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The monovalent copper tin phosphate $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$

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Abstract

The monovalent copper tin phosphate $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ was obtained by different chemical ways and its crystallographic data (Nasicon-type $\text{R}\bar{3}\text{c}$) specified. The material was characterized by diffuse reflectance, Mössbauer spectroscopy and ^{31}P MAS-NMR spectrum. Thermogravimetric measurements are consistent with the existence of the redox $\text{Cu}^{2+}/\text{Cu}^+$ system in the network. A structural determination by applying the Rietveld method showed common features with homologous compounds $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$ ($\text{M}=\text{Ti}, \text{Zr}$) and $\text{NaSn}_2(\text{PO}_4)_3$. This material can play an interesting part from the catalytic point of view in various reactions.

1. Introduction

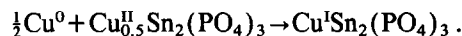
Monovalent copper phosphates with formula $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$ ($\text{M}=\text{Ti}, \text{Zr}$) and Nasicon-type structure [1], have been extensively studied with respect to their conduction, exchange, catalytic or luminescent properties [2–7]. These properties are related to the copper distribution in various sites of the three-dimensional framework formed by $[\text{PO}_4]$ tetrahedra sharing corners with $[\text{MO}_6]$ octahedra. As an example, $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ shows luminescent properties [6], while the homologous $\text{Cu}^{\text{I}}\text{Ti}_2(\text{PO}_4)_3$ does not. This difference in behaviour can be explained by monovalent copper pairing ($\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}=2.40 \text{ \AA}$) evidenced by an EXAFS study in the $\text{M}(1)$ site of the Nasicon structure for the first compound, whereas for $\text{Cu}^{\text{I}}\text{Ti}_2(\text{PO}_4)_3$ such aggregates are not allowed because of the small size at the $\text{M}(1)$ site [8–10]. Moreover, an oscillatory catalytic activity has been observed, related to the migration of Cu^+ ions and to their reduction in $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ essentially [5].

In this context, it was interesting to extend these

studies to monovalent copper tin phosphate $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ and first to solve its structure by the Rietveld profilation method.

2. Experimental

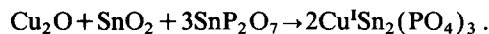
$\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ was prepared by reaction at 800°C , during 24 h, of metallic copper on a sample of $\text{Cu}_{0.5}\text{Sn}_2(\text{PO}_4)_3$, according to:



This reaction was carried out in a vacuum sealed tube. $\text{Cu}_{0.5}^{\text{II}}\text{Sn}_2(\text{PO}_4)_3$ was previously obtained either by firing a stoichiometric mixture of CuO , SnO_2 and $(\text{NH}_4)_2\text{HPO}_4$ at 700°C , or by the following process. The slow addition of a $\text{NH}_4\text{H}_2\text{PO}_4$ solution under constant stirring to 2N HNO_3 solution of CuO and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, produces a gel which is progressively heated at 70°C . The obtained powder is just calcined at 400°C , then at 700°C during 15 h.

As for the homologous phosphates $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$

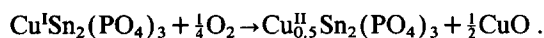
(M = Ti, Zr), $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ can also be obtained directly from Cu_2O , SnO_2 and SnP_2O_7 mixed in stoichiometric proportions and heated in a vacuum sealed tube at 900°C according to:



$\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ is a clear grey powder.

3. Thermogravimetric analysis

A thermogravimetric investigation of $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ has been performed in air between room temperature and 650°C and leads in a first step to the formation of $\text{Cu}_{0.5}^{\text{II}}\text{Sn}_2(\text{PO}_4)_3$ and CuO according to the reversible reaction:



As shown in Fig. 1, after a weak release of absorbed water, oxidation begins at 340°C and finishes at 480°C ($\Delta m = +0.15\%$). Beyond 500°C , the obtained $\text{Cu}_{0.5}^{\text{II}}\text{Sn}_2(\text{PO}_4)_3$ reacts with CuO to restore the starting compound. At 650°C only $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ is present.

