

# Tl<sub>1-x</sub>Na<sub>x</sub>Nb<sub>2</sub>PO<sub>8</sub> and Related Compounds, Isostructural with Ca<sub>0.5+x</sub>Cs<sub>2</sub>Nb<sub>6</sub>P<sub>3</sub>O<sub>24</sub>

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Received July 25, 2001; in revised form November 30, 2001; accepted November 30, 2001

Compounds  $A_{2/3}A'_{1/3}M_2XO_8$  ( $A = \text{Tl, Rb, Cs}$ ;  $A' = \text{Na, Ag}$ ;  $M = \text{Nb, Ta}$ ;  $X = \text{P, As}$ ) have been synthesized using the ceramic method. The sodium and potassium compounds ( $A = \text{Na}$  and  $\text{K}$ ) have been prepared by an ion exchange reaction starting from their thallium analogues. These materials are isotypic with  $\text{Tl}_{1-x}\text{Na}_x\text{Nb}_2\text{PO}_8$  ( $x = 0.21$ ) the structure of which has been determined by using X-ray single-crystal data. The space group is  $R32$ , the cell constants are  $a_H = 13.369(2)$ ,  $c_H = 10.324(3)$  Å and  $z = 9$ . This compound is isostructural with  $\text{Ca}_{0.5+x}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$ . Its three-dimensional framework  $[\text{Nb}_2\text{PO}_8]_n$ , built up from  $\text{NbO}_6$  octahedra and corner-sharing  $\text{PO}_4$  tetrahedra, delimits tunnels running along  $c_H$  and cavities accommodating  $\text{TI}^+$  and  $\text{Na}^+$  cations, respectively. The  $\text{K}_{2/3}\text{Na}_{1/3}\text{Nb}_2\text{PO}_8$  structure, refined using X-ray powder data, showed that  $\text{K}^+$  cations are spread like the  $\text{TI}^+$  ones over many sites, but more excentred from the tunnel axis. The isotypy of these compounds is also revealed by the similarity of the infrared and Raman spectra. The nonlinear optical study showed a behavior similar to that of the KDP for all the compounds. The ionic conductivity measurements gave high activation energies and low conductivity values for these materials. © 2002 Elsevier Science (USA)

**Key Words:** structure; thallium; niobium; tantalum; phosphate; arsenate; Rietveld; infrared; Raman; nonlinear optics; ionic conductivity.

## INTRODUCTION

Inorganic materials built up of  $\text{MO}_6$  octahedra and  $\text{XO}_4$  tetrahedra offer a wide field of investigation because of the interesting physical properties they may present, and their potential use in several applications such as ionic conductivity (1, 2), ion exchange reactions (3, 4), catalysis, or optics (5). The investigation of several systems, the characterization,

and the structure determination of the isolated compounds arise as the first step to propose new materials likely to exhibit at least one of the above properties.

In this context, one can mention the works conducted on the systems  $A-M-P-O$  ( $A = \text{alkali metal}$  and  $M = \text{Nb, Mo}$ ) which have shown the existence of compounds with mixed-valent metal cations (6) exhibiting interesting magnetic and electrical properties (7).

During our investigation of the  $\text{Tl}_2\text{O-Nb}_2\text{O}_5\text{-P}_2\text{O}_5$  system, two compounds (8, 9) have been isolated. The compound of the present work contains in addition a small amount of sodium accidentally delivered by the combustion boat wherein the synthesis was performed.

This paper reports on the crystal structure of  $\text{Tl}_{1-x}\text{Na}_x\text{Nb}_2\text{PO}_8$ , and on the compounds of the family with formula  $A_{2/3}A'_{1/3}M_2XO_8$  ( $A = \text{Na, K, Tl, Rb, Cs}$ ;  $A' = \text{Na, Ag}$ ;  $M = \text{Nb, Ta}$ ; and  $X = \text{P, As}$ ), isotypic with  $\text{Ca}_{0.5+x}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$  (10). The anionic framework delimiting tunnels communicating with cavities, and the acentric space group in which these compounds crystallize, make ionic conductivity and nonlinear optics (NLO) properties worthy to be investigated.

## EXPERIMENTAL

### Preparations

In an alumina combustion boat, a solid state reaction starting from  $\text{Tl}_2\text{CO}_3$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$  in the molar ratio of 3/3/4 was carried out in two steps: first at 300°C for 4 hours to let the ingredients decompose, and then at 700°C for 1 day. The resulting product contains a minor phase existing in needle-shaped colorless crystals. Preliminary energy dispersive X-ray spectroscopy analysis showed the existence of Tl, Nb, and P in a molar ratio of about 1/2/1, with in addition a small amount of sodium.

Powdered samples of  $A_{2/3}A'_{1/3}M_2XO_8$  ( $A = \text{Tl, Rb, Cs}$ ;  $A' = \text{Na, Ag}$ ;  $M = \text{Nb, Ta}$ ;  $X = \text{P, As}$ ) were prepared

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starting from (Rb<sub>2</sub>CO<sub>3</sub>/Tl<sub>2</sub>CO<sub>3</sub>/Cs<sub>2</sub>CO<sub>3</sub>), (NaNO<sub>3</sub>/AgNO<sub>3</sub>), (Nb<sub>2</sub>O<sub>5</sub>/Ta<sub>2</sub>O<sub>5</sub>), and (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>/NH<sub>4</sub>H<sub>2</sub>AsO<sub>4</sub>) mixed in the proper molar ratio. Thoroughly ground, these mixtures were slowly heated in alumina combustion boats and re-ground every 100°C. The upper temperature (700°C) was kept for 1 day. A mole excess of 10% of A<sub>2</sub>CO<sub>3</sub> (A = Tl, Rb, Cs) and NH<sub>4</sub>H<sub>2</sub>XO<sub>4</sub> (X = P, As) was added before the ultimate thermal treatment to make the residual metal oxide react.

