

Structural and vibrational study of titanium Monophosphates $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ (M = Mn, Ni)

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Abstract: This work is a systematic study of titanium phosphates compounds $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ (M = Mn, Ni), which are characterized by X-ray diffraction (XRD), IR spectrometry, Raman and scanning electron microscopy. Indeed, the crystalline structures of the two compounds were determined in the orthorhombic system, with space group Pmmm (Z = 4); the determined unit cell parameters are: a = 14.59 Å, b = 13.31 Å, c = 2.6 Å for $\text{Na}_{0.5}\text{Mn}_{0.25}\text{Ti}_2(\text{PO}_4)_3$, and a = 14.60 Å, b = 13.31 Å, c = 2.67 Å for $\text{Na}_{0.5}\text{Ni}_{0.25}\text{Ti}_2(\text{PO}_4)_3$.

The structures, compared to that of $\text{Li}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$, are constructed from $[\text{TiO}_6]$ octahedra and $[\text{PO}_4]$ tetrahedra connected by sharing angles along the c axis. The cations M = Mn^{2+} , Ni^{2+} , are located in half of the antiprismatic infection sites and are ordered.

Keywords: Titanium; Phosphates; XRD; IR; Raman; MEB.

1. Introduction

Habit is taken now, by researchers or engineers, materials are classified into two categories according to their function:

The materials are known as "structure", used mainly for mechanical and/or thermomechanical (construction of buildings, land vehicles, aerospace, space, etc.)

The materials called physical properties other than mechanical characterizing Electric (metals, functional "for which they are conductors, superconductors, semiconductors), dielectrics (capacitors, ferroelectric memories, multiferroic / dielectric magneto couplings), magnetic (permanent magnets, memories, etc), optical (luminescence, electroluminescence, nonlinear properties of the waveguide, colored pigments, lasers etc.), biological (biomaterials, contrast agents in medical imaging / NMR vectors combining magnetic transporting drugs and hyperthermia, etc.), thermoelectric and photovoltaic (energy conversion), electrochemical for production (fuel cells) and energy storage (batteries), etc.

Ferroelectric materials are of growing interest because of their applications, some of which have reached the industrial stage a long time ago: capacitors with high permittivity, electromechanical transducers, infrared sensors, electro-optical modulators. The areas of most recent use are those

processing and optical storage of information. Some examples of applications of these materials are:

The production of capacitors with high dielectric constant, so miniaturizable.

The manufacture of thermistors using strong variations in capacitance as a function of temperature.

Replacement of quartz in ultrasonic generators (direct piezoelectric effect).

The inverse piezoelectric effect is also used for converting a mechanical effect into an electrical effect.

The use of remnant polarization in option for storing information in computer memories;

The use in nonlinear optics Travel frequency doublers are ferroelectric compounds;

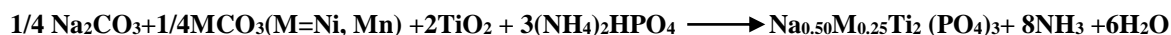
The holographic memories using the variations in the refractive index resulting from load-displacement.

The use of pyroelectric detector retinas in "pyricons" (taking heat for TV tube).

Inorganic phosphates are one of the most interesting types of new inorganic materials, mainly because of the ability of the PO_4^{3-} tetrahedral group to bind to other structural units¹⁻¹⁰.

In this work, we are interested in the structural and vibrational study of series of titanium monophosphate $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ (M = Mn, Ni) by X-ray diffraction (XRD), IR absorption spectrometers and Raman scattering and scanning

electron microscopy. It is to note that Titanium monophosphate has not been studied.



In the preparation, the titanium oxide "TiO₂", carbonates "M^{II}CO₃", and ammonium hydrogen phosphate "(NH₄)₂HPO₄" were used as precursors. These reagents are milled for one hour in a porcelain mortar in order to achieve good homogenization and the finest particle size possible.

