

Investigation of the glass–crystal transition of $\text{Na}_5\text{Ti}(\text{PO}_4)_3$

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Abstract

$\text{Na}_5\text{Ti}(\text{PO}_4)_3$ can exist in both crystalline and vitreous forms. The glass–crystal transition was investigated using several techniques. The crystallization process involves two steps corresponding to the successive formation of $\text{Na}_4\text{TiO}(\text{PO}_4)_2$ and $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ crystals.

The latter new phosphate belongs to the Nasicon-type family ($a_h = 9.061 \pm 0.002 \text{ \AA}$, $c_h = 21.734 \pm 0.004 \text{ \AA}$, space group $R32$). Its structure can be described as a three-dimensional framework containing TiO_6 and NaO_6 octahedra sharing common corners with the PO_4 tetrahedral groups. The titanium and sodium atoms are distributed with a 2-2 ordering along the c axis. This arrangement creates two different M_2 sites.

1. Introduction

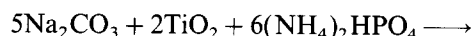
Transparent glasses with relatively large non-linearities are promising materials for all optical switching applications [1]. The choice of composition is mainly dictated by the possibility of an increase in the non-linear index coefficient n_2 . Various parameters have to be considered such as high damage threshold, ultrafast response time, wave guide formation process *etc.*

A preliminary investigation of the $\text{Na}_2\text{O}-\text{TiO}_2-\text{P}_2\text{O}_5$ system was recently reported [2]. P_2O_5 was selected as a glass-forming oxide, and TiO_2 as the hyperpolarizable entity, and sodium ions were introduced to make the possible ion exchange easier. The glass-forming region was found to comprise the composition 50% Na_2O , 20% TiO_2 and 30% P_2O_5 (mole per cent). The crystallization of this glass leads to the formation of a new Nasicon-type phosphate of identical composition. The present paper describes the process of crystallization as well as the structure of the crystalline phase.

2. Experimental details

Glasses were prepared as described elsewhere [2]. The crystallized form of $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ is obtained by heating the glass of identical composition at 700°C or by standard solid state preparation from a mixture of Na_2CO_3 , TiO_2 and $(\text{NH}_4)_2\text{HPO}_4$.

The reaction



is completely achieved after three thermal treatments respectively at 300°C for 4 h, 500°C for 6 h and 750°C for 15 h.

Slow cooling of the liquid of identical composition from 850°C to room temperature (RT) leads to the simultaneous formation of $\text{Na}_4\text{TiO}(\text{PO}_4)_2$ and $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ crystals. Suitable crystals of the latter phase were isolated for a complete structural determination.

3. Results

The differential thermal analysis curve shows two glass transition temperatures T_{g1} and T_{g2} respectively at 414 and 507°C , and two exothermic peaks T_{c1} and T_{c2} at 462 and 547°C . The melting point is observed at about 800°C (Fig. 1). The X-ray diffraction (XRD) patterns of samples heated between T_{c1} and T_{c2} reveal the existence of $\text{Na}_4\text{TiO}(\text{PO}_4)_2$ and $\text{Na}_4\text{P}_2\text{O}_7$ in addition to a remaining vitreous phase. Above T_{c2} only the new phase $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ is detected. Therefore, T_{c2} corresponds to crystallization of the last amorphous phase and to the formation of the new phosphate.

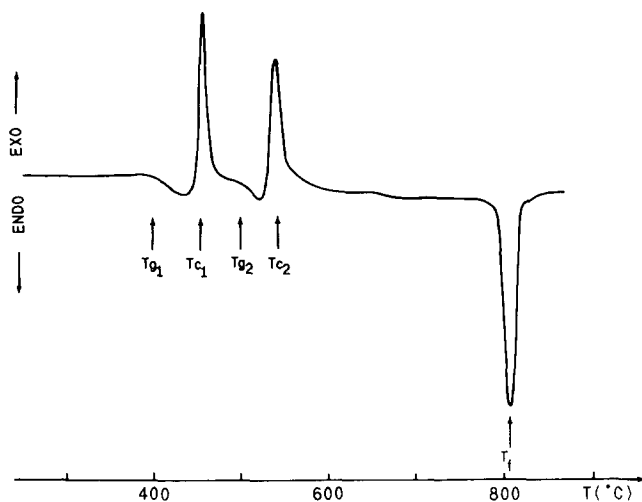


Fig. 1. Differential thermal analysis curve of the 50 mol% Na_2O , 20 mol% TiO_2 , 30 mol% P_2O_5 glass.

4. The structure of $\text{Na}_5\text{Ti}(\text{PO}_4)_3$

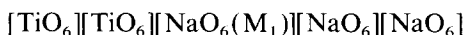
Here we summarize the description of the structure of $\text{Na}_5\text{Ti}(\text{PO}_4)_3$, details of which will be published elsewhere [3].

At room temperature the XRD pattern of $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ can be indexed assuming a hexagonal cell ($a_h = 9.061 \pm 0.002 \text{ \AA}$, $c_h = 21.734 \pm 0.004 \text{ \AA}$, $Z = 6$, $d_{\text{exp}} = 2.84$, $d_x = 2.89$).