It is noteworthy that:

— tantalum could not be combined with arsenic, rubidium, or cesium to accommodate the same structural type as the title compound,

— Tl<sub>2/3</sub>Na<sub>1/3</sub>Nb<sub>2</sub>AsO<sub>8</sub> was accompanied by an important nonidentified impurity,

— the thallium compounds present a continuous Nb–Ta solid solution,

— we did not try to prepare all the silver series of compounds.

The preparation of K<sub>2/3</sub>Na<sub>1/3</sub>M<sub>2</sub>PO<sub>8</sub> and NaM<sub>2</sub>PO<sub>8</sub> (M = Nb, Ta) was carried out starting from the homologous thallium compounds by a cationic exchange reaction: the Tl<sub>2/3</sub>Na<sub>1/3</sub>M<sub>2</sub>PO<sub>8</sub> (M = Nb, Ta) materials were mixed with a large excess of the desired alkali chloride. They were then placed in a combustion boat inside a silica tube connected to a vacuum pump, and heated for 1 day at 460°C. The energy dispersive X-ray spectroscopy analysis and the weight loss calculations are in agreement with a quantitative exchange reaction after two/four recyclings for the niobium- and the tantalum-potassium compounds, respectively. The sodium compounds NaM<sub>2</sub>PO<sub>8</sub> require a higher number of recyclings, and a higher reaction temperature (550°C) is needed for the compound with M = Nb.

*Tl<sub>1-x</sub>Na<sub>x</sub>Nb<sub>2</sub>PO<sub>8</sub> Refinement*

The MolEN software package (11) and SHELX program (12) were used for data reduction, intensity analysis, and refinements, respectively.

First, the atom positions of the Ca<sub>0.5+x</sub>Cs<sub>2</sub>Nb<sub>6</sub>P<sub>3</sub>O<sub>24</sub> compound (R32 space group) were taken as a starting set, and the refinements led to a highly agitated thallium atom, and to a Fourier map with several peaks close to that of the starting thallium atom (note that the choice of the noncentrosymmetric R32 space group is also supported by the NLO results reported below). The Fourier peaks were then considered as thallium positions and the refinements were carried out on their multipliers and on that of the sodium atom. The refinement results were in concordance with an electroneutral formula, while the R and wR<sub>2</sub> agreement factors decreased significantly to the values 0.0489 and 0.1005, respectively, when the sodium, niobium, and phosphorus anisotropic thermal factors were refined. The highest peak observed in the Fourier map (1 e/Å<sup>3</sup>) was refined as

**TABLE 1**  
**Crystallographic and Experimental Data of the Compound**  
**Tl<sub>1-x</sub>Na<sub>x</sub>Nb<sub>2</sub>PO<sub>8</sub> (x = 0.21)**

Equipment	Four-circle CAD4 diffractometer
Radiation	λ(MoKα) = 0.70073 Å
Space group	R 3 2
a <sub>H</sub> (Å)	13.345(2)
c <sub>H</sub> (Å)	10.324(3)
z	9
Number of reflections for unit cell measurements	25
2θ range for unit cell measurements	12.56 < θ < 13.42
Crystal dimensions (mm <sup>3</sup> )	0.09 × 0.04 × 0.04
Measured reflections	1317
Unique reflections	644
Number of parameters	51
Scan mode	ω – 2θ
Scan width	0.65 + 0.79 tg θ
Recording angular range	1.5 < θ < 25
Absorption coefficient μ (mm <sup>-1</sup> )	20.795
Absorption correction type	Empirical ψ-scan
R <sub>1</sub> /wR <sub>2</sub>	0.0489/0.1005
Extinction parameter	1.17 × 10 <sup>-4</sup>

a thallium position without any significant improvement. Tables 1 and 2 summarize the data collection conditions, the refinement results, and the atomic coordinates, respectively.

It is noteworthy that the refinements considering a fully occupied sodium site led to an abnormally high thermal factor for that atom and an increase of the reliability factors. For an electroneutral formula, the sum of the occupancy factors of the thallium atoms exceeds the value of 0.33 encountered for Cs<sup>+</sup> in Ca<sub>0.5+x</sub>Cs<sub>2</sub>Nb<sub>6</sub>P<sub>3</sub>O<sub>24</sub>. Consequently, there is a narrow domain where, starting from the nominal formula with x = 0.33 (compound of the cited

**TABLE 2**  
**Tl<sub>1-x</sub>Na<sub>x</sub>Nb<sub>2</sub>PO<sub>8</sub> (x = 0.21) Atomic Coordinates and Thermal Parameters**

Atom	Site	x	y	z	Multiplier	U/U <sub>eq</sub>
Tl(1)	18f	0.6969(7)	0.999(2)	0.911(2)	0.187(7)	0.086(4)
Tl(2)	9e	0.6194(5)	0	½	0.27(2)	0.044(2)
Tl(3)	9d	0.700(2)	0	0	0.048(7)	0.04(2)
Tl(4)	18f	0.690(2)	0.963(2)	0.869(3)	0.05(2)	0.01(1)
Na	3a	0	0	0	0.64(2)	0.013(5)*
Nb	18f	0.5222(1)	0.1619 (1)	0.0143(2)	1.0	0.0063(4)*
P	9d	0.2287(4)	0	0	1.0	0.006(1)*
O(1)	18f	0.1491(9)	0.9765(9)	0.1180(8)	1.0	0.010(2)
O(2)	9e	0.153(2)	0	½	1.0	0.020(4)
O(3)	18f	0.3450(7)	0.1070(8)	0.0267(9)	1.0	0.008(2)
O(4)	9d	0.475(1)	0	0	1.0	0.009(3)
O(5)	18f	0.6795(8)	0.2181(8)	0.0313(9)	1.0	0.011(2)

Note. For starred atoms, U<sub>eq</sub> = 1/3 ∑<sub>i</sub> ∑<sub>j</sub> U<sub>i</sub> U<sub>j</sub> a<sub>i</sub><sup>\*</sup> · a<sub>j</sub><sup>\*</sup> · a<sub>i</sub><sup>\*</sup> · a<sub>j</sub><sup>\*</sup>.

above family), Na can be substituted by Tl, each on its site, until a limit composition that was not determined in this work. Nevertheless, X-ray characterization showed the powdered compound with  $x = 0$  not to exhibit the same structural type.

