

Glass–Crystal Transformation of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ Phosphate

S. KRIMI^{1,2}, A. EI JAZOULI^{1*}, A. LACHGAR³ AND J. R. RAMOS - BARRADO⁴

¹Laboratoire de Chimie des Matériaux Solides, Faculté des Sciences Ben M'Sik, Avenue Idriss El Harti, B.P. 7955, Casablanca, Morocco.

²Département de Chimie, Faculté des Sciences Ain Chock, Casablanca, Morocco.

³Department of Chemistry, Wake Forest University, Winston – Salem, North Carolina 27109, USA.

⁴Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Málaga, Spain.

*Corresponding author: a.eljazouli@univh2m.ac.ma

Abstract

$\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ phosphate exists in both crystalline and vitreous forms. The glass – crystal transformation was investigated using DTA, XRD, Raman spectroscopy and ionic conductivity. The crystalline phase which belongs to the Nasicon type family structure, space group $R\bar{3}$, contains isolated TiO_6 octahedra whereas the corresponding glass contains Ti-O-P and Ti-O-Ti linkages. The Mg^{2+} ions are located in the framework for the crystalline phase while in the glass they are in the modifying network.

INTRODUCTION

Within a research program on the titanium phosphates we have isolated numerous compounds which are promising materials in the field of solid state chemistry [1-5]. We have recently initiated a survey of the $\text{Na}_2\text{O} - \text{MO} - \text{TiO}_2 - \text{P}_2\text{O}_5$ system ($\text{M} = \text{Mg}, \text{Ca}, \text{Cd}, \text{Sr}$) [5]. Glass and crystalline phosphates of composition $\text{Na}_{5-2x}\text{M}_x\text{Ti}(\text{PO}_4)_3$ have been obtained. The purpose of this paper is to describe the glass – crystal transformation of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$.

EXPERIMENTAL

Colourless $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ phosphate glass was prepared in Pt crucible, from Na_2CO_3 , MgO, TiO_2 and $(\text{NH}_4)_2\text{HPO}_4$ as starting materials, by a conventional melt-quenching method as described elsewhere[5]. The powder crystalline samples of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ was obtained by heating the glass of identical composition at 650°C or by standard solid state preparation as described elsewhere [1]. The X-ray diffraction (XRD) data were collected at room temperature with a Philips PW1710 diffractometer ($\text{CuK}\alpha$). Thermal properties were investigated by DTA (SETARAM MDTA-85, $5^\circ\text{C}/\text{mn}$). The Raman spectra were recorded using the microprobe on the XY Dilor Multichannel instrument. 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 10 Hz to 3 MHz and the temperature range was between 373K and 673K.

RESULTS AND DISCUSSION

The vitreous transition and recrystallization temperatures are 500°C and 522°C respectively. The melting point is observed at about 800°C . Recrystallization of the glass leads to the formation of a new crystalline phase of identical composition. The X-ray diffraction patterns of glass and crystalline forms are given in figure 1. The XRD pattern of crystalline phase can be indexed assuming a hexagonal cell $a_h = 8.792(2) \text{ \AA}$, $c_h = 22.039(3) \text{ \AA}$, $Z = 6$, $d_{\text{exp}} = 2.91(2)$

and $d_{\text{cal}} = 2.88$. The single crystal X-ray analysis shows that the structure belongs to the Nasicon - type family (S. G.: $R\bar{3}$). It consists of three-dimensional network of PO_4 tetrahedra and AO_6 octahedra ($A = \text{Ti}, \text{Mg}$) sharing corners. The TiO_6 octahedra are isolated from each other and so are the PO_4 tetrahedra. Na^+ cations partially occupy the sites usually labelled M1 and M2. Details of the structure analysis will be published elsewhere [6].

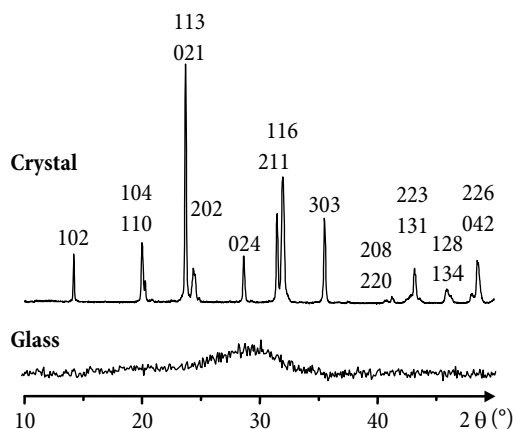


Figure 1: XRD of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$

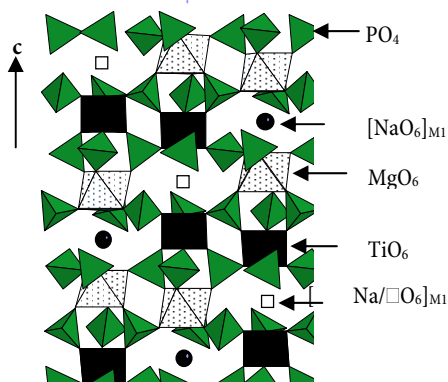
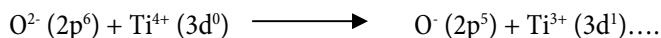


Figure 2: The structure of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$

The Raman spectra, at 300 K, of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ in both crystalline and vitreous forms are compared to that of the oxyphosphate $\text{Mg}_{0.5}\text{TiOP}_4$ [7] (figure 3). The structure of the latter belongs to the KTP family. The peaks observed at the high wave-numbers are attributed to the vibration of P - O bonds. The strong peak observed between 700 and 800 cm^{-1} in the $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ glass is absent in the Nasicon titanium phosphates and is attributed to the oxyphosphate titanium structure indicating the formation of -Ti-O-Ti-O- chains in the glass. The broad peaks at high energy in glass form are sharp in the crystalline phases. The bands observed between 400 and 700 cm^{-1} are attributed to O-P-O deformation and Ti-O vibrations.

