Synthesis and structural characterization of phosphate-based Nasiglasses
Na$_3$Ca$_{1-x}$Mn$_x$Ti(PO$_4$)$_3$ (0 ≤ x ≤ 1)

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Abstract
Nasiglasses with formula Na$_3$Ca$_{1-x}$Mn$_x$Ti(PO$_4$)$_3$ (0 ≤ x ≤ 1) were synthesized and structurally characterized by DTA, PXRD, EPR, Raman, and density measurements. The density of these glasses increases while the molar volume remains practically constant when manganese replaces calcium, indicating that manganese ions are located in the interstitial sites of the framework, in good agreement with the small variation of the glass transition temperature, observed between the extreme compositions (ΔT ≈ 23 °C). Crystallization of the glasses at 650 °C leads to the formation of crystalline phases belonging to the Nasicon family. The structure of these crystalline phases consists of three dimensional framework built of PO$_4$ tetrahedra sharing corners with AO$_6$ octahedra (A = Ca/Mn, Ti); Na$^+$ ions occupy the interstitial sites. EPR study of glasses shows that Mn$^{2+}$ ions occupy octahedral sites, with predominantly ionic bonding between Mn$^{2+}$ and O$^{2-}$ ions. Raman spectroscopy study shows that the glasses contain P$_2$O$_5$ and PO$_4$ groups, and short -Ti-O-Ti-O-Ti- chains. The presence of these chains indicates that the TiO$_6$ octahedra are linked to each other through corners, unlike in the corresponding crystalline phases where they are connected to each other via PO$_4$ tetrahedra. All results obtained for the glassy materials indicate that Mn$^{2+}$ and Ca$^{2+}$ ions act as glass modifiers, unlike in the crystalline compounds where they are part of the framework.

1. Introduction
Metal phosphates in both crystalline and glassy forms are extensively studied for their potential applications. They can be used as hosts for radioactive elements which makes them useful in removal of radioactive elements from nuclear waste [1,2], as cathodes in lithium ion batteries [3,4], as sunscreens for UV radiation absorption [5,6], as pigments [7-10], as lasers and light emitting diodes (LEDs) components [11,16], and last but not least as biomaterials [17,22]. Phosphate glasses possess a series of interesting properties such as low glass transition temperatures, low melting and softening temperatures, high electrical conductivity and interesting dielectric properties [23], large thermal expansion coefficients [24], and high optical transparency window over UV, visible and infrared wavelength range [25]. Introduction of divalent manganese ions (Mn$^{2+}$) in phosphates leads to materials with interesting electrochemical, optical, thermochemical, and electric-dielectric properties [3,14,26-28]. The diverse properties and applications of phosphate glasses depend on their structure, which is based on the distribution of PO$_4$ tetrahedra in the vitreous network. Connection of these tetrahedra by vertices gives rise to different phosphate groups depending on the value of O/P ratio. So, the glass structure can be formed by
a cross-linked network where each PO₄ is linked to three others (vitreous P₂O₅, O/P = 2.5), infinite metaphosphate chains where each PO₄ is linked to two others (vitreous NaPO₃, O/P = 3), or by small diphosphate P₂O₇²⁻ (O/P = 3.5) and monophosphate PO₄³⁻ (O/P = 4) anions [29]. We previously reported the study of glasses belonging to the Na₂O-TiO₂-P₂O₅ system [30]. This ternary system includes the composition Na₃Ti(PO₄)₂ (50 mol. % Na₂O - 20 mol. % TiO₂ - 30 mol. % P₂O₅), which exists in both glassy and crystalline forms [31, 32]. The crystalline form belongs to the Nasicon family (Nasicon is the acronym of Natrium super ionic conductor) [33, 34]. Many compounds of this family can be prepared in the glassy form; they are called Nasiglass (Na super ionic glass) [35]. Substitution of sodium in Na₃Ti(PO₄)₂ by calcium or manganese led to formation of new crystalline and vitreous compounds Na₃₀₂₅Ca₅Ti(PO₄)₂₃ (0 ≤ x ≤ 1 ) [36, 37] and Na₃₀₂ₓMnₓTi(PO₄)₂₃ (0 ≤ x ≤ 1) [38]. The composition x = 1 corresponds to the compounds Na₃CaTi(PO₄)₃ and Na₃MnTi(PO₄)₃. The structure of their crystalline form consists of a three dimensional framework built of PO₄ tetrahedra sharing corners with AO₆ octahedra (A = Ca/Mn, Ti); Na⁺ ions occupy interstitial sites. Ti⁴⁺, Ca²⁺, and Mn²⁺ ions belong to the framework of these crystalline materials [39-41]. Raman study of glassy form of Na₃CaTi(PO₄)₃ showed the presence of short -Ti-O-Ti-O-Ti- chains [37]. In order to have more information on the structure of the glass, we substituted manganese for calcium and used Mn²⁺ ion as paramagnetic local probe. The present paper reports the synthesis and structural characterization of Na₃Ca₁₋ₓMnₓTi(PO₄)₃ (0 ≤ x ≤ 1) system (30 mol. % Na₂O – 20(1-x) mol. % CaO – 20x mol. % MnO – 20 mol. % TiO₂ – 30 mol. % P₂O₅; 0 ≤ x ≤ 1).