### $K_{2/3}Na_{1/3}Nb_2PO_8$ Refinements

Data collection has been conducted on an INEL diffractometer ( $CuK\alpha_1$ ,  $\lambda = 1.54059 \text{ \AA}$ ). The investigated domain was  $15 < 2\theta < 114.7^\circ$ , from which some regions were excluded ( $28.20^\circ$ – $28.50^\circ$ ,  $96.60^\circ$ – $97.40^\circ$ , and  $105.10^\circ$ – $106.00^\circ$ ) due to the instrumental limitation.

The refinements were carried out by the Rietveld method (13) using the GSAS program (14, 15). Some peaks were not indexed until a second phase ( $Nb_2O_5$ ) (16), present at a percentage of about 5%, was considered in the refinements.

The hypothesis of a  $K^+$  cation in the same site as  $Cs^+$  in  $Ca_{0.5+x}Cs_2Nb_6P_3O_{24}$  (10) led to very high  $K^+$  anisotropic thermal factors that do not define an ellipsoid. The thallium compound atomic positions were then taken as a starting set. A soft constraint concerning the P–O distances to be near to the average value of  $1.53 \text{ \AA}$  was also applied.

The last refinements, considering 282 reflections, converged to the agreement factors  $R_p = 0.0320$ ,  $wR_p = 0.0448$ , and  $R(F^2) = 0.0536$ . At this stage, a difference Fourier map was featureless with minima and maxima which did not exceed  $1 e/\text{\AA}^3$ . Figure 1 presents experimental and calculated X-ray powder patterns. The atomic positions (Table 3) are very close to that obtained for the thallium homologue compound.

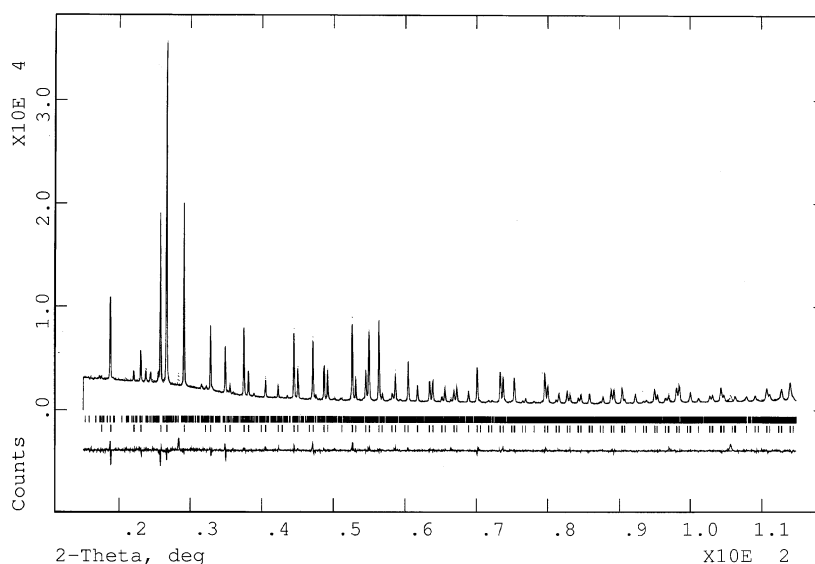


FIG. 1. Profile after Rietveld refinement for  $K_{2/3}Na_{1/3}Nb_2PO_8$ : experimental (---), calculated (—), and difference on the same scale.

TABLE 3  
 $K_{2/3}Na_{1/3}Nb_2PO_8$  Atomic Coordinates and Thermal Parameters

Atom	Site	x	y	z	Multiplier	$B/B_{eq}$
K(1)	18f	0.706(3)	0.990(4)	0.909(3)	0.184(3)	4.6(6)
K(2)	9e	0.67(2)	0	$\frac{1}{2}$	0.072(7)	9.5(7)
K(3)	9d	0.76(1)	0	0	0.069(7)	9.4(7)
K(4)	18f	0.645(5)	0.958(4)	0.864(4)	0.078(3)	0.6(7)
Na	3a	0	0	0	1.0	1.7(5)
Nb	18f	0.5215(2)	0.1621(2)	0.0146(2)	1.0	1.28*
P	9d	0.2276 (5)	0	0	1.0	0.84*
O(1)	18f	0.1462(8)	0.9793(9)	0.1162(7)	1.0	1.1(1)
O(2)	9e	0.145(2)	0	$\frac{1}{2}$	1.0	0.8(1)
O(3)	18f	0.3482(8)	0.1065(8)	0.020(1)	1.0	1.1(1)
O(4)	9d	0.475(2)	0	0	1.0	1.1(1)
O(5)	18f	0.6795(9)	0.2176(9)	0.033(1)	1.0	1.2(1)

Note. For starred atoms,  $B_{eq} = \frac{1}{3} \sum_i \sum_j U_i U_j a_i \cdot a_j$ ,  $B = 8\pi^2 U$ .

### Vibrational Study

The infrared spectra were carried out on a Perkin Elmer spectrum 1000 apparatus, on pressed pellets of the powdered samples dispersed in KBr. The Raman scattering spectra were recorded on powdered samples, on a Dilor XY spectrometer using the 514.5 nm wavelength radiation emitted by an ionized argon laser as excitation.

### NLO Study

The measurements were carried out on a Kurtz and Perry apparatus (17). An Nd:YAG laser having a pulse power of

250 mJoules, a pulse width of 10 nsec, with a frequency of 10 Hz, and a diameter of 4 mm was used.