The mixture is placed in a crucible and undergoes several heat treatments, at increasing temperatures, between each grinding operation, to ensure their homogeneity and promote solid state diffusion.

They are finally brought to a temperature of 1050°C for 5 hours. The Na_{0.5}M_{0.25}Ti₂(PO₄)₃ (M = Mn, Ni) powders are yellow and red.

X-ray diffraction. Powder diffraction patterns for the two title compounds were collected with a SIEMENS D 5000 diffractometer using Cu K_α radiation (λ = 1.5406 Å). The experimental 2θ range was from 5 to 70° (2θ) with a step size of 0.017° and a counting time of 160.9603s per step.

The microstructure and the morphology of the samples were characterized using scanning electron microscopy (SEM, Hitachi S-3500N). The samples were sputtered with a thin layer of carbon before SEM analysis at magnifications from 5x and imaging was conducted at a voltage of 20 kV.

2. Experimental

The compounds Na_{0.5}M_{0.25}Ti₂(PO₄)₃ (M = Mn, Ni) are synthesized by a solid reaction method.

The Raman spectrum was recorded under the Raman dispersive microscope DXR2 (Thermo scientific). Excitation was accomplished with the Laser 633 nm line of an argon-ion laser. Incident power was approximately 3 mW at the source, and 10% of that at the sample. The infrared spectra were recorded using a Bruker tensor-27 FTJR Spectrometer. The infrared spectrum was recorded at room temperature on pellets containing the milled product dispersed in a KBr matrix (about 1% by mass of compound).

3. Result and Discussion

3.1. Crystal structure description

The X-ray diffractograms of the two studied compounds at room temperature are shown in Figure 1, which show that the compounds crystallised in a pure phase without detectable impurity. These profiles are similar to those of sodium and titanium of the same Nasicon structure Na_{0.5}M_{0.25}Ti₂(PO₄)₃ (M = Mn, Ni) reported previously¹¹⁻¹⁴.

The unit-cell parameters were calculated using the following programs: Dicol06, Mc-Mesh, Ito, and Treor¹⁵. The data obtained from the analysis of powder X-ray diffractograms of the two compounds are shown in Tables 1 and 2.

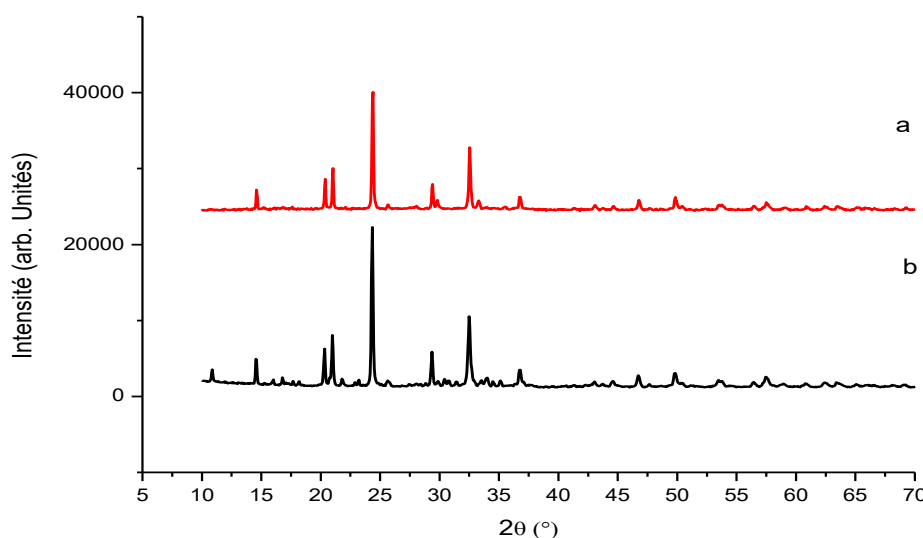


Figure 1. XRD diagrams of sintered powders: a) Na_{0.5}Mn_{0.25}Ti₂(PO₄)₃, b) Na_{0.5}Ni_{0.25}Ti₂(PO₄)₃