The reversible reaction $\text{Cu}^{2+} + e^- \leftrightarrow \text{Cu}^+$ underlines the stability of the covalent framework $[\text{Sn}_2(\text{PO}_4)_3]^-$, which allows various cationic substitu-

tions and justifies its potential catalytic properties.

The divalent copper tin phosphate $\text{Cu}_{0.5}^{\text{II}}\text{Sn}_2(\text{PO}_4)_3$, which structure derives from the monoclinic Nasicon-type variety, has been characterized by EPR ($g_{\parallel} = 2.27$; $g_{\perp} = 2.09$) and by magnetic measurements. The thermal variation of the reciprocal susceptibility obeys the Curie law between 4 and 300 K with the Curie constant ($C = 0.39$) close to the theoretical value (0.375), without notable influence of the temperature-independent paramagnetism.

4. Spectroscopic and crystallographic investigations

$\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ crystallizes in the rhombohedral system ($R\bar{3}c$) and is isomorphous with $\text{NaZr}_2(\text{PO}_4)_3$. This is confirmed by the ^{31}P MAS-NMR spectra, which are rigorously similar to those of Nasicon-type phosphates (Fig. 2). The only single ^{31}P resonance line (-26.7 ppm) clearly indicates that all the P atoms are crystallographically equivalent, as expected from the space group $R\bar{3}c$ [12].

The measured density ($d_{\text{exp}} = 4.12 \pm 0.05$ g/cm³) is in good agreement with the theoretical one: $d_{\text{mes}} = 4.12$ g/cm³ for six $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ groups per unit cell. The parameters of the usual hexagonal cell are compared

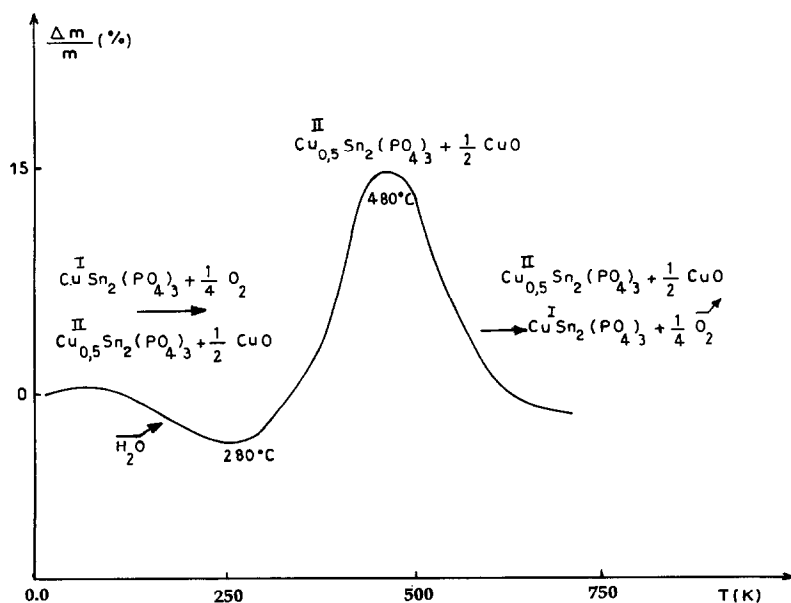


Fig. 1. Thermogravimetric analysis of $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$.

