

## Synthesis and Study of New Compounds $(M^I)(N^{IV})_2(PO_4)_3$ with Nasicon-like Structure ( $M = Ag, Cu; N = Ge, Hf, Sn, Ti, Zr$ )

J.-M. WINAND, A. RULMONT,\* AND P. TARTE

*Institut de Chimie, B06, Université de Liège, B-4000 Liège 1, Belgium*

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Compounds  $(M^I)(N^{IV})_2(PO_4)_3$  ( $M = Ag, Cu; N = Ge, Hf, Sn, Ti, Zr$ ) have been synthesized using solid-state reactions. Attempts to synthesize  $CuGe_2(PO_4)_3$  did not succeed. All other compounds have Nasicon-like structure (space group  $R\bar{3}c$ ).  $AgGe_2(PO_4)_3$ ,  $AgHf_2(PO_4)_3$ ,  $CuSn_2(PO_4)_3$ , and  $CuHf_2(PO_4)_3$  are described for the first time. Cell parameters, vibrational spectra, and ionic conductivities are given. Silver compounds have higher conductivities than, but the same spectral behavior as, corresponding sodium compounds. The spectra of copper compounds show significant differences, perhaps because of peculiar localization of copper in the structure. © 1993 Academic Press, Inc.

### Introduction

Compounds with Nasicon-like structure have been intensively studied over the last 10 years because of their properties as ionic conductors, ceramics with low thermal expansion, and luminescent materials.

Numerous compounds with formula  $(M^I)(N^{IV})_2(PO_4)_3$  ( $N = Ge, Hf, Sn, Ti, Zr$ ) belong to this family. Many works have been devoted to those with  $M = Li$ , or  $Na$ , but compounds with  $M = Ag$  or  $Cu$  have been more rarely studied. Even if some data are available about  $AgSn_2(PO_4)_3$  (1, 2),  $AgZr_2(PO_4)_3$  (3, 4),  $AgTi_2(PO_4)_3$  (5-7),  $CuTi_2(PO_4)_3$  (7-11), and  $CuZr_2(PO_4)_3$  (12-14), ionic conductivities or vibrational spectra have not been measured in most of these studies. Moreover, no attempt to synthesize other possible compounds ( $AgGe_2(PO_4)_3$ ,  $AgHf_2(PO_4)_3$ ,  $CuGe_2(PO_4)_3$ ,  $CuSn_2(PO_4)_3$ ,  $CuHf_2(PO_4)_3$ ) has been carried out. Consequently, our aim was to check the existence of  $(Ag, Cu)(N^{IV})_2(PO_4)_3$  ( $N = Ge, Hf, Sn, Ti, Zr$ ) compounds and to study them using X-ray powder diffraction, vibrational spec-

troscopies, and ionic conductivity measurements.

### Experimental

All syntheses have been carried out using conventional solid-state reaction technique; reagents ( $Ag_2CO_3$ ,  $CuCl$ ,  $M^{IV}O_2$ ,  $(NH_4)_2HPO_4$ ,  $ZrOCl_2 \cdot 8H_2O$ ), weighed in stoichiometric quantities, were well-mixed and ground in an agate mortar, and progressively fired up to temperatures between 900 and 1000°C (silver compounds) or between 1000 and 1200°C (copper compounds). This temperature was maintained for 3 or 4 days, with intervening mixing and grinding, until no change was detected by X-ray diffraction.

Observed and calculated weight-losses were in fairly good agreement.

Our equipment for X-ray and vibrational spectroscopies has been previously described (15).

Electrical conductivities were measured using the complex impedance method, with a Hewlett-Packard 4192 A impedancemeter; we have already discussed in detail the accuracy of this method (16).

\* To whom correspondence should be addressed.

It has been showed previously that, in such compounds, the conductivity was mainly of ionic origin (4).