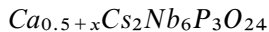
The laser beam ( $\lambda = 1.06 \mu\text{m}$ ) irradiates the powdered sample, which consequently transmits in the visible domain ( $\lambda/2 = 0.503 \mu\text{m}$ ). The detected second harmonic signal is amplified by a photomultiplier and displayed on an oscilloscope; it is compared to that of a reference material: the potassium dihydrogenophosphate (KDP).

### Ionic Conductivity

The experiments were performed on annealed pressed disks of the compounds. AC conductivity of each sample was measured by the complex impedance method, using a precision LCR meter (SOLARTRON 1255), in the frequency range between 1.5 and 65536 Hz, at a temperature ranging from 300 to 550°C.

## RESULTS AND DISCUSSION

### Structural Features and Relationship with



Tl<sub>1-x</sub>Na<sub>x</sub>Nb<sub>2</sub>PO<sub>8</sub> and K<sub>2/3</sub>Na<sub>1/3</sub>Nb<sub>2</sub>PO<sub>8</sub> are isotypic with Ca<sub>0.5+x</sub>Cs<sub>2</sub>Nb<sub>6</sub>P<sub>3</sub>O<sub>24</sub> (10). Their anionic framework, built up of NbO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra sharing corners, results from the stacking along *c*<sub>H</sub> (Fig. 2) of infinite [Nb<sub>2</sub>PO<sub>8</sub>] layers connected to each other by Nb–O–Nb or Nb–O–P strings. The resulting 3D anionic framework forms large tunnels running along *c*<sub>H</sub> communicating with cavities through six-sided brownmillerite windows. Tunnels and cavities accommodate Tl<sup>+</sup>/K<sup>+</sup> and Na<sup>+</sup> cations, respectively.

The interatomic distances and the polyhedral coordination angles in the thallium and potassium compounds are close to the (calcium, cesium) ones: all exhibit highly distorted NbO<sub>6</sub> octahedra (Table 4) and almost regular PO<sub>4</sub> tetrahedra. The main difference with respect to the cesium compound consists of the statistical occupation of many sites close to each other by Tl<sup>+</sup> cations with high thermal motion. Such Tl<sup>+</sup> behavior has been previously observed (18). This is probably due to a stereochemical activity of the lone pair 6s<sup>2</sup> of Tl<sup>+</sup> (19), leading to more excentred positions from the tunnel axis.

Another difference concerning cations should be noticed: in Ca<sub>0.5+x</sub>Cs<sub>2</sub>Nb<sub>6</sub>P<sub>3</sub>O<sub>24</sub>, the niobium cation is mixed valent. The positive charge deficiency is counterbalanced by a surplus of Ca<sup>2+</sup> cations, while the occupancy factor of the cesium site is 0.33, whereas in Tl<sub>1-x</sub>Na<sub>x</sub>Nb<sub>2</sub>PO<sub>8</sub> the niobium atom is strictly pentavalent and the mode of occupation of the Tl<sup>+</sup> and Na<sup>+</sup> sites is quite different from those of Cs<sup>+</sup> and Ca<sup>2+</sup> in Ca<sub>0.5+x</sub>Cs<sub>2</sub>Nb<sub>6</sub>P<sub>3</sub>O<sub>24</sub>. Indeed, while the sodium atom does not fully occupy its site, the thallium cations are spread over many sites close to each other, with a sum of the occupancy factors exceeding the value of  $\frac{1}{3}$ .

The K<sup>+</sup> cations in K<sub>2/3</sub>Na<sub>1/3</sub>Nb<sub>2</sub>PO<sub>8</sub>, like Tl<sup>+</sup> in Tl<sub>1-x</sub>Na<sub>x</sub>Nb<sub>2</sub>PO<sub>8</sub>, are also spread over many sites next to each other, because of the preparation method carried out to obtain this material (exchange reaction starting from the thallium analogous compound). This compound cannot be prepared using the direct method; this is probably due to the small K<sup>+</sup> ionic radius.

Because of its small size, K<sup>+</sup> adopts, especially for K(3) and K(4), dissymmetrical environments with largely

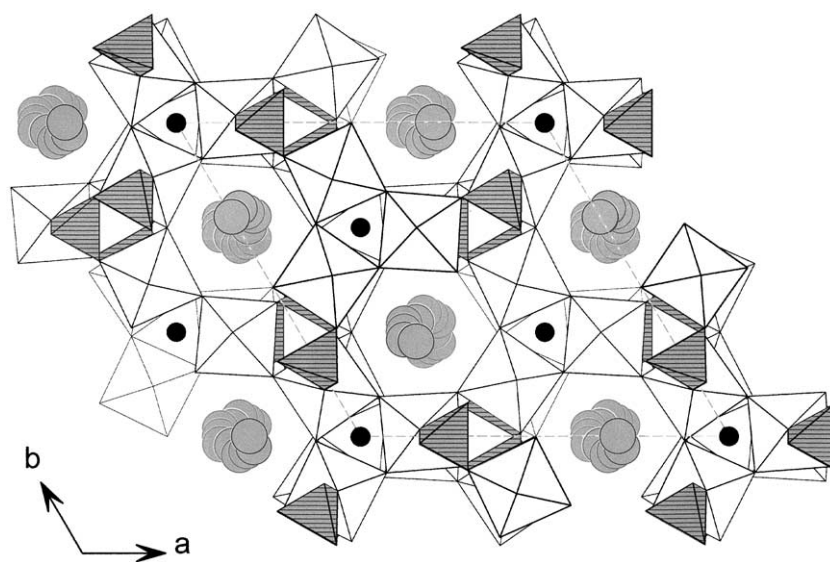


FIG. 2. Projection of the structure along the *c* axis.