Table 1. X-Ray Diffractogram Stripping of $\text{Na}_{0.5}\text{Mn}_{0.25}\text{Ti}_2(\text{PO}_4)_3$.

h k l	dobs (Å)	dcal (Å)	dobs-dcal (Å)	2θobs	2θcal	2θobs-2θcal
120	6.04683	6.05041	-0.00358	14.637	14.629	0.009
130	4.24619	4.24310	0.00309	20.904	20.919	-0.015
400	3.64784	3.64946	-0.00162	24.381	24.370	0.011
240	3.02618	3.02735	-0.00117	29.493	29.482	0.012
340	2.74833	2.74668	0.00165	32.554	32.574	-0.020
121	2.44227	2.44312	-0.00084	36.770	36.757	0.013
431	1.93987	1.93875	0.00113	46.792	46.821	-0.029
251	1.82515	1.82555	-0.00040	49.928	49.916	0.012
800	1.82553	-0.00038	49.917	0.011	-	-
061	1.70615	1.70656	-0.00041	53.678	53.664	0.014
840	1.60048	1.60063	-0.00015	57.540	57.534	0.006

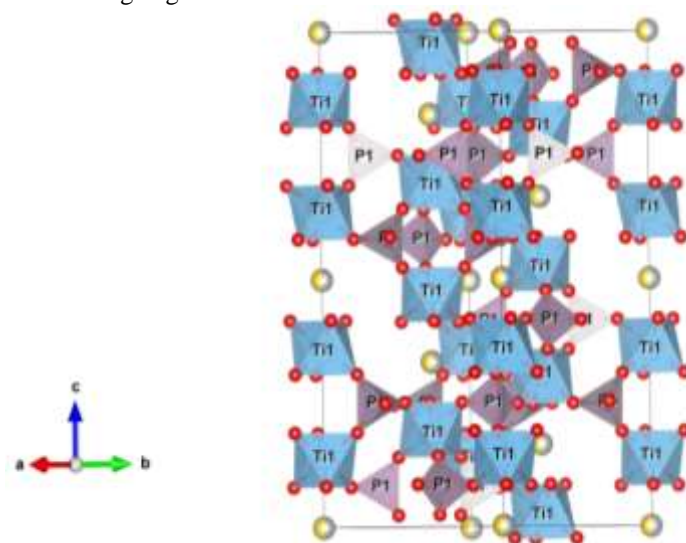
Table 2. X-Ray Diffractogram Stripping of $\text{Na}_{0.5}\text{Ni}_{0.25}\text{Ti}_2(\text{PO}_4)_3$.

h k l	dobs (Å)	dcal (Å)	dobs-dcal (Å)	2θobs	2θcal	2θobs-2θcal
1 2 0	6.08151	6.07897	0.00255	14.554	14.560	-0.006
1 3 0	4.25492	4.25717	-0.00225	20.860	20.849	0.011
4 0 0	3.65294	3.65631	-0.00337	24.347	24.324	0.023
2 4 0	3.03726	3.03404	0.00322	29.383	29.415	-0.032
3 4 0	2.75183	2.75168	0.00015	32.511	32.513	-0.002
5 3 0	2.44135	2.44220	-0.00085	36.785	36.771	0.013
4 3 1	1.94211	1.94149	0.00062	46.735	46.751	-0.016
8 0 0	1.82666	1.82612	0.00054	49.884	49.899	-0.016
0 6 1	1.70851	1.70902	-0.00051	53.598	53.581	0.017
8 4 0	1.60103	1.60120	-0.00017	57.518	57.512	0.007

The bibliographical study shows that the two compounds have a Nasicon structure ¹⁴.