2. Experimental details

Glassy samples of Na₃Ca₁₋ₓMnₓTi(PO₄)₃, 0 ≤ x ≤ 1, were prepared by the conventional melt-quenching technique, using analytical grade reagents NaH₂PO₄, CaCO₃, TiO₂ and MnO. Before weighing the reagents, CaCO₃ is dried at 350°C and TiO₂ at 600°C, during 4 hours, in order to remove any traces of water and adsorbed gases, then kept in dry atmosphere. The overall chemical reaction is summarized in the following equation:

\[
3\text{NaH}_2\text{PO}_4 + (1-x)\text{CaCO}_3 + x\text{MnO} + \text{TiO}_2 \rightarrow \text{Na}_3\text{Ca}_{1-x}\text{Mn}_x\text{Ti(PO}_4)_3 + 3\text{H}_2\text{O} + (1-x)\text{CO}_2
\]

Stoichiometric amounts of reagents, required to obtain 10g of the glass, were ground in a porcelain mortar then transferred to a platinum crucible. The mixture was heated at 200°C (4h) and 600°C (6h) to eliminate H₂O and CO₂ gases. The temperature was then progressively raised to 1050°C with a heating rate of 10 °C/min, and held for 20 min at this temperature. The melt was then quenched to room temperature in air. Homogeneous glasses without bulbs were obtained. Na₃CaTi(PO₄)₃ is colorless while glasses containing manganese are brown (Figure 1). The brown color becomes more intense when the manganese content increases. Crystallization of glasses consists of heating powders of the previously prepared samples for 12 hours at 650°C (temperature close to the crystallization temperature Tc of the glasses). Crystalline form of Na₃CaTi(PO₄)₃ has a white color, while the compounds containing manganese have a brownish color as seen in Figure 1.

| Glassy samples | | | | | | |
|----------------|---|---|---|---|---|
| Crystalline samples | | | | | | |
| x | 0 | 0.01 | 0.05 | 0.25 | 0.50 | 0.75 | 1 | |

**Figure 1**: Photographs of glassy and crystalline Na₃Ca₁₋ₓMnₓTi(PO₄)₃ (0 ≤ x ≤ 1) samples.

Density measurements were performed on blocks of glasses, using Archimedes’ Principle, on an analytical balance (±0.1 mg) with an attached density kit. Diethyl phthalate was used as the immersion liquid. The density (\(\rho\)) was obtained from the following equation:

\[\rho = \left[ m_w / (m_i - m_t) \right] \rho_l\]
where \( m_a \) is the mass of the sample in air, \( m_l \) is the mass of the sample fully immersed in the liquid, and \( \rho_l \) is the density of liquid used (diethyl phthalate) at room temperature. Measurements were done three times for each composition, and the error is within \( \pm 0.03 \text{ g/cm}^3 \). The molar volume \( (V_m = M/\rho) \) of glasses was calculated from the molecular weight \( (M) \) and density \( (\rho) \).