**TABLE 4**  
Main Interatomic Distances (Å)

Compound	Nb–O(1 <sup>iii</sup> )	Nb–O(2 <sup>i</sup> )	Nb–O(3)	Nb–O(4)	Nb–O(5)	Nb–O(5 <sup>ii</sup> )
Tl	2.077(8)	1.895(1)	2.100(8)	1.929(3)	1.851(9)	2.024(9)
K	2.094(7)	1.905(3)	2.05(1)	1.934(4)	1.86(1)	2.021(9)

Oxygen atom	The Tl–O and K–O distances				
	Tl(1)	K(1)	Oxygen atom	Tl(2)	K(2)
O(3 <sup>vii</sup> )	3.00(2)	2.89(4)	O(3 <sup>xiii</sup> )	2.86(1)	3.5(2)
O(5 <sup>viii</sup> )	3.09(2)	3.10(4)	O(3 <sup>xiv</sup> )	2.86(1)	3.5(2)
O(4 <sup>ix</sup> )	3.11(2)	3.29(3)	O(5 <sup>xv</sup> )	2.90(1)	3.17(8)
O(3 <sup>x</sup> )	3.18(2)	3.23(4)	O(5 <sup>xvi</sup> )	2.90(1)	3.17(8)
O(1 <sup>xi</sup> )	3.25(2)	3.25(2)	O(4 <sup>xvii</sup> )	3.40(2)	3.06(6)
O(5 <sup>xii</sup> )	3.27(2)	3.11(3)	O(4 <sup>xviii</sup> )	3.40(2)	3.06(6)
O(5 <sup>ix</sup> )	3.29(2)	3.47(4)	O(5 <sup>xvii</sup> )	—	3.4(2)
O(4 <sup>xii</sup> )	3.48(2)	3.50(4)	O(5 <sup>xviii</sup> )	—	3.4(2)

Oxygen atom	Tl(3)	K(3)	Oxygen atom	Tl(4)	K(4)
O(3 <sup>xviii</sup> )	2.94(2)	2.81(2)	O(3 <sup>vii</sup> )	2.71(2)	2.95(4)
O(3 <sup>xix</sup> )	2.94(2)	2.81(2)	O(5 <sup>xii</sup> )	2.89(2)	3.30(5)
O(4)	3.00(3)	—	O(5 <sup>viii</sup> )	2.97(2)	2.62(4)
O(5)	3.07(2)	—	O(3 <sup>xvii</sup> )	3.05(3)	3.28(5)
O(5 <sup>iv</sup> )	3.07(2)	—	O(1 <sup>xi</sup> )	3.36(3)	—
O(1 <sup>xx</sup> )	3.43(3)	2.83(9)	O(4 <sup>ix</sup> )	3.42(2)	2.97(5)
O(1 <sup>xxi</sup> )	3.43(3)	2.83(9)	O(1 <sup>xxiii</sup> )	3.44(3)	—
O(1 <sup>xxv</sup> )	—	3.27(9)	O(4 <sup>ii</sup> )	3.45(2)	—
O(1 <sup>xxvi</sup> )	—	3.27(9)	O(1 <sup>xxix</sup> )	—	3.48(5)
O(5 <sup>xxvii</sup> )	—	3.47(6)	—	—	—
O(5 <sup>xxiii</sup> )	—	3.47(6)	—	—	—

Note. Symmetry codes. (i):  $\frac{2}{3} - x + y, \frac{1}{3} - x, -\frac{2}{3} + z$ . (ii):  $1 - x + y, 1 - x, z$ . (iii):  $\frac{2}{3} - x, -\frac{2}{3} - x + y, \frac{1}{3} - z$ . (iv):  $x - y, -y, -z$ . (v):  $x, y - 1, z$ . (vi):  $1 + x - y, 1 - y, -z$ . (vii):  $1 - x, 1 - x + y, 1 - z$ . (viii):  $x - y, 1 - y, 1 - z$ . (ix):  $x, 1 + y, 1 + z$ . (x):  $1 - y, 1 + x - y, 1 + z$ . (xi):  $y, 1 + x, 1 - z$ . (xii):  $\frac{4}{3} - x + y, \frac{2}{3} - x, \frac{2}{3} + z$ . (xiii):  $\frac{1}{3} + y, -\frac{1}{3} + x, \frac{2}{3} - z$ . (xiv):  $\frac{2}{3} - x + y, \frac{1}{3} - x, \frac{1}{3} + z$ . (xv):  $\frac{4}{3} - x, \frac{2}{3} - x + y, \frac{2}{3} - z$ . (xvi):  $\frac{2}{3} - y, -\frac{2}{3} + x - y, \frac{1}{3} + z$ . (xvii):  $\frac{4}{3} - x + y, \frac{2}{3} - x, \frac{2}{3} + z$ . (xviii):  $1 - y, x - y, z$ . (xix):  $1 - x, -x + y, -z$ . (xx):  $-x + y, -x, z$ . (xxi):  $y, x, -z$ . (xxii):  $\frac{1}{3} + x, \frac{2}{3} + y, \frac{2}{3} + z$ . (xxiii):  $1 - x, -x + y, 1 - z$ . (xxiv):  $\frac{2}{3} + y, -\frac{2}{3} + x, \frac{1}{3} - z$ . (xxv):  $2 - y, 1 + x - y, z$ . (xxvi):  $1 - x, -1 - x + y, -z$ . (xxvii):  $\frac{4}{3} - x + y, \frac{2}{3} - x, -\frac{1}{3} + z$ . (xxviii):  $\frac{2}{3} + y, -\frac{2}{3} + x, \frac{1}{3} - z$ . (xxix):  $\frac{4}{3} - y, \frac{2}{3} + x - y, \frac{2}{3} + z$ .

excentred positions from the tunnel axis in comparison with Tl<sup>+</sup> (Fig. 3).