X-ray powder diagrams have been indexed by comparison with other Nasicon-like compounds;  $hkl$  indices were assigned in a first step and cell parameters were then calculated by a least-squares method. We consider that the resulting cell is acceptable only if it complies with the accuracy criteria listed in a previous work (17).

## Results

### X-Ray Diffraction

We have never obtained a crystalline pure single phase in the case of  $\text{CuGe}_2(\text{PO}_4)_3$ , whatever the synthetic method used (direct solid state synthesis, or transformation into a glassy phase by oil quenching and subsequent thermal devitrification by annealing). The infrared spectra show bands inconsistent with the production of a pure orthophosphate phase and the X-ray powder pattern shows no similarity with a Nasicon-type compound.

Except for this case, all syntheses have succeeded; silver compounds are white, copper compounds are green (for  $N = \text{Sn}$ ,  $\text{Hf}$ ,  $\text{Zr}$ ) or brown (for  $N = \text{Ti}$ ). Their X-ray powder diagrams can be indexed with fairly good precision with hexagonal-rhombohedral Nasicon-like cells (space group  $R\bar{3}c$ ); cell parameters are listed in Table I (data about  $\text{Li}$  and  $\text{Na}$  compounds are given for comparison). For compounds previously described, our cell parameters are in good agreement with those reported in the literature.

In the case of  $\text{CuZr}_2(\text{PO}_4)_3$ , Yao and Fray (12) have reported that they did not obtain a pure compound, but a mixture of two phases, one unknown and the other with Nasicon-like structure. We confirm this result (whatever the synthesis temperature) when the synthesis is carried out using zirconium oxide as starting reagent. On the contrary, an X-ray pure phase is obtained if zirconium oxychloride (more reactive than

the oxide) is used as a reagent. However, this compound is not completely pure because its infrared spectrum shows a weak (but significant) band near  $730\text{ cm}^{-1}$  (Fig. 1) which probably corresponds to a P–O–P vibration, likely due to a small quantity of pyrophosphate.

The corresponding X-ray pure hafnium compound can also be synthesized starting from the oxide, but the same band near  $730\text{ cm}^{-1}$  is also present in its infrared spectrum (Fig. 1).

### Vibrational Spectroscopies

*Silver compounds.* As has been observed in a previous work concerning the  $\text{Na}$  and  $\text{K}$  compounds ( $M^I$ )  $(N^{IV})_2(\text{PO}_4)_3$  (18), the shape of the spectra is very much influenced by the cationic substitution on the  $M^I$  and on the  $N^{IV}$  sites, so that it is often difficult or impossible to determine the correspondence between the different peaks.

We can note that the spectra of silver compounds strongly depend on the electronic structure of the tetravalent ion (main or transition element) (Figs. 2 and 3). This behavior is quite similar to what has been previously observed in the case of the corresponding  $\text{Na}$  and  $\text{K}$  compounds (18).

*Copper compounds.* Discussing the case of Copper compounds is more difficult, first because the synthesis of  $\text{CuGe}_2(\text{PO}_4)_3$  did not succeed, and second because the strong coloration of the other copper compounds makes difficult the recording of Raman spectra using an  $\text{Ar}^+$  laser. We can, however, note that the infrared spectrum of  $\text{CuSn}_2(\text{PO}_4)_3$  shows only one band near  $1200\text{ cm}^{-1}$  instead of a well-separated doublet for other compounds whose tetravalent ions belong to a main family (i.e.,  $(\text{Ag}, \text{Na}, \text{K})(\text{Sn}, \text{Ge})_2(\text{PO}_4)_3$ ).