Figure 4 shows diffuse reflectance spectra of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ in both glassy and crystalline forms. The strong absorption is due to the electronic transfer:



The values of the absorption threshold (E_g/eV) are 3.35 for the glass and 3.54 for the crystalline phase. Those of TiO_2 and the oxyphosphate $\text{Mg}_{0.5}\text{TiO}(\text{PO}_4)$ are respectively 3.00 eV and 3.37 eV [7]. The evolution of E_g 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 $\text{Mg}_{0.5}\text{TiOP}_4$ and to six PO_4 in $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ (Figure 5). 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 $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ the value of E_g (3.35 eV) is close to that obtained for $\text{Mg}_{0.5}\text{TiOP}_4$ (3.37 eV) 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 the vitreous $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ is based on $-\text{Ti}-\text{O}-\text{P}-$ and $-\text{Ti}-\text{O}-\text{Ti}-$ linkages.

The curves $\log \sigma T$ versus $(10^3/T)$ for the crystalline and vitreous forms of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ are given in figure 6. The conductivity variation follows the Arrhenius law. The values of the activation energy are 0.70 eV for the crystalline phase and 0.84 eV for the glass form. The high value of the activation energy obtained for the vitreous phosphate imply that the Mg^{2+} ions are located in the modifying network, unlike the crystalline phase where the divalent ions (Mg^{2+}) are in the framework.

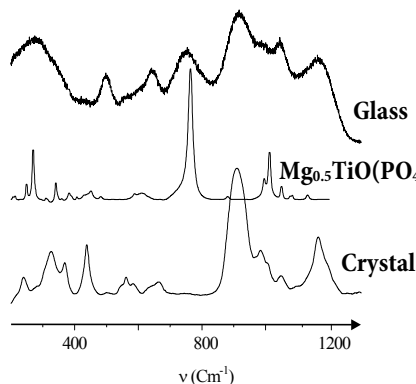


Figure 3: Raman spectra of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ and $\text{Mg}_{0.5}\text{TiO}(\text{PO}_4)$

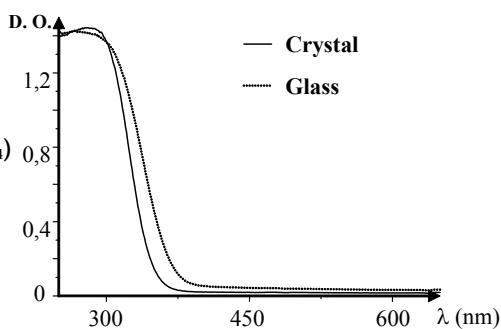


Figure 4: Diffuse reflectance spectra of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$

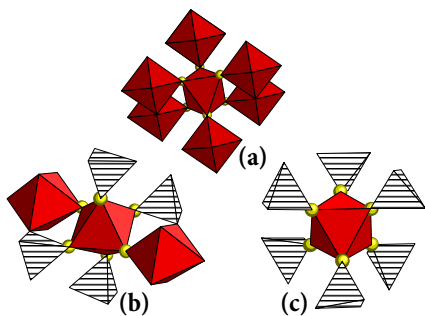


Figure 5: Titanium environment in TiO_2 (a), $\text{Mg}_{0.5}\text{TiO}(\text{PO}_4)$ (b) and Nasicon $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$ (c)

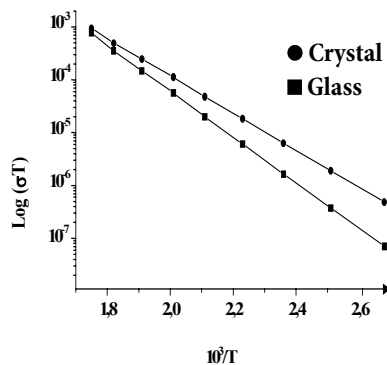


Figure 6: Arrhenius plots of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$

CONCLUSION

In this work we have investigated the glass-crystal transformation of $\text{Na}_3\text{MgTi}(\text{PO}_4)_3$. The structure of the crystalline phases belongs to the Nasicon family. The divalent cations participate to the framework which is formed by AO_6 octahedra ($A = \text{Ti}, \text{Mg}$) sharing their corners only with PO_4 tetrahedra. The interstitial sites are partially occupied by sodium. The structure of the glass is based on -Ti-O-P- and -Ti-O-Ti- linkages. The high values of activation energy obtained for the glass indicate that the divalent ions are located in the modifying network.

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