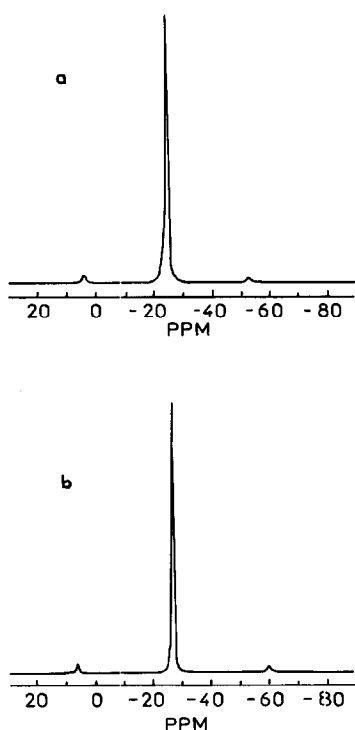


Fig. 2. ^{31}P MAS-NMR spectra of (a) $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ and (b) $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$.

to those of the homologous $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$ ($\text{M}=\text{Ti}$, Zr) in Table 1.

The observed increase of volume of the hexagonal cells of $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$ ($\text{M}=\text{Ti}$, Sn , Zr) agrees with the rising ionic radius M^{4+} . A similar evolution was observed for the phosphates $\text{NaM}_2(\text{PO}_4)_3$ ($\text{M}=\text{Ti}$, Sn , Zr) [14], in which the $\text{M}(1)$ site is occupied by Na^+ ions.

The Mössbauer spectrum of $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ is characteristic of $\text{Sn}(\text{IV})$ in an octahedral environment, with an isomer shift of 0.379 mm/s with regard to SnO_2 (Fig. 3). The diffuse reflectance spectrum of

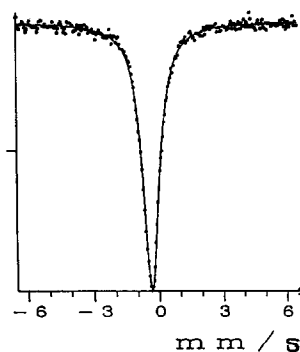


Fig. 3. Mössbauer spectrum of $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$.

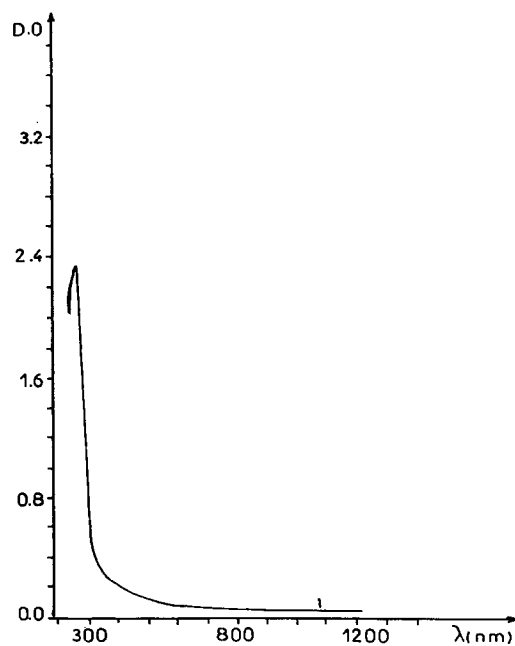


Fig. 4. Diffuse reflectance spectra of $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$.

Table 1
Parameters of the hexagonal cell for the $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$ ($\text{M}=\text{Ti}$, Zr) compounds

$\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$	Ionic radius (\AA) [13]	a_h ($\pm 0.005 \text{ \AA}$)	c_h ($\pm 0.03 \text{ \AA}$)	V ($\pm 5 \text{ \AA}^3$)
$\text{M}=\text{Ti}$	0.74	8.530	21.36	1346
$\text{M}=\text{Sn}$	0.83	8.588	21.96	1403
$\text{M}=\text{Zr}$	0.86	8.870	22.10	1512

$\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ shows an intense band assigned to electron transfer $\text{O}^{2-} \rightarrow \text{Sn}^{4+}$ (Fig. 4). This transfer occurs at a lower energy than that of $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ ($\text{O}^{2-} \rightarrow \text{Zr}^{4+}$; 230 nm) due to the more covalent character of the Sn–O bond. No absorption is evidenced in the region 600–1400 nm, excluding the presence of divalent copper ions in the material. There is a broadening of the bottom of the charge transfer band (400 nm) assigned to the $\text{Cu}^+ \rightarrow \text{Sn}^{4+}$ transfer. This phenomenon, already observed in $\text{Cu}^{\text{I}}\text{Ti}_2(\text{PO}_4)_3$ [15], indicates a localization of the lowest excited levels of the $3d^9 4s^1$ configuration (Cu^+) in the conduction band and would explain the absence of luminescence for $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ under UV excitation.