Despite the occupation by K<sup>+</sup> of very large sites, K<sub>2/3</sub>Na<sub>1/3</sub>Nb<sub>2</sub>PO<sub>8</sub> is very stable. Indeed, neither significant weight loss nor thermal effect was noticed when a thermal analysis experiment was carried out up to 1000°C. In addition, the X-ray pattern of the resulting powder does not exhibit any alteration of the material. Similar results have been observed on K<sub>2/3</sub>Na<sub>1/3</sub>Ta<sub>2</sub>PO<sub>8</sub> and NaM<sub>2</sub>PO<sub>8</sub> (M = Nb, Ta), also prepared using a cationic exchange reaction.

The Compounds of the Family with Formula

$A_{2/3}A'_{1/3}M_2XO_8$  (A = Na, K, Tl, Rb, Cs; A' = Na, Ag; M = Nb, Ta; and X = P, As)

*X-ray characterization.* The examination of the X-ray powder patterns of the compounds with the formula  $A_{2/3}A'_{1/3}M_2XO_8$  showed these materials to be isotypic with Tl<sub>1-x</sub>Na<sub>x</sub>Nb<sub>2</sub>PO<sub>8</sub>. Table 5 reports the unit cell parameters of the compounds of the family which can be divided into two groups: the phosphate compounds exhibiting nearly equivalent parameter values, and the arsenate ones presenting slightly higher parameters.

*IR and raman characterizations.* The isotypy of the above-cited compounds with Tl<sub>1-x</sub>Na<sub>x</sub>Nb<sub>2</sub>PO<sub>8</sub> is corroborated by a vibrational study since the infrared spectra (Fig. 4) and the Raman ones (Fig. 5) exhibit similar peaks in intensities and in positions as shown for three representative

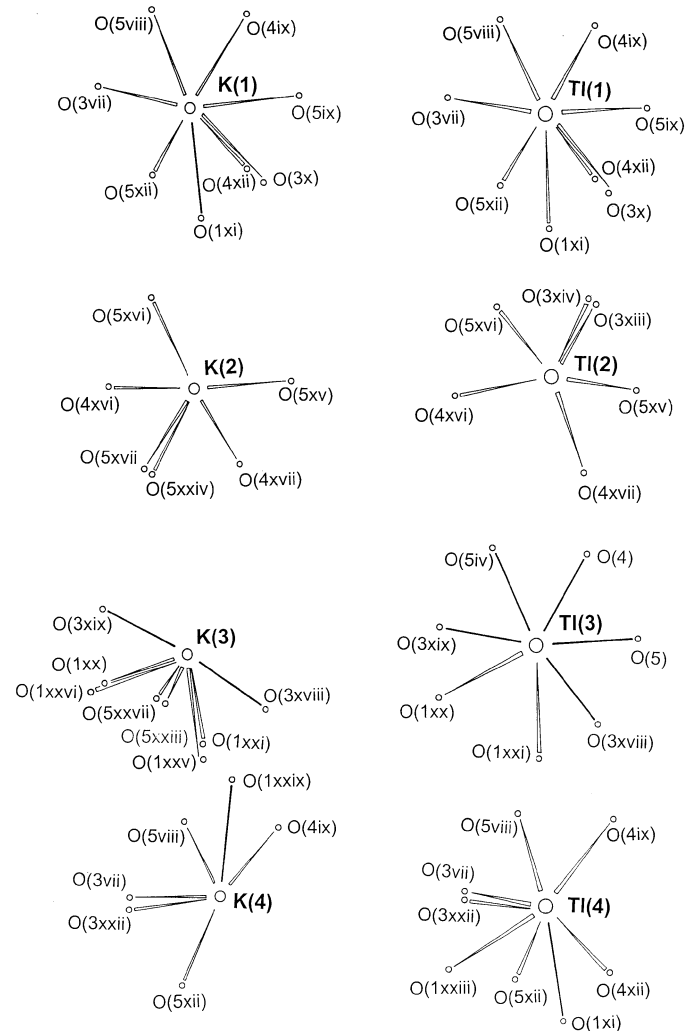


FIG. 3. K<sup>+</sup> and Tl<sup>+</sup> environments.

**TABLE 5**  
**Unit Cell Constants**

Compound	<i>a</i> <sub>H</sub> (Å)	<i>c</i> <sub>H</sub> (Å)	<i>V</i> (Å <sup>3</sup> )
Tl <sub>2/3</sub> Na <sub>1/3</sub> Nb <sub>2</sub> PO <sub>8</sub>	13.305(4)	10.297(5)	1578(2)
Tl <sub>2/3</sub> Na <sub>1/3</sub> Ta <sub>2</sub> PO <sub>8</sub>	13.307(4)	10.321(3)	1583(2)
Tl <sub>2/3</sub> Na <sub>1/3</sub> NbTaPO <sub>8</sub>	13.320(4)	10.330(4)	1587(2)
Rb <sub>2/3</sub> Na <sub>1/3</sub> Nb <sub>2</sub> PO <sub>8</sub>	13.351(3)	10.338(2)	1597(1)
Cs <sub>2/3</sub> Na <sub>1/3</sub> Nb <sub>2</sub> PO <sub>8</sub>	13.393(5)	10.357(4)	1609(2)
K <sub>2/3</sub> Na <sub>1/3</sub> Nb <sub>2</sub> PO <sub>8</sub>	13.344(2)	10.332(2)	1593(2)
K <sub>2/3</sub> Na <sub>1/3</sub> Ta <sub>2</sub> PO <sub>8</sub>	13.309(2)	10.336(2)	1586(2)
Rb <sub>2/3</sub> Na <sub>1/3</sub> Nb <sub>2</sub> AsO <sub>8</sub>	13.482(2)	10.465(2)	1647(2)
Cs <sub>2/3</sub> Na <sub>1/3</sub> Nb <sub>2</sub> AsO <sub>8</sub>	13.561(5)	10.531(5)	1677(2)
Tl <sub>2/3</sub> Ag <sub>1/3</sub> Nb <sub>2</sub> PO <sub>8</sub>	13.380(2)	10.322(2)	1600(2)
Tl <sub>2/3</sub> Ag <sub>1/3</sub> Ta <sub>2</sub> PO <sub>8</sub>	13.352(5)	10.332(2)	1595(2)
NaTa <sub>2</sub> PO <sub>8</sub>	13.317(4)	10.323(2)	1585(2)
NaNb <sub>2</sub> PO <sub>8</sub>	13.349(2)	10.327(2)	1594(1)

compounds; the arsenic compounds just differ by the expected lower frequency range of the AsO<sub>4</sub> internal modes.