Differential scanning calorimetry (DSC Q2000, heating rate 10 °C/min, accuracy \( \pm 5\)°C) was used to determine the glass transition and crystallization temperatures of the glasses \( (T_g, T_c) \). Crushed glass powders (~20 to 40 mg) were transferred to platinum crucibles and the curves were recorded in air atmosphere.

Powder X-ray diffraction (PXRD) patterns were recorded at room temperature with a powder diffractometer (PANalytical X’Pert Pro) using Cu K\( \alpha \) radiation (1.54 Å). Raman spectra were recorded on small pieces of glasses, on a confocal micro-Raman Labram (Horiba/Jobin-Yvon) spectrophotometer with a backscattering mode, at room temperature, in the range 150-1800 cm\(^{-1} \). The excitation source was a 532 nm continuous laser. A holographic Notch filter was used to reject the Rayleigh diffusion. The backscattered light was collected through a 100x objective and selectively transmitted toward a cooled CCD detector. EPR spectra were recorded at room temperature with a Bruker spectrometer operating at the X-band frequency (9.7 GHz).

3. Results and discussion

3.1. PXRD of glasses

The amorphous state of glasses was checked by PXRD. The absence of any sharp peak in the diffraction patterns of Na\(_3\)Ca\(_{1-x}\)Mn\(_x\)Ti(PO\(_4\))\(_3\) \((0 \leq x \leq 1)\) glasses (Figure 2) confirms their amorphous state.

![Figure 2: PXRD patterns of glassy Na\(_3\)Ca\(_{1-x}\)Mn\(_x\)Ti(PO\(_4\))\(_3\) (0 \leq x \leq 1)](image)

3.2. Density and molar volume

The density and molar volume of glasses depend upon many factors such as structure, coordination number, cross-link density, and dimensionality of interstitial spaces [42]. If the molar volume remains constant, we can conclude that the cations introduced are located in the interstitial sites of the framework. A decrease in the molar volume shows that the introduced cations occupy sites available within the framework, and strengthens the network as it bridges the oxide ions. An increase in molar volume is indicative of a network expansion. The values of molar mass \( (M = 0.3 M_{Na2O} + 0.2(1-x) M_{CaO} + 0.2x M_{MnO} + 0.2 M_{TiO2} + 0.3M_{P2O5}; 0 \leq x \leq 1) \), density \( (\rho) \) and molar volume \( (V_m) \) for the studied glasses are reported in table 1. With an increase in MnO content, the molar weight and the density increase while the molar volume remains practically constant, within the accuracy of the measurements. The increase of the molar mass and the density is due to replacement of low molecular weight Ca\(^{2+}\) by Mn\(^{2+}\). The fact that the molar volume remains practically constant, when MnO concentration...
increases, indicates that Mn\(^{2+}\) ions occupy the interstitial sites, and don't participate to the glass framework. Thus, one can conclude that MnO acts as glass modifier.

3.3. DSC study

DSC thermograms of the glasses studied are shown in Figure 3. All glasses exhibit an endothermic change due to glass transition, followed by an exothermic peak due to crystallization of the glass. Data in Table 1 show that the values of the glass transition temperature (\(T_g\)) and crystallization temperature (\(T_c\)) decrease with increasing MnO content. However the variation of \(T_g\) between the extreme compositions (\(\Delta T_g = 23 \pm 10^\circ C\)) is not as important as those observed in Na\(_2\)O-MnO-P\(_2\)O\(_5\) (\(\Delta T_g = 120^\circ C\)) and K\(_2\)O-MnO-P\(_2\)O\(_5\) (\(\Delta T_g = 185^\circ C\)) glasses [27, 43]. It is established that the variation of glass transition temperature is strictly related to the nature of bonding in the vitreous network. A large variation of \(T_g\) shows a strong modification of the glass structure. The small variation of \(T_g\) observed for Na\(_3\)Ca\(_{1-x}\)Mn\(_x\)Ti(PO\(_4\))\(_3\) (0 \(\leq x \leq 1\)) glasses indicates that non significant change occurred in their structure. This behavior is due to the fact that, Mn\(^{2+}\) ions are located in the interstitial sites, and don’t participate to the glass framework, in good agreement with the non-variation of the molar volume of these glasses.

