasses

4 Conclusion

In this work we have investigated the glass - crystal transformation of $Na_{(5-2x)}M^{II}_xTi(PO_4)_3$. (M= Mg, Ca, Cd, Sr). The structure of the crystalline phases (for M = Mg, Ca, Cd) belongs to the Nasicon family. The divalent cations participate to the framework which is formed by AO_6 octahedra (A=Ti, Ca, Na) sharing their corners only with PO_4 tetrahedra. The interstitial sites are partially occupied by sodium.

The structure of the glasses is based on Ti-O-P and Ti-O-Ti linkages. The high values of activation energy obtained for the glasses indicate that the divalent ions are located in the modifying network.

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