The crystallographic formula can be described as that of $[\text{Na}_{0.50}] \text{M}^{\text{I}} [\text{M}_{0.25}] \text{M}^{\text{II}} [\text{Ti}_2] \text{A} (\text{PO}_4)_3$ ($\text{M} = \text{Mn}, \text{Ni}$). The structure consists of a three-dimensional framework of $[\text{PO}_4]$ tetrahedra and $[\text{TiO}_6]$ octahedra sharing angles.

Figure 2 represents the crystal structure of the $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ projected on the (0, 1, 0) plane. It is stated that Titanium ion occupies the octahedral site of isolated TiO_6 , which binds to PO_4 groups by sharing vertices. The sequence of PO_4 tetrahedra and TiO_6 polyhedra delimit the tunnels where the M ($\text{M} = \text{Mn}, \text{Ni}$) cations are located.

**Figure 2.** Three-dimensional arrangement of $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ ($\text{M} = \text{Mn}, \text{Ni}$) on (100) plane

➤ **The TiO₆ coordination polyhedron:**

Titanium atom Ti (1) is surrounded by six oxygen atoms (Figure 3) and occupies the center of a six coordinate octahedron. Note that each octahedron [TiO₆] is bound by the 4 octahedra via the [PO₄]

tetrahedra and that the Ti-O distances are of the order of 1.5225 Å.

These distances already known in the literature are typical of monophosphate and close to the distances found in Mn_{0.50}Ti₂(PO₄)₃ (<P - O> = 1,562 (6) Å)¹⁴⁻¹⁶.

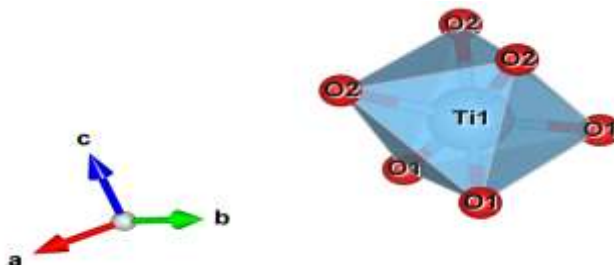


Figure 3. TiO₆ polyhedra chains in the structure of Na_{0.5}M_{0.25}Ti₂(PO₄)₃ on the (0, 1, 0) plane.

➤ **The PO₄ coordination polyhedron**

It is present in the form of a tetrahedron represented in Figure 4 where the phosphorus atom is surrounded by 4 oxygen atoms. Three oxygens of this group are

in common with two TiO₆ groups. The phosphorus - oxygen distances are between 1.522 Å and 1.585 Å. These distances are in good agreement with the literature¹⁶.

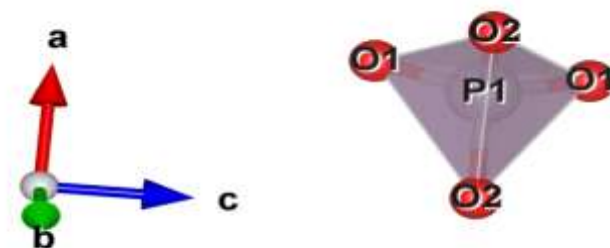


Figure 4. PO₄ polyhedra chains in the structure of Na_{0.5}M_{0.25}Ti₂(PO₄)₃ (M = Mn, Ni).

3.2. Infrared Absorption Spectrum of Na_{0.5}M_{0.25}Ti₂(PO₄)₃ (M = Mn, Ni)

The infrared absorption spectrum allowed to characterize the compound and to verify the nature of the inserted species. The characteristic absorptions of the compound are shown in Figure 5. Based on crystal structure data, the factor group analysis for PO₄ anions internal vibration modes in this crystal are carried out (Table 3).