Table 1. Density (\(\rho\)), molar mass (\(M\)), molar volume (\(V_m\)), glass transition temperature (\(T_g\)) and crystallization temperature (\(T_c\)) of Na\(_3\)Ca\(_{1-x}\)Mn\(_x\)Ti(PO\(_4\))\(_3\) (0 \(\leq x \leq 1\)) glasses.

<table>
<thead>
<tr>
<th>x</th>
<th>(\rho) (g/cm(^3) ± 0.03)</th>
<th>(M) (g/mol)</th>
<th>(V_m) (cm(^3)/mol ± 0.4)</th>
<th>(T_g) ((^\circ)C ± 5)</th>
<th>(T_c) ((^\circ)C ± 5)</th>
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<tr>
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<tr>
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<td>601</td>
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<tr>
<td>0.75</td>
<td>2.95</td>
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<td>31.0</td>
<td>479</td>
<td>608</td>
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<td>91.34</td>
<td>31.0</td>
<td>475</td>
<td>576</td>
</tr>
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</table>

Figure 3: DSC curves of Na\(_3\)Ca\(_{1-x}\)Mn\(_x\)Ti(PO\(_4\))\(_3\) (0 \(\leq x \leq 1\)) glasses.
3.4. Powder X-ray diffraction of the crystalline materials

The PXRD patterns of the crystalline Na₃Ca₁₋ₓMnₓTi(PO₄)₃ materials, obtained by crystallization of the glasses at 650°C, are shown in Figure 4, for the compositions x = 0 and 1, as examples. They can be indexed in the trigonal system, space group R32. The values of the equivalent hexagonal cell parameters (aₕ = 8.961 Å; cₕ = 21.929 Å for x = 0 and aₕ = 8.813 Å; cₕ = 21.748 Å for x = 1) are consistent with the Nasicon-type structure [33, 34]. The very low intensity extra peaks are attributed to NaTi₂(PO₄)₃ and Ca₂P₂O₇. These impurities are probably due to a low weight loss during the synthesis of glasses at high temperature, implying a slight deviation from the theoretical composition. Details of the crystalline structure of Na₃Ca₁₋ₓMnₓTi(PO₄)₃ compositions will be described elsewhere. It consists of a 3D network of PO₄ tetrahedra and AO₆ (A = Ti, Ca/Mn) octahedra sharing corners (Figure 5). Within this covalent framework exist two additional cationic sites, usually labeled M1 and M2, where the sodium ions are located. The M1 site is a trigonal antiprism sharing faces with two AO₆ octahedra. The M2 site is a large cage bounded by 8 oxygens. The decrease of the cell parameters when manganese replaces calcium in the octahedral sites can be explained by the size of Mn²⁺ (0.82 Å), which is smaller than that of Ca²⁺ (1.00 Å).

Figure 4: PXRD patterns of crystalline Na₃Ca₁₋ₓMnₓTi(PO₄)₃ (x = 0, 1) (*: NaTi₂(PO₄)₃ ; : Ca₂P₂O₇; {)

Figure 5: Structure of crystalline Na₃Ca₁₋ₓMnₓTi(PO₄)₃ (x = 0, 1) compounds.
3.5. EPR spectroscopy

Figure 6 presents the EPR spectra of Na$_3$Ca$_{1-x}$Mn$_x$Ti(PO$_4$)$_3$ (0 ≤ x ≤ 1) glasses. All spectra show a strong signal centered at g = 2.0. Spectra of glasses with low manganese concentrations (x = 0.01; 0.05) are characterized by a hyperfine structure (hfs) which consists of six multiplets centered at g = 2.0, with a hyperfine coupling constant A = 90 G. Additional weaker signals are observed at lower magnetic fields, g = 3.3 and g = 4.3, for the low concentrations (x = 0.01, 0.05, 0.25).

