

Tin-containing nasicon-related compounds: a new mixed valence compound, $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$, containing Sn^{4+} and Sn^{2+} and lithium incorporation within $\text{CuSn}_2\text{P}_3\text{O}_{12}$

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Abstract

The new mixed valence Sn^{4+} – Sn^{2+} compound of composition $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$ contains highly ionic Sn^{2+} species within the Type I sites in the channels of the nasicon-related structure. Treatment of the compound $\text{CuSn}_2\text{P}_3\text{O}_{12}$ with butyl lithium results in the replacement of Cu^+ in the Type I sites by Li^+ and the reduction of Cu^+ to metallic copper. © 1997 Elsevier Science B.V.

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1. Introduction

Compounds of composition $\text{AM}_2^{4+}\text{P}_3\text{O}_{12}$ have three-dimensional linked channel networks resulting from the corner sharing of PO_4 tetrahedra with the MO_6 octahedra [1–4]. The A ions can occupy either distorted octahedral coordination within the channels in sites between two MO_6 octahedra along the c-axis (called the Type I sites) thus forming ribbons of $\text{O}_3\text{MO}_3\text{AO}_3\text{MO}_3$, or larger sites (called the Type II sites) with eight to ten co-ordinating oxygen ions located between the ribbons. The structure is versatile and amenable to substitution on the A, M or phosphorous sites. The occupancy of the Type I and II sites can be varied from four to zero and the compound of composition $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ which is called nasicon has attracted considerable interest because of its high sodium-ion mobility [1,2].

There have been relatively few reports of nasicon-related compounds which contain tin. We report here on the preparation of a new mixed valence tin compound of composition $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$ which contains highly ionic Sn^{2+} ions in the Type I sites. We also report on the treatment of the compound $\text{CuSn}_2\text{P}_3\text{O}_{12}$, where Cu^+ is located in the Type I sites, with butyl lithium which

results in the replacement of Cu^+ by Li^+ and the reduction of Cu^+ to copper metal.

2. Experimental details

The compound $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$ was prepared by the sequential heating of ground stoichiometric mixtures of tin(II) oxide, tin(IV) oxide and ammonium dihydrogen phosphate at 200°C (12 h), 600°C (6 h), 900°C (5 h) and 1000°C (5 h) in alumina boats under flowing nitrogen. An identical product was also prepared under similar reaction conditions using elemental tin, tin(IV) oxide and ammonium dihydrogen phosphate.

The compound $\text{CuSn}_2\text{P}_3\text{O}_{12}$ was prepared as previously described [5] by the calcination of stoichiometric quantities of copper(I) chloride, tin (IV) oxide and ammonium dihydrogen phosphate at 1000°C for 4 days. Lithium was intercalated within $\text{CuSn}_2\text{P}_3\text{O}_{12}$ by treating the finely powdered $\text{CuSn}_2\text{P}_3\text{O}_{12}$ with an excess of butyl lithium (1.3 M solution in hexane) in an argon filled glove box. The mixture was allowed to stand for 30 min and the product removed by filtration and dried in air.

X-ray powder diffraction data were recorded with a Siemens D5000 diffractometer using CuK_α radiation. ^{119}Sn Mössbauer spectra were recorded at 298 K and 77 K with a microprocessor-controlled Mössbauer spectrometer using

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Table 1
X-ray powder diffraction data for $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$

<i>hkl</i>	$d_{\text{obs}}/\text{\AA}$	$d_{\text{calc}}/\text{\AA}$	<i>I/I</i> ₀
102	6.072	6.082	9
104	4.482	4.485	31
110	4.141	4.137	94
113	3.647	3.641	44
201	3.546	3.540	5
204	3.048	3.041	28
107	2.990	2.987	4
116	2.817	2.812	100
211	2.699	2.690	9
108	2.672	2.668	7
214	2.458	2.450	11
109	2.397	2.407	36
302	2.342	2.339	3
303	2.290	2.281	7
208	2.249	2.242	7
304	2.195	2.206	3
1010	2.180	2.190	6
217	2.097	2.090	6
209	2.078	2.080	11
222	2.036	2.036	20
1011	2.007	2.007	4
310	1.989	1.987	2
311	1.979	1.980	13
224	1.942	1.946	10
225	1.887	1.887	8
315	1.829	1.824	28
316	1.760	1.764	16
320	1.642	1.644	9
323	1.607	1.607	5
3011	1.573	1.573	17

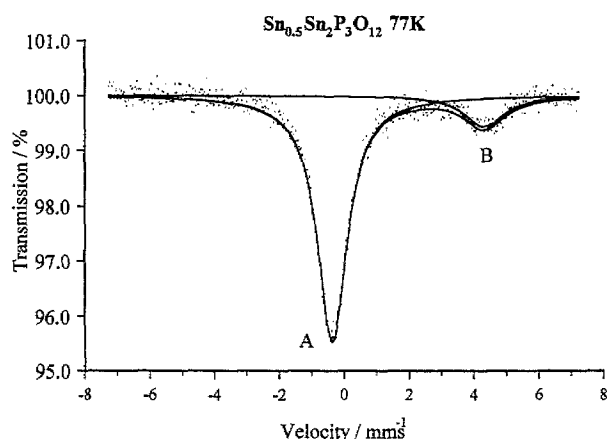


Fig. 1. ^{119}Sn Mössbauer spectrum recorded at 77 K from the compound $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$