5. Structural investigation

A refinement of the structure of $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ was carried out by the Rietveld profilation method. The initial atomic coordinates are those found for $\text{NaZr}_2(\text{PO}_4)_3$, but a general position for Cu^+ ion around the center of the M(1) site in the Nasicon structure is assumed (Table 2), as for $\text{Cu}^{\text{I}}\text{Ti}_2(\text{PO}_4)_3$.

The final refinement gives satisfactory reliability

Table 2

Reduced coordinates of $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$

	Position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{iso} (Å ²)
Cu	36f	0.070	0.104	0.000	2.62
Sn	12c	0.000	0.000	0.144	0.70
P	18e	0.289	0.000	0.250	1.30
O(1)	36f	0.183	0.980	0.191	2.04
O(2)	36f	0.189	0.165	0.085	1.95

factors $R_p = 4.32\%$, $R_{wp} = 5.91\%$ and $R_B = 3.14\%$. The refined parameters of the hexagonal cell are $a_h = 8.808 \pm 0.009$ Å and $c_h = 21.95 \pm 0.01$ Å. A comparison of the experimental and calculated diffractograms of $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ is shown in Fig. 5. The main interatomic distances are listed in Table 3.

The interatomic distances obtained for $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ reveal a distribution and a surrounding for monovalent copper comparable with those found for the homologous phases $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$ (M=Ti, Zr) [8] and for the high temperature form of $\text{NaSn}_2(\text{PO}_4)_3$. As a consequence, the Cu–O distances are characterized by two short distances (2.07 Å, 2.12 Å), two medium distances (2.51 Å, 2.58 Å) and two long distances (2.91 Å, 2.95 Å) (Fig. 6). This copper surrounding is a compromise between the