EPR of divalent manganese was investigated in a variety of glass system [44 - 46]. The d$^5$ electronic configuration of Mn$^{2+}$ ion has a $^6S_{5/2}$ ground state in the free ion and possesses zero orbital angular momentum. The hyperfine splitting of 2I+1 = 6 lines, arises from the interaction between the spin of the unpaired 3d$^5$ electrons (S = 5/2) with the spin of the $^{55}$Mn nucleus, I($^{55}$Mn, 100%) = 5/2. This isotropic signal at g = 2.0 is due to Mn$^{2+}$ ions in an environment close to octahedral symmetry. The hfs line-width increases with the MnO content, from x = 0.01 to x = 0.05, due to the increase of the dipolar interaction. The hyperfine structure disappears when MnO content increases (x > 0.05). The strongly distorted versions of the octahedral vicinity, subjected to strong crystal field effects, give rise to absorptions at g = 4.3 and 3.3. These absorptions are less intense than the one at g = 2.0 and appear only for low concentrations of manganese (x = 0.01, 0.05 and 0.25). There is a relatively small concentration of Mn$^{2+}$ ions involved in such structural units. The same behavior in the low concentration range was observed for other glass systems [44, 46].

The structure of Na$_3$Ca$_{1-x}$Mn$_x$Ti(PO$_4$)$_3$ (0 ≤ x ≤ 1) glasses shows an evolution from structural units involving Mn$^{2+}$ ions in well-defined vicinities, to structural units containing clustered magnetic ions. The change of the shape of g = 2.0 EPR-spectra when the content of manganese ions increases revealed this evolution. The line intensities at g = 4.3 and 3.3 are small enough and indicate a relative low concentration of isolated Mn$^{2+}$ ions involved in structural units strongly distorted of the octahedral vicinities.
3.6. Raman spectroscopy

Figure 7 shows the Raman spectra of Na$_{2}$Ca$_{1-x}$Mn$_x$Ti(PO$_4$)$_3$ (0 ≤ x ≤ 1) glasses in the frequency region between 100 and 1800 cm$^{-1}$. Table 2 gives Raman wave-numbers and their assignments. Figure 8 represents the Raman spectra of the crystalline compounds NaTi$_2$(PO$_4$)$_3$, LiTiO(PO$_4$) and Cs$_2$MnP$_2$O$_7$, which belong respectively to Nasicon (monophosphate), oxyphosphate, and diphosphate families. The crystalline structure of NaTi$_2$(PO$_4$)$_3$ [33] and LiTiO(PO$_4$) [47–50] is based on a 3D framework built of TiO$_6$ octahedra and PO$_4$ tetrahedra sharing corners; this 3D framework has cavities where Na$^+$ and Li$^+$ ions are located. In both compounds, the PO$_4$ tetrahedra are isolated from each other. The TiO$_6$ octahedra are rather regular and isolated from each other in NaTi$_2$(PO$_4$)$_3$ (Ti-O distances : 1.90–2.00 Å), while in LiTiO(PO$_4$) they are linked to each other by corners to form -Ti-O-Ti-O-Ti-O- infinite chains with alternating short (1.70 Å) and long (2.28 Å) Ti-O bonds; these chains are connected by PO$_4$ tetrahedra. The structure of Cs$_2$MnP$_2$O$_7$ diphosphate contains P$_2$O$_7$ groups [51]. For NaTi$_2$(PO$_4$)$_3$, in which PO$_4$ tetrahedra, as well as TiO$_6$ octahedra, are isolated from each other, no peak is observed in 700–800 cm$^{-1}$ region, in good agreement with previous Raman studies of iso-structural titanium phosphates [36, 37, 52]. In contrast, Raman spectra of titanyl oxyphosphates show a strong peak in this region, at 745 cm$^{-1}$ for NaTiOPo$_4$ [53, 54], 783 cm$^{-1}$ for LiTiOPo$_4$ [50], and ≈ 750 cm$^{-1}$ for M$_{0.5}$TiOPO$_4$ (M=Mg, Co, Ni) [36, 55, 56]. This strong peak is associated with Ti-O bond. It can be attributed to synchronous vibrations of all Ti-O bonds of the -Ti-O-Ti-O-Ti- chains as previously reported by Bamberger et al. [53, 54]. The Raman spectrum of Cs$_2$MnP$_2$O$_7$ shows a strong and sharp peak at 1020 cm$^{-1}$ and a strong one at 700 cm$^{-1}$, attributed respectively to asymmetric and symmetric stretching vibrations of P-O bonds in P-O-P bridge ($v_1$ and $v_3$ modes) [51].