This shows that the nature of the monovalent ion has a strong influence on the  $\text{PO}_4$  stretching vibrations. A similar conclusion had already been deduced from a comparative study of  $\text{Na}$ ,  $\text{K}$ ,  $\text{Rb}$ , and  $\text{Cs}$  compounds (18). The peculiar behavior of  $\text{Cu}$  compounds could tentatively be explained on

TABLE I

$M^{IV}(N^{IV})_2(PO_4)_3$  COMPOUNDS ( $M = Ag, Cu; N = Ge, Hf, Sn, Ti, Zr$ ):  
CELL PARAMETERS ( $\text{\AA}$ ), ACTIVATION ENERGY (kJ/mole), AND  
ELECTRICAL CONDUCTIVITY ( $\Omega^{-1} \text{cm}^{-1}$ )

Compound	<i>a</i>	<i>c</i>	$E_a$	$\sigma_{600 \text{ K}}$
CuGe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	No single phase obtained			
CuSn <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.605(1)	21.930(5)	57	$7.1 \times 10^{-5}$
CuTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.531(2)	21.336(9)	57	$2.0 \times 10^{-4}$
CuZr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.876(2)	22.146(7)	57	$2.6 \times 10^{-4}$
CuHf <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.840(2)	22.128(8)		
AgGe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.066(1)	21.819(5)	57	$2.4 \times 10^{-5}$
AgSn <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.459(1)	22.683(6)	58	$3.6 \times 10^{-5}$
AgTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.475(2)	22.106(8)	51	$1.2 \times 10^{-3}$
AgZr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.818(1)	22.870(5)	38	$8.7 \times 10^{-4}$
AgHf <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.760(1)	22.794(6)		
NaGe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.094(1)	21.519(7)	98.5	$2.8 \times 10^{-7 a}$
NaSn <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.502(1)	22.472(6)	55.5	$6.4 \times 10^{-7 a}$
NaTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.486(2)	21.779(3)	45.5	$2.3 \times 10^{-5 a}$
NaZr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.801(1)	22.752(5)	45.5	$7.5 \times 10^{-5 a}$
NaHf <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.772(1)	22.662(4)	49.5	$4.9 \times 10^{-5 a}$
LiGe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.274(2)	20.450(6)	58	$2.5 \times 10^{-5 a}$
LiSn <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.650(1)	21.487(5) <sup>a</sup>		
LiTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.509(2)	20.853(9)	38	$1.5 \times 10^{-3 a}$
LiHf <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	8.815(1)	22.016(3)	36.5	$3.9 \times 10^{-4 a}$

<sup>a</sup> According to (20).

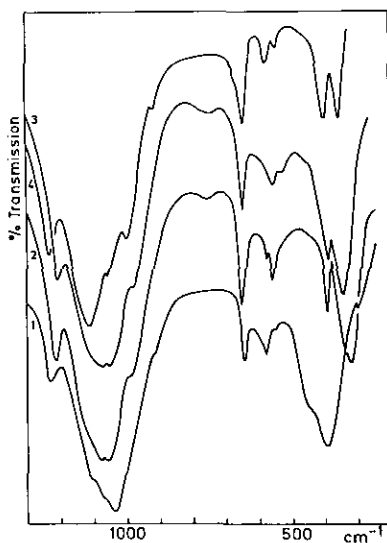


FIG. 1. Infrared spectra of  $Cu(N^{IV})_2(PO_4)_3$  compounds: [1]  $CuTi_2(PO_4)_3$ , [2]  $CuHf_2(PO_4)_3$ , [3]  $CuZr_2(PO_4)_3$ , and [4]  $CuSn_2(PO_4)_3$ .

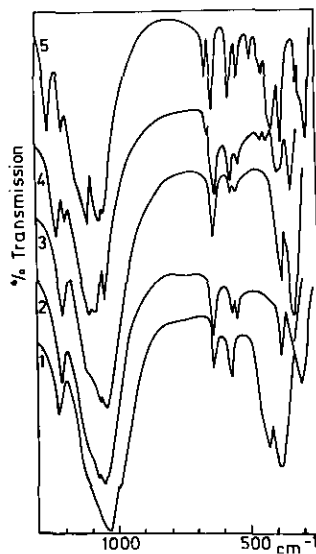


FIG. 2. Infrared spectra of  $Ag(N^{IV})_2(PO_4)_3$  compounds: [1]  $AgTi_2(PO_4)_3$ , [2]  $AgHf_2(PO_4)_3$ , [3]  $AgZr_2(PO_4)_3$ , [4]  $AgSn_2(PO_4)_3$ , and [5]  $AgGe_2(PO_4)_3$ .