Table 2
 ^{119}Sn Mössbauer parameters recorded from $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$

	298 K		77 K	
	δ/mms^{-1}	Spectral area %	δ/mms^{-1}	Spectral area %
Sn^{4+}	-0.35	93	-0.36	85
Sn^{2+}	4.30	7	4.34	15

a $\text{Ca}^{119\text{m}}\text{SnO}_3$ source. The drive velocity was calibrated with a ^{57}Co -Rh source and a natural iron foil. All the spectra were computer fitted. The ^{119}Sn Mössbauer chemical isomer shift data are quoted relative to tin(IV) oxide.

Copper K-edge extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) data were recorded in transmission mode at 298 K on Station 7.1 at the Daresbury Laboratory Synchrotron Radiation Source under operating conditions of 2 GeV and an average current of 200 mA. The data were analyzed using the programmes Excalib, Exback, and Excurv 90.

3. Results and discussion

3.1. $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$

The X-ray powder diffraction pattern recorded from the white nasicon-related compound of composition $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$ was best indexed to a hexagonal unit cell $a=b=8.27\pm0.01$ Å, $c=23.00\pm0.05$ Å (Table 1).

The ^{119}Sn Mössbauer spectrum is shown in Fig. 1 and the ^{119}Sn Mössbauer parameters are collected in Table 2. The absorption with a chemical isomer shift δ of -0.35 mms^{-1} may be assigned to the Sn^{4+} ions on the structural sites. The highly negative chemical isomer shift is notable, indeed it approaches the value recorded [6] from $\text{CuSnF}_6\cdot 4\text{H}_2\text{O}$ ($\delta=-0.45$ mms^{-1}) which is the most negative ^{119}Sn Mössbauer chemical isomer shift yet recorded. Interestingly, the chemical isomer shift is similar to that recorded [7] from SnP_2O_7 ($\delta=-0.39$ mms^{-1}) which has been described [7] as one of the most ionic Sn^{4+} compounds currently known, and it would appear that the highly negative chemical isomer shift for the Sn^{4+} ions in $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$ may be associated with the structural Sn^{4+} ions forming strong bonds with the octahedrally coordinated oxygen atoms. The resonant absorption at δ 4.30 mms^{-1} is consistent with the presence of Sn^{2+} . The low intensity of the absorption precluded the fitting of a quadrupole split absorption. The highly positive chemical isomer shift is similar [8,9] to that of Sn^{2+} when incorporated within nasicon-related $\text{NbTiP}_3\text{O}_{12}$ and approaches the value of 4.84 mms^{-1} predicted for an ideal Sn^{2+} ion with a pure $5s^2$ electronic configuration [10]. The increase in spectral area at low temperature of the absorption corresponding to Sn^{2+} (Table 2) is indicative of the large difference in recoil-free fractions at 298 K and 77 K and

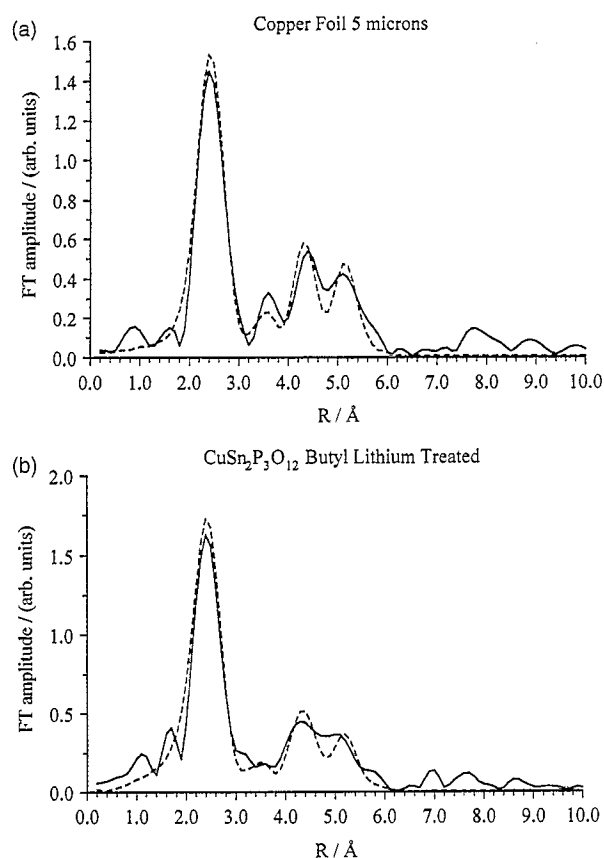


Fig. 2. Copper K-edge EXAFS recorded from (a) copper foil and (b) $\text{CuSn}_2\text{P}_3\text{O}_{12}$ following treatment with butyl lithium.

the phenomenon is similar to that observed [9] in spectra recorded over a range of temperatures from $\text{Sn}_x\text{NbTiP}_3\text{O}_{12}$ ($0 < x < 0.5$). These materials were shown by X-ray powder diffraction [8] to contain Sn^{2+} in the Type I sites with longer distances between the Sn^{2+} ion and the surrounding oxygen atoms of the channel than would normally be expected. Hence the ^{119}Sn Mössbauer chemical isomer shift data recorded for Sn^{2+} in $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$ at 298 K and 77 K may be associated with a highly ionic Sn^{2+}

species interacting only weakly with the oxygen atoms of the Type I sites of the nasicon-related structure.