The assignments were done on the basis of previous knowledge of niobium, tantalum, phosphate, and arsenate compounds (20–27), and on comparing spectra of several compounds of the family with different pentavalent cations. The vibrational study carried out on the compounds of the above-cited family did not show a meaningful difference with different monovalent cations. Indeed, the fractional occupancy factors of these cations are too small to consider a real interaction with the anionic framework. The discussion was then limited only to three compounds.

The examination of these spectra permits us to propose the assignment displayed in Table 6. In the IR spectra (Fig. 4), the multiple bands from 397 to 687 cm<sup>-1</sup>, for the phosphorus compounds Tl<sub>2/3</sub>Na<sub>1/3</sub>M<sub>2</sub>PO<sub>8</sub> (*M* = Nb, Ta), and from a lower frequency range to 668 cm<sup>-1</sup> for Rb<sub>2/3</sub>Na<sub>1/3</sub>Nb<sub>2</sub>AsO<sub>8</sub>, should be assigned to *X*-O-*X* bending modes coupled also with the *v*<sub>as</sub> *M*-O stretching mode (*M* = Nb, Ta) (Table 6). Below these frequency ranges, the *M*-O-*M* and *M*-O-*X* bending vibrations are observed. The whole network vibrations appear in a frequency range further below.

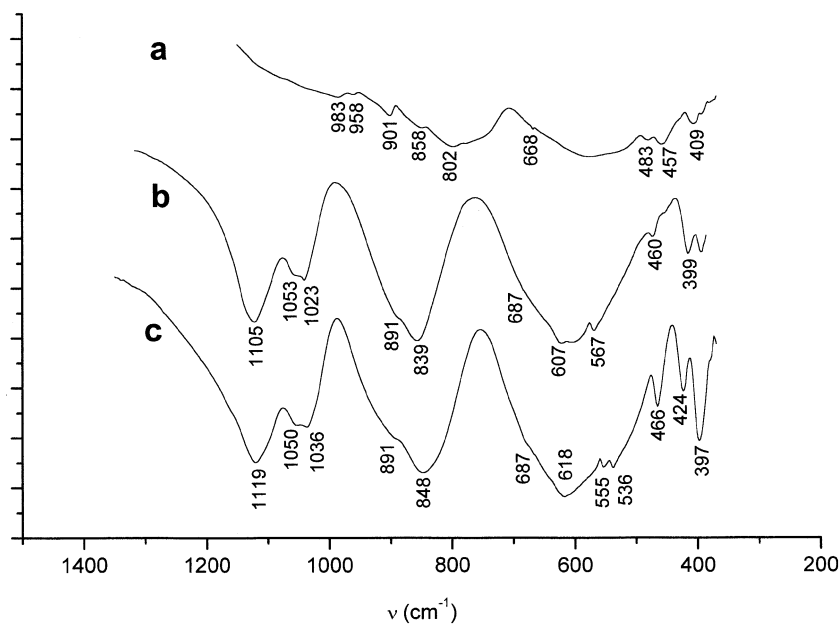
Concerning the Raman spectra (Fig. 5), one can observe, above 600 cm<sup>-1</sup>, a great similarity between the Tl<sub>2/3</sub>Na<sub>1/3</sub>Nb<sub>2</sub>PO<sub>8</sub> and Tl<sub>2/3</sub>Na<sub>1/3</sub>Ta<sub>2</sub>PO<sub>8</sub> spectra, with shifts rarely exceeding the precision of the measurements (4 cm<sup>-1</sup>).

The *M*-O stretching modes, either in infrared or in Raman, appear in relatively high ranges because of the highly distorted MO<sub>6</sub> octahedra (Table 4), which is in agreement with previous results in the literature (26, 27).

*Physical Properties*

*Nonlinear optical properties.* The NLO test performed on the title compounds family shows a behavior similar to that of the reference compound (KDP), with second harmonic generation yields ranging from 0.8 for Cs<sub>2/3</sub>Na<sub>1/3</sub>Nb<sub>2</sub>AsO<sub>8</sub> to 1.3 for Tl<sub>2/3</sub>Na<sub>1/3</sub>Ta<sub>2</sub>PO<sub>8</sub>.

The optical nonlinearity is mainly due to the magnitude of the bond polarizabilities (28), which appears in the distorted MO<sub>6</sub> octahedra of this family of compounds.



**FIG. 4.** Infrared spectra of (a) Rb<sub>2/3</sub>Na<sub>1/3</sub>Nb<sub>2</sub>AsO<sub>8</sub>, (b) Tl<sub>2/3</sub>Na<sub>1/3</sub>Nb<sub>2</sub>PO<sub>8</sub>, and (c) Tl<sub>2/3</sub>Na<sub>1/3</sub>Ta<sub>2</sub>PO<sub>8</sub>.