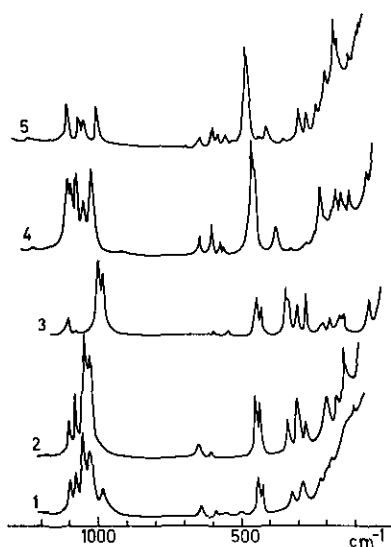


FIG. 3. Raman spectra of  $\text{Ag}(\text{N}^{\text{IV}})_2(\text{PO}_4)_3$  compounds: [1]  $\text{AgGe}_2(\text{PO}_4)_3$ , [2]  $\text{AgSn}_2(\text{PO}_4)_3$ , [3]  $\text{AgTi}_2(\text{PO}_4)_3$ , [4]  $\text{AgZr}_2(\text{PO}_4)_3$ , and [5]  $\text{AgHf}_2(\text{PO}_4)_3$ .

the basis of a recently described structural feature; in  $\text{CuTi}_2(\text{PO}_4)_3$ ,  $\text{Cu}^+$  ions are localized in the octahedral site usually occupied by monovalent ions, but they do not lie in the center of the coordination polyhedron (10, 11).

This could modify the strength of some chemical bonds and consequently the vibrational spectra. We can also note that the cell parameters of Cu compounds (Table I) do not comply with the empirical rule observed for other Nasicon-like ( $M^{\text{I}}$ )  $(\text{N}^{\text{IV}})_2(\text{PO}_4)_3$  compounds. In the whole series  $\text{Li} \rightarrow \text{Na} \rightarrow \text{Ag} \rightarrow \text{K}$ , increasing the size of  $M$  induces an increase of the  $c$ -axis and a smaller decrease of the  $a$ -axis (18). On the contrary, variations of cell parameters are unpredictable when  $\text{Li}^+$  is substituted by  $\text{Cu}^+$ , despite the almost equal ionic radii of these two ions in sixfold coordination (respectively 0.76 and 0.77 Å (19)). For Ti and Hf compounds, we note an increase of both parameters, but an increase of  $c$  and a decrease of  $a$  in the case of Sn compounds.

**High-frequency IR band.** The spectra of these Nasicon-like compounds present a IR band of rather high frequency (near 1200

$\text{cm}^{-1}$ ). This high frequency has been tentatively explained by the large value of the  $\text{P}-\text{O}_1-\text{N}^{\text{IV}}$  angle (18).

We can also note that, according to group theory (18), crystal modes arising from  $\nu_1$  and  $\nu_3$  belong to the same pair of representations. In all Raman modes,  $\nu_1$  and  $\nu_3$  are coupled, but, in the IR spectra, there are two  $A_{2u}$  modes with only  $\nu_3$  components. The high-frequency bands observed in IR are likely to be the  $A_{2u}$  modes because:

- the high frequency value could be correlated with the absence of  $\nu_1$  contribution
- the corresponding bands of  $g$ -symmetry are absent or very weak in Raman spectra.