3.2. $\text{Li/CuSn}_2\text{P}_3\text{O}_{12}$

The lattice parameters recorded from the light green compound $\text{CuSn}_2\text{P}_3\text{O}_{12}$ $a=b=8.52\pm0.01$ Å, $c=21.79$ Å + 0.05 Å resembled those previously reported [5]. The ^{119}Sn Mössbauer spectrum recorded at 298 K was best fitted to a single absorption with a chemical isomer shift δ of -0.37 mm s^{-1} which is similar to that recorded from the structural Sn^{4+} ion in $\text{Sn}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$ (vide supra). The result indicates that the Sn^{4+} ions in the structural octahedral sites of these nasicon-related phases have electronic environments which are highly influenced by their coordination to oxygen atoms covalently bonded to phosphorous (vide supra). The copper K-edge EXAFS recorded from $\text{CuSn}_2\text{P}_3\text{O}_{12}$ showed the copper to be coordinated by three oxygen atoms at 1.98 Å and another oxygen atom at 2.75 Å. The results indicate that the Cu^+ ion does not occupy the center of the Type I interstitial site; and correlate well with the conclusions of a vibrational spectroscopic study of the compound [5]. In this respect it is pertinent to note that the octahedral Type I site in materials of composition $\text{M}^{n+}\text{M}_2^{+}\text{P}_3\text{O}_{12}$ has been described [3] as being trigonally elongated along [001] and the EXAFS data are consistent with the Cu^+ ion being displaced towards one of the shared faces of the SnO_6 octahedra to achieve lower immediate oxygen coordination. Such a displacement has been identified in similar sites in structurally related $\text{M}^{n+}\text{M}_2^{+}\text{M}^{4+}\text{P}_3\text{O}_{12}$ phases [8]. No evidence was found for the existence of Cu^+-Cu^+ pairs which have been envisaged [11] to exist in the related compound of composition $\text{CuZr}_2\text{P}_3\text{O}_{12}$.

The treatment of $\text{CuSn}_2\text{P}_3\text{O}_{12}$ with butyl lithium gave a black solid with a nasicon-related structure $a=b=8.44+0.01$ Å, $c=22.34+0.05$ Å. The ^{119}Sn Mössbauer spectrum was identical to that recorded from $\text{CuSn}_2\text{P}_3\text{O}_{12}$ and gave no evidence for the incorporation of lithium giving rise to the reduction of Sn^{4+} .

Table 3

Best fit parameters to copper K-edge EXAFS recorded from $\text{CuSn}_2\text{P}_3\text{O}_{12}$ following treatment with butyl lithium and from a 5 μm copper foil

Material	Atom Type	$R(\text{\AA})$	$2\sigma^2(\text{\AA}^2)$
$\text{CuSn}_2\text{P}_3\text{O}_{12}$	30	1.98	0.029
	10	2.75	0.012
	2 Sn	3.15	0.029
	2 Sn	4.64	0.027
$\text{CuSn}_2\text{P}_3\text{O}_{12}$ treated with butyl lithium	12 Cu	2.50	0.032
	6 Cu	3.55	0.052
	16 Cu	4.40	0.038
	8 Cu	5.26	0.025
Copper foil	12 Cu	2.50	0.032
	6 Cu	3.53	0.045
	16 Cu	4.36	0.033
	8 Cu	5.21	0.018

The Fourier transform of the copper K-edge EXAFS data recorded from $\text{CuSn}_2\text{P}_3\text{O}_{12}$ treated with butyl lithium is shown in Fig. 2 together with that recorded from a 5 μm copper foil. The best fit parameters are given in Table 3. The results show that treatment of $\text{CuSn}_2\text{P}_3\text{O}_{12}$ with butyl lithium results in the reduction of Cu^+ to the face centred cubic copper metal. The copper K-edge XANES recorded from the butyl lithium treated $\text{CuSn}_2\text{P}_3\text{O}_{12}$ was also similar to that recorded from the copper foil and endorses the EXAFS results. The ^7Li magic angle spinning NMR spectrum recorded from $\text{CuSn}_2\text{P}_3\text{O}_{12}$ treated with butyl lithium showed a resonance at 0 ppm, compared to LiCl in aqueous solution, consistent with the presence of Li^+ . The results therefore indicate that the Cu^+ ions in off centred positions in the Type I sites of $\text{CuSn}_2\text{P}_3\text{O}_{12}$ are reduced by the incorporation of Li^+ and segregate to the exterior of the nasicon-related structure.

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