PO₄³⁻ vibrational modes analysis

As the Raman and IR spectra of Na_{0.5}M_{0.25}Ti₂(PO₄)₃ phosphates are mostly dominated by internal vibrations of the PO₄³⁻ groups and, in order to facilitate assignments of different vibrations modes, we have performed a factor group analysis of PO₄³⁻ internal vibrations, correlating the point group of the 'free' ion (T_d) with its site-group (C_s) and its factor group (D_{2h}) (Table 3).

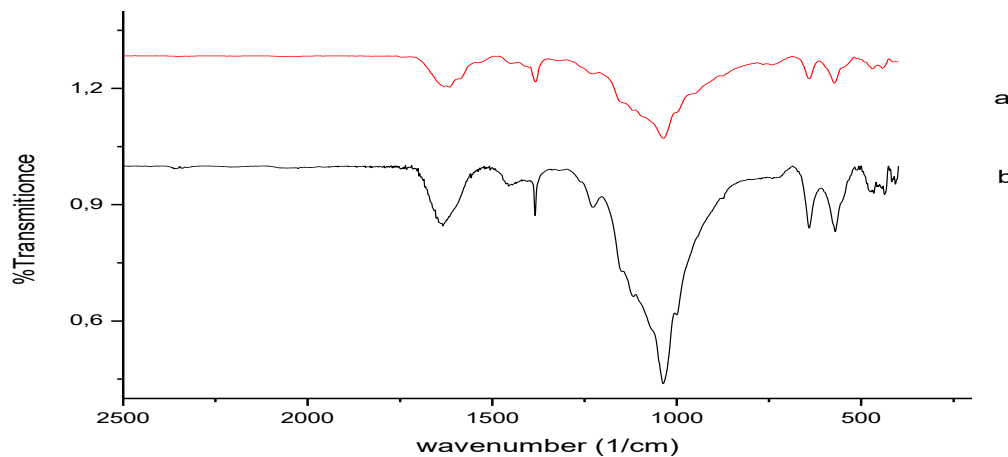


Figure 5. Infrared spectra of: a) Na_{0.5}Mn_{0.25}Ti₂(PO₄)₃, b) Na_{0.5}Ni_{0.25}Ti₂(PO₄)₃

Table 3. Internal vibrational modes correlation of PO₄ (T_d→C_s→D_{2h}).

	Molecular group: T _d	Site group C _s	Factor group D _{2h}
1 ν ₁	1 A ₁ (Ra)	6A'(Raman) 3A''(IR)	A _g (Ra)
1 ν ₂	1E (Ra)		B _{1g} (Ra)
1 ν ₃ , 1 ν ₄	2F ₂ (Ra, IR)		B _{2g} (Ra)
			B _{3g} (Ra)
			A _u (IR)
			B _{1u} (IR)
			B _{2u} (IR)
			B _{3u} (IR)

Due to the site effect, the lowering of the symmetry of the anion during the transition from the T_d molecular group to the C_s site group leads to an increase in the degeneracy of the A₁, E and F₂ modes. That only the modes "gerade" [ν₁ (A₁)]

would be active at Raman by becoming of symmetry A_g, B_{1g}, B_{2u}, B_{3u}, in the group factor D_{2h}. With regard to the "unmonitored" modes of symmetry F₂ and E are inactive modes in Raman but which are active in IR, with symmetry A''.

Table 4. IR data for Na_{0.5}M_{0.25}Ti₂(PO₄)₃ (M = Mn, Ni), band positions and assignments are in cm⁻¹.

band Positions	Attributions
500	δ _s OPO ⁻ (ν ₂ : symmetric deformation)
669	δ _{as} OPO ⁻ (ν ₄ : asymmetric deformation)
1316	ν _s PO (ν ₁ : symmetric stretching)
1410	ν _{as} PO (ν ₃ : asymmetric stretching)

The assignment of characteristic bands observed in the compound's spectra (Table 4) is made based on factor group analysis, and previous results made on homologous compounds.