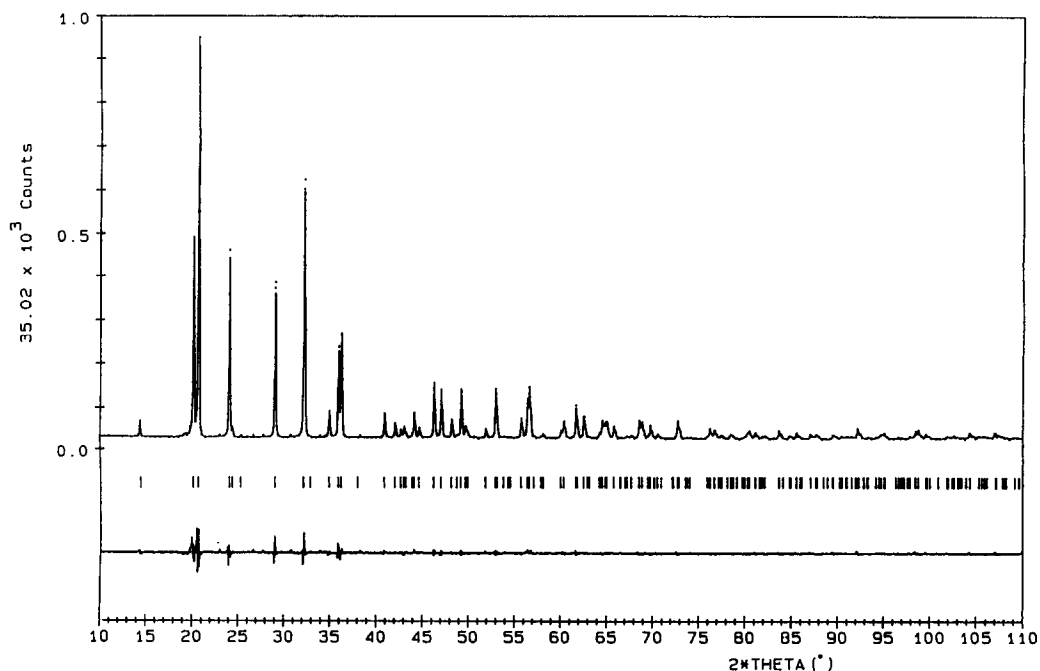


Fig. 5. Observed and calculated diffractograms of $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$.

Table 3

Interatomic distances (Å) for $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$

Cu–O ₂	2.07	Sn–O ₁ (3)	1.96	O ₁ –O ₂	2.44
Cu–O ₂	2.12	Sn–O ₂ (3)	2.00	O ₁ –O ₂	2.57
Cu–O ₂	2.51			O ₁ –O ₂	2.54
Cu–O ₂	2.58	Cu–P	2.99	O ₁ –O ₂	2.80
Cu–O ₂	2.91			O ₁ –O ₁	2.88
Cu–O ₂	2.95	P–O ₁ (2)	1.53	O ₂ –O ₂	2.85
Cu–O ₁	2.87	P–O ₁ (2)	1.54	O ₂ –O ₂	2.50
Cu–O ₁	2.99			O ₂ –O ₂	2.66

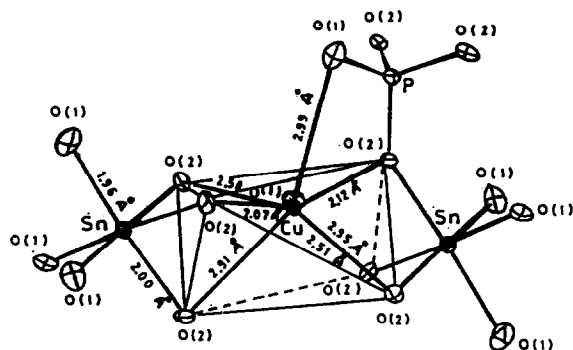


Fig. 6. Oxygen surrounding copper and tin atoms.

usual linear coordination and the octahedral geometry of the M(1) site of the Nasicon structure. The tetrahedra (PO_4) are nearly regular. The distances (1.59 Å) between the symmetrical positions of Cu in M(1) sites are similar to those obtained for $\text{Cu}^{\text{I}}\text{Ti}_2(\text{PO}_4)_3$, but much smaller than in the case of $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ (2.40 Å).

The absence of copper pairing ($\text{Cu}^+ - \text{Cu}^+$) possibility in the M(1) site, also explains why the phosphates $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ and $\text{Cu}^{\text{I}}\text{Ti}_2(\text{PO}_4)_3$ do not show luminescent properties.

6. Conclusion

The monovalent copper tin phosphate $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ crystallizes in a Nasicon-type structure ($R\bar{3}c$), like $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$ ($\text{M} = \text{Zr}, \text{Ti}$) and $\text{NaSn}_2(\text{PO}_4)_3$. From a structural point of view, the size of the M(1) site is very similar to that of $\text{Cu}^{\text{I}}\text{Ti}_2(\text{PO}_4)_3$ and can explain the non-luminescent properties of this material. The strongly covalent framework $[\text{Sn}_2(\text{PO}_4)_3]^-$ allows the reversible oxido-reduction reaction $\text{Cu}^{2+} + e^- \leftrightarrow \text{Cu}^+$ without

modifying the 3D character of the structure. $\text{Cu}^{\text{I}}\text{Sn}_2(\text{PO}_4)_3$ is a potential candidate for catalysis in the general context of a study which is now in progress.

Acknowledgement

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