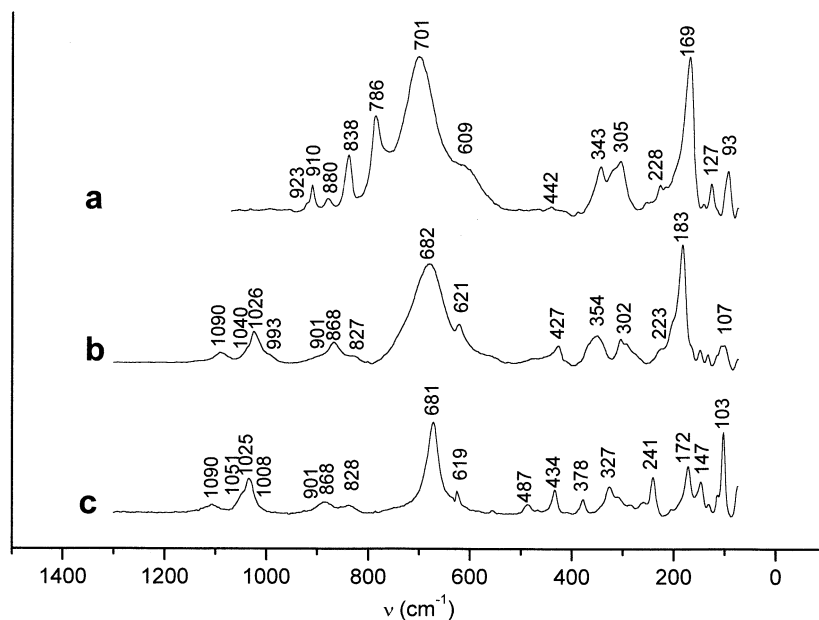


FIG. 5. Raman spectra of (a)  $\text{Rb}_{2/3}\text{Na}_{1/3}\text{Nb}_2\text{AsO}_8$ , (b)  $\text{Tl}_{2/3}\text{Na}_{1/3}\text{Nb}_2\text{PO}_8$ , and (c)  $\text{Tl}_{2/3}\text{Na}_{1/3}\text{Ta}_2\text{PO}_8$ .

Note that the silver compounds  $\text{Tl}_{2/3}\text{Ag}_{1/3}\text{M}_2\text{PO}_8$  ( $M = \text{Nb}, \text{Ta}$ ) decomposed under the laser beam.

**Ionic conductivity.** A three-dimensional framework with large tunnels, wherein highly agitated thallium cations reside with a statistical occupation of many sites, could give rise to good cationic mobility. Despite these characteristics, investigation of the ion conduction properties of the thallium compound  $\text{Tl}_{2/3}\text{Na}_{1/3}\text{Nb}_2\text{PO}_8$  and also of those of the whole family was unsatisfactory. Indeed, these compounds exhibited high activation energies and low conductivity values at  $300^\circ\text{C}$ , ranging from 0.95 to 1.26 eV and  $6.26 \times 10^{-9}$  to  $2.81 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ , respectively.

## CONCLUSION

$\text{Tl}_{1-x}\text{Na}_x\text{Nb}_2\text{PO}_8$  ( $x = 0.21$ ) and the related family of compounds with formula  $A_{2/3}A'_{1/3}M_2XO_8$  ( $A = \text{Na}, \text{K}, \text{Tl}, \text{Rb}, \text{Cs}$ ;  $A' = \text{Na}, \text{Ag}$ ;  $M = \text{Nb}, \text{Ta}$ ;  $X = \text{P}, \text{As}$ ) are isotypic with the  $\text{Ca}_{0.5+x}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$ . It appears that their framework accommodates a large number of cations.

The impact of the highly distorted  $\text{NbO}_6$  and  $\text{TaO}_6$  octahedra on the vibrational study appears in the  $M\text{-O}$  stretching modes with peaks centered at relatively high frequency ranges.

The NLO measurements exhibited similar properties for all the compounds over the whole family of materials, with

TABLE 6  
Spectral Data and Band Assignments of P–O(As–O) and Nb–O(Ta–O) Stretching Modes

	$\text{Tl}_{2/3}\text{Na}_{1/3}\text{Nb}_2\text{PO}_8$		$\text{Tl}_{2/3}\text{Na}_{1/3}\text{Ta}_2\text{PO}_8$		$\text{Rb}_{2/3}\text{Na}_{1/3}\text{Nb}_2\text{AsO}_8$	
	IR	Raman	IR	Raman	IR	Raman
$\nu_3 = \nu_{\text{as}}(\text{X-O})(\text{cm}^{-1})$ (1017 for free $\text{PO}_4$ , 878 for free $\text{AsO}_4$ (23))	1105 s 1053 m 1023 m	1090 w 1040 w 1026 m 993 vw	1119 vw 1050 m 1036 m	1090 vw 1051 sh 1025 m 1008 sh	983 vw 958 vw 901 w	923 sh 910 m 880 w
$\nu_1 = \nu_{\text{s}}(\text{X-O})(\text{cm}^{-1})$ (938 for free $\text{PO}_4$ , 837 for free $\text{AsO}_4$ (23))	891 sh	901 vw 868 w	891 sh	901 vw 868 w	802 m	786 s —
$\nu_{\text{s}}(\text{M-O})(\text{cm}^{-1})$	839 s	827 w	848 s	828 w	859 s	838 m
$\nu_{\text{as}}(\text{M-O})(\text{cm}^{-1})$	687 sh	682 s 621 m	687 sh	681 s 619 m	668 sh	701 s 609 sh

Note. For bands and lines, s strong, m medium, w weak, vw very weak and sh shoulder.

harmonic yields not sufficiently important to propose such materials as serious candidates for practical application in this domain.

Highly agitated thallium cations with statistical occupation of many sites located in large tunnels are not sufficient—contrary to what is expected—to make the studied compounds good ionic conductors.

#### ACKNOWLEDGMENTS

The crystal data collection was performed in the “Laboratoire de Cristallographie de la Faculté des Sciences de Tunis.” We are grateful to Professor A. Driss who supervised this experiment. We would like also to thank Professor T. Jouini for helpful discussions. We are indebted to M. Souchaud, from Institut des matériaux Jean Rouxel, Nantes, for conductivity measurements.

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