Infrared spectroscopy analysis reveals several bands, in particular, those attributable to PO₄³⁻ ions. The results are shown in Table 4.

This spectrum has four distinct frequency domains:

✚ Domain I: between 1460 and 980 cm⁻¹ due to the antisymmetric and symmetrical vibration of the PO₄³⁻ ion.

✚ Domain II: between 660 and 500 cm⁻¹ corresponds to the antisymmetric vibrations of deformation of the PO₄³⁻ ion.

✚ Domain III: between 450 and 400 cm⁻¹ due to the symmetrical vibration of the PO₄³⁻ ion.

✚ In the FTIR spectrum, we have automatically subtracted the CO₂ bands from atmosphere absorption, although weak artefacts originated by

CO₂ are still present in the corrected data around 2300 cm⁻¹¹⁸.

Based on the frequencies of the internal modes of the PO₄³⁻¹⁹ ion, in the first frequency domain, we assign the frequency lines 1131, 1074, 1020 and 1001 cm⁻¹ to the antisymmetric vibrations of the ion PO₄³⁻. The 982 cm⁻¹ frequency line is due to the symmetric valence vibrations relative to the PO₄³⁻ ion. The frequency bands 650, 621 and 550 cm⁻¹ correspond to the vibrations of anti-symmetric deformation of the PO₄³⁻ ion. Similarly, the frequency lines 439, 401 and 349 cm⁻¹ are due to symmetrical deformation vibrations of the two PO₄³⁻ ions. The lines of frequency lower than 401 cm⁻¹ are due to the external vibrations of PO₄³⁻ ions, TiO groups²⁰.

3.3. Raman scattering spectrum of Na_{0.5}M_{0.25}Ti₂(PO₄)₃ (M = Mn, Ni).

The Raman scattering spectrum of Na_{0.5}M_{0.25}Ti₂(PO₄)₃ is shown in Figure 6.

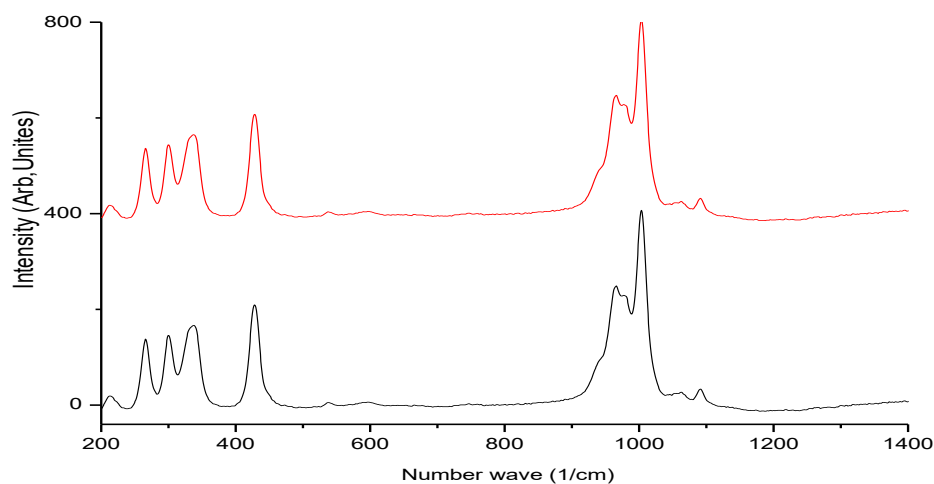


Figure 6. Raman scattering spectra of: a) $\text{Na}_{0.5}\text{Mn}_{0.25}\text{Ti}_2(\text{PO}_4)_3$, b) $\text{Na}_{0.5}\text{Ni}_{0.25}\text{Ti}_2(\text{PO}_4)_3$