![Raman spectra of Na$_{2}$Ca$_{1-x}$Mn$_x$Ti(PO$_4$)$_3$ (0 ≤ x ≤ 1) glasses.](image)

The peaks observed for Na$_2$Ca$_{1-x}$Mn$_x$Ti(PO$_4$)$_3$ (0 ≤ x ≤ 1) glasses, in the high frequency region 830 – 1250 cm$^{-1}$ are due to monophosphate (PO$_4$) and diphosphate (P$_2$O$_7$) groups. The peak at ~1033 cm$^{-1}$, relatively sharp, is due to P$_2$O$_7^{4-}$ diphosphate ions [51]. The strong peak at ~750 cm$^{-1}$ is assigned to Ti-O vibrations in the -Ti-O-Ti-O- chains [50, 52 - 56], which indicates that the glass structure contains TiO$_6$ octahedra linked by corners and form short -Ti-O-Ti-O- chains. These chains are certainly linked to phosphate groups to form -Ti-O-P- linkages. The peaks observed between 400 and 640 cm$^{-1}$ are attributed to O-P-O and P-O-P deformations ($\delta_2$ and $\delta_3$ PO$_4$ modes) and Ti-O vibrations of TiO$_6$ octahedra. The peaks observed below 300 cm$^{-1}$ are attributed to lattice vibrations. As can be observed from Figure 7 and Table 2, no significant change is observed in the spectra, when manganese replaces calcium, indicating that Mn$^{2+}$ ions don't modify significantly the glass structure and occupy the interstitial sites of the framework, in good agreement with glass transition temperature and molar volume variations. We can then conclude that Mn$^{2+}$ and Ca$^{2+}$ ions act as network modifiers in the glasses, unlike in the crystalline phases where they are part of the framework.
Table 2. Raman wave numbers (cm$^{-1}$) peak assignments of Na$_3$Ca$_{1-x}$Mn$_x$Ti(PO$_4$)$_3$ (0 ≤ x ≤ 1) glasses (w: weak, vw: very weak, m: medium, s: strong, vs: very strong).

<table>
<thead>
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<th>x = 0</th>
<th>x = 0.25</th>
<th>x = 0.5</th>
<th>x = 0.75</th>
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<td>1034</td>
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<tr>
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<td>740 s</td>
<td>741</td>
<td>743</td>
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<td>590 vw</td>
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4. Conclusion
Na$_3$Ca$_{1-x}$Mn$_x$Ti(PO$_4$)$_3$ (0 ≤ x ≤ 1) phosphates can be prepared in both crystalline and glassy forms. The crystalline materials belong to the Nasicon family. Their structure consists of a 3D network of PO$_4$ tetrahedra and AO$_6$ [A = Ti, Ca/Mn] octahedra sharing corners; Na$^+$ ions occupy interstitial sites. EPR study of glasses shows that Mn$^{2+}$ ions occupy octahedral sites, with predominantly ionic character of the bonding between Mn$^{2+}$ and O$^2$ ions. Raman spectroscopy study shows that the glasses contain PO$_4$ and P$_2$O$_7$ groups, and short -Ti-O-Ti-O-Ti- chains. The presence of these chains indicates that the TiO$_6$ octahedra are linked to each other through corners, unlike in the corresponding Nasicon crystalline phases where they are isolated and connected to each other via PO$_4$ tetrahedra. All results obtained for the glassy materials indicate that MnO and CaO oxides act as glass modifiers.

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