The space group $R32$ is compatible with the observed reflections (hkl), $-h + k + l = 3n$ and $(hhl):l = 2n$, as well as with a positive test of second harmonic generation (SHG = $1.064 \mu\text{m}/0.532 \mu\text{m}$).

The structure was solved using standard diffraction techniques and calculations. It consists of a three-dimensional network of PO_4 tetrahedra and AO_6 octahedra ($A \equiv \text{Ti}, \text{Na}$) sharing common corners. These octahedra are occupied successively by the titanium and sodium atoms with a 2-2 ordering along the c axis (Fig. 2).

The site usually labelled M_1 , an elongated antiprism, shares common faces with a TiO_6 octahedron and an NaO_6 octahedron, giving rise to infinite chains parallel to the $[001]$ direction with the following distribution:



This cationic ordering creates two different M_2 sites within the three-dimensional framework where the remaining sodium atoms are located: they are surrounded by eight oxygen atoms with relatively large Na-O distances in the range $2.437\text{--}2.904 \text{ \AA}$.

These data can be analysed in the context of the structural evolution of the Nasicon-type phosphates.

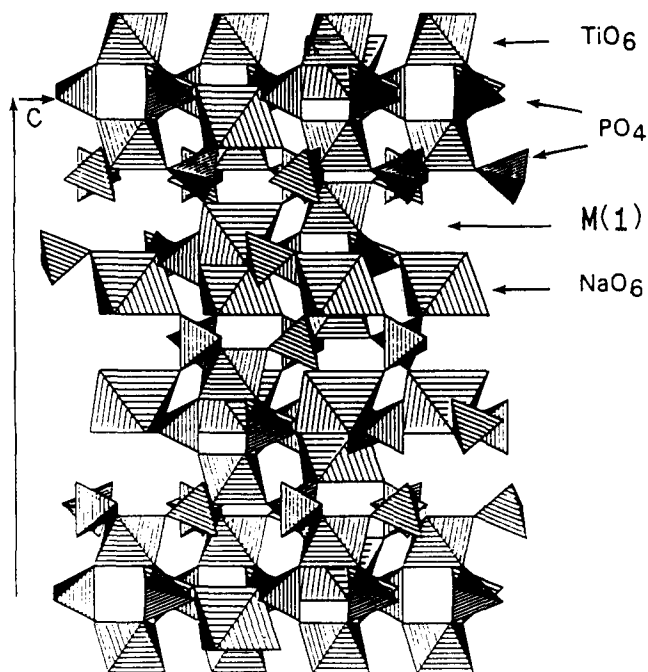


Fig. 2. A perspective drawing of the $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ structure.

This structure was described initially by Hagman and Kierkegaard [4] for $\text{NaA}_2(\text{PO}_4)_3$ ($A \equiv \text{Ti}, \text{Ge}, \text{Zr}$) phosphates in which only the M_1 site is occupied by the sodium atom.

The rules governing the variations in cell parameters of the Nasicon-type phosphates have already been established [5]: (i) the a parameter is directly correlated with the size of the cation located at the octahedral A site and with the proportion of sodium in position M_2 ; (ii) the c parameter increases with the size of the A^{n+} ion and the strength of the $\text{Na}^+(M_1) - A^{n-}$ electrostatic repulsion.

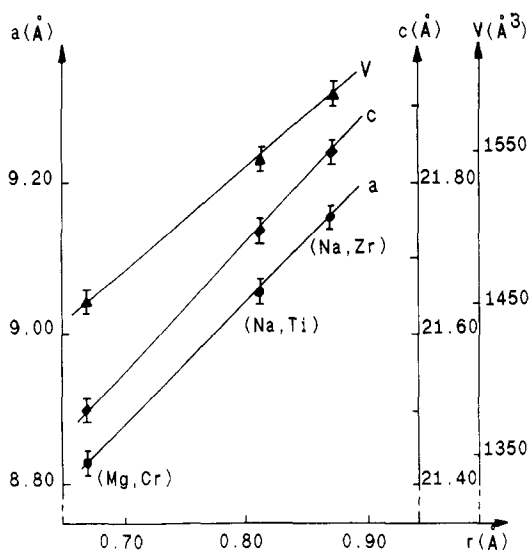


Fig. 3. Cell parameters and volume variations vs. mean A ionic radii of sodium-rich Nasicon-type phosphates.

Figure 3 compares the variation in structural data of Nasicon-type phosphates for which the mean charge of the A cations is 2.5. The linear variation of these parameters *vs.* the mean A cation ionic radii is in fair agreement with the cationic distribution found for $\text{Na}_5\text{Ti}(\text{PO}_4)_3$.

Acknowledgments

The authors wish to thank F. Estager, University of Bordeaux, for assisting in the structure determination and J. C. Achddou, Laboratoire de Physico Chimie des

Matériaux de Montpellier, for carrying out the SHG test.

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