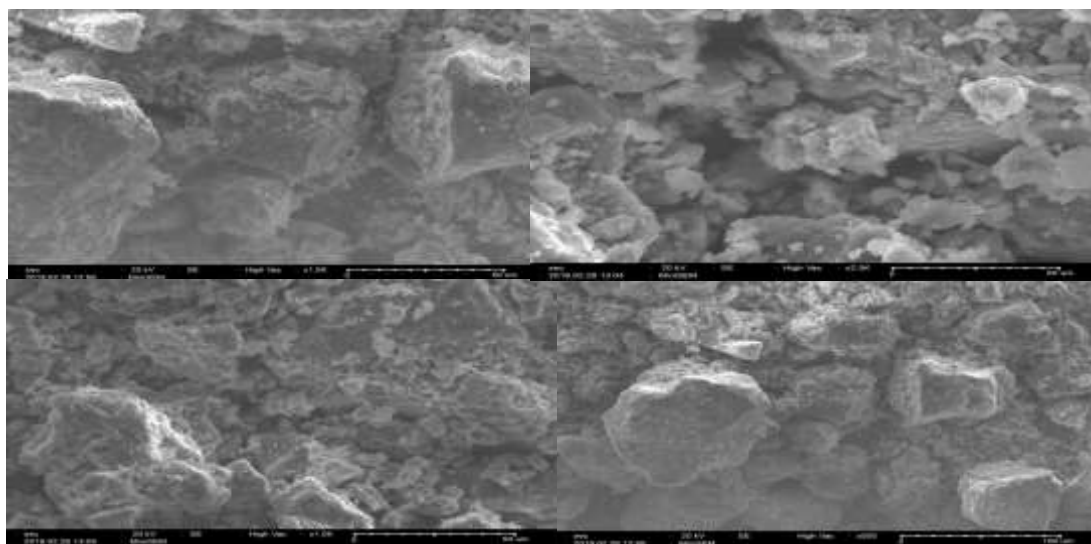
Based on the frequencies of the internal modes of the PO_4^{3-} ion, in the first frequency domain, we assign the frequency bands 1131, 1074, 1020 and 1001 cm^{-1} to the antisymmetric vibrations of the PO_4^{3-} ion. The 982 cm^{-1} frequency line is due to the symmetric valence vibrations relative to the PO_4^{3-} ion. The frequency bands 650, 621 and 550 cm^{-1} correspond to the vibrations of anti-symmetric deformation of the PO_4^{3-} ion. Similarly, the frequency lines 439, 401 and 349 cm^{-1} are due to symmetrical deformation vibrations of the two PO_4^{3-}

ions. Frequency lines less than 401 cm^{-1} are due to external vibrations of PO_4^{3-} ions, TiO groups¹⁷.

3.4 Surface analysis by SEM

The scanning electron microscopy (SEM) analysis of the samples of the solid solution made it possible to determine the state of its surface. The observation is made on the sample surface compacted and sintered at 600°C for 4h (Figure 7).

Figure 7. Surface view photograph by Scanning Electron Microscopy (SEM) of the solid solution of



$\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ (M = Mn, Ni)

Figure 7 shows that the image was taken by the scanning microscope (SEM) of the compounds of $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$, which are in the form of platelets with well-defined faces is homogeneous.

Conclusion

In this work, we have been interested in synthesizing a pure phase of titanium phosphate based on sodium

" $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ " by the solid synthesis method. The X-ray diffraction spectra of the $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ compound, obtained at temperatures above 900°C , show main lines assignable to pure phases.

The titanium Monophosphates $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ (M = Mn, Ni) was obtained as a powder. It crystallizes in the orthorhombic system, space group Pmmm, Z=4, and is an isotype of $\text{Li}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$.

Infrared absorption and Raman scattering spectra, as well as scanning electron microscopy surface analysis of this phosphate, have been established and interpreted. They provided additional Physico-chemical information for X-ray diffraction studies. The scanning electron microscope (MEB) of $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ ($\text{M} = \text{Mn}, \text{Ni}$) determines the homogeneity of the structure.

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