#### Electrical Conductivity

In the cases of sodium or silver compounds, the ionic conductivity depends strongly on the electronic structure of the tetravalent ion (main or transition element) (Table I, Fig. 4; Ref. (20)). Similarly, in the Nasicon-like solid solutions  $\text{Na}_{1+x}(\text{N}^{\text{III}})_x\text{Zr}_{2-x}(\text{PO}_4)_3$ , the ionic conductivity was higher when the trivalent ion was a transition element (15). In the case of Ag

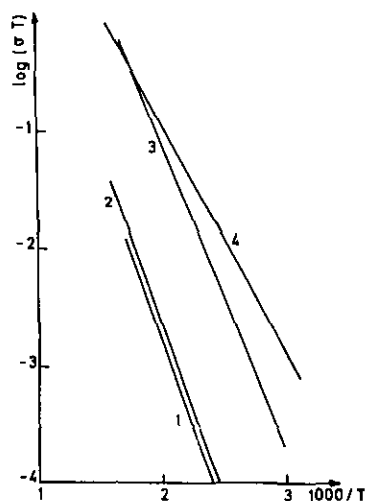


FIG. 4. Ionic conductivity of  $\text{Ag}(\text{N}^{\text{IV}})_2(\text{PO}_4)_3$  compounds: [1]  $\text{AgGe}_2(\text{PO}_4)_3$ , [2]  $\text{AgSn}_2(\text{PO}_4)_3$ , [3]  $\text{AgTi}_2(\text{PO}_4)_3$ , and [4]  $\text{AgZr}_2(\text{PO}_4)_3$ .

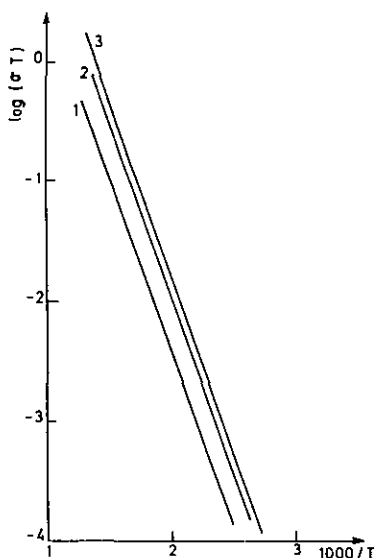


FIG. 5. Ionic conductivity of  $\text{Cu}(\text{N}^{\text{IV}})_2(\text{PO}_4)_3$  compounds: [1]  $\text{CuSn}_2(\text{PO}_4)_3$ , [2]  $\text{CuTi}_2(\text{PO}_4)_3$ , and [3]  $\text{CuZr}_2(\text{PO}_4)_3$ .

$\text{Ge}_2(\text{PO}_4)_3$ , low conductivity could be due to the small volume of the cell (suggesting that the bottleneck could be too narrow to allow an easy migration). However, such a simple explanation is not relevant when comparing the Sn and Ti compounds. In fact, some interatomic distances and angles probably depend on the electronic structure of the tetravalent ion  $N$ , thus explaining the differences observed in the vibrational spectra. This could also induce a shrinkage of the bottlenecks (even if the cell parameters increase), thus explaining the differences observed in ionic conductivity measurements. However, the magnitude of this last phenomenon also depends strongly on the nature of the mobile (monovalent) ion; it is more dramatic in the case of Na compounds (20) than for Ag compounds; for the three Cu compounds studied here, it is no more noticeable (Table 1).

We also note that the ionic conductivities of silver compounds are always higher than those of the corresponding sodium containing substances, despite the smaller ionic

radius of  $\text{Na}^+$  ion (1.02 Å against 1.15 for  $\text{Ag}^+$  (19)) which suggests that  $\text{Na}^+$  would be able to pass easier through the bottlenecks. This is certainly not fortuitous because it is well-known that some of the best ionic conductors (as  $\text{RbAg}_4\text{I}_5$ ) are silver compounds. According to the literature, this could tentatively be explained by the higher polarizability of silver ion (4).

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