

Lithium intercalation in $\text{Cu}^{\text{II}}_{0.5}\text{Ti}_2(\text{PO}_4)_3$

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Abstract

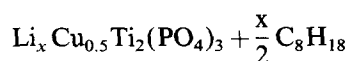
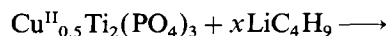
Lithium intercalation by a soft chemistry chemical route of the Nasicon-type derived phosphate $\text{Cu}^{\text{II}}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ leads to a new phase $\text{Li}_x\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ with a broad range of composition ($0 \leq x \leq 3.5$). The c_h parameter of the equivalent hexagonal cell increases with lithium content whereas a_h remains constant. Electron paramagnetic resonance spectra and magnetic susceptibility measurements allow the reduction process of both titanium(IV) and copper(II) ions to be deduced.

1. Introduction

Copper and titanium phosphates $\text{Cu}_x\text{Ti}_2(\text{PO}_4)_3$ ($x = 0.5, \text{Cu}^{\text{II}}; x = 1, \text{Cu}^{\text{I}}$) have been extensively studied owing to their potential catalytic properties [1–4]. A neutron diffraction study showed that $\text{Cu}^{\text{I}}\text{Ti}_2(\text{PO}_4)_3$ had a Nasicon-type structure (hexagonal cell $R\bar{3}c$) [5, 6]. Oxidation of this compound allowed us to obtain $\text{Cu}^{\text{II}}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ with a structure derived from the monoclinic low temperature Nasicon variety. The intercalation of lithium in this phosphate has been studied by a soft chemistry route. We present the results of electron paramagnetic resonance (EPR) and magnetic investigations of the materials obtained.

2. Experimental details

$\text{Cu}^{\text{II}}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ was obtained by oxidation of $\text{Cu}^{\text{I}}\text{Ti}_2(\text{PO}_4)_3$ at 500 °C [7, 8]. After washing in nitric acid solution to remove CuO the isolated phosphate was calcined at 600 °C for 15 h. Lithiation was carried out with a solution of *n*-butyllithium in hexane. A weighted sample of $\text{Cu}^{\text{II}}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ is immersed in hexane and the *n*-butyllithium is added under stirring in an argon filled glove box. An instantaneous colour change occurs. The reaction is the following:



After being left for several days, to ensure complete reaction, the solid phase was filtered, washed with hexane, dried under vacuum and characterized by X-ray diffraction. Several compositions were obtained ($0 \leq x \leq 3.5$). Chemical analysis for lithium, copper, titanium and phosphorus rates was carried out in the CNRS Laboratory (Vernaison).

3. Crystallographic study

All X-ray diffraction patterns were indexed in the monoclinic system derived from the low temperature variety of Nasicon by doubling *c*. Parameters of the monoclinic and hexagonal equivalent cells are given in Table 1. It is seen that a_h remains nearly constant while c_h rises with the size reduction of Cu^{II} and Ti^{IV} involving larger ions in the cell (Fig. 1).

4. Electron paramagnetic resonance investigation

The EPR parameters are collected in Table 2. For $\text{Li}_{0.5}\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ the spectrum is characteristic at any temperature of a very low Cu^{II} content. For $0.5 \leq x \leq 2$, at 4 K the spectra detect the presence of a hyperfine structure (ϵCu^{2+}) and a signal due to Ti^{3+} for $1 \leq x \leq 2$. For higher lithium contents no signal appears at room temperature. The EPR spectrum at liquid helium temperature confirms the reduction of Ti^{IV} to Ti^{III} with a typical value of $g = 1.86$ (Fig. 2).

TABLE 1. Parameters of the $\text{Li}_x\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ phases ($0 \leq x \leq 3.5$)

x	$a_h (\pm 0.02 \text{ \AA})$	$c_h (\pm 0.05 \text{ \AA})$	$a_m (\pm 0.04 \text{ \AA})$	$b_m (\pm 0.02 \text{ \AA})$	$c_m (\pm 0.04 \text{ \AA})$	$\beta (\pm 0.06^\circ)$
0	8.41	21.88	14.51	8.38	17.60	123.34
0.5	8.38	22.36	14.51	8.38	17.77	122.99
1	8.38	22.55	14.51	8.38	17.88	122.77
2	8.38	22.83	14.51	8.38	18.03	122.47
2.5	8.39	22.93	14.53	8.39	18.10	122.36
3	8.39	23.00	14.53	8.39	18.13	122.29
3.5	8.39	23.06	14.53	8.39	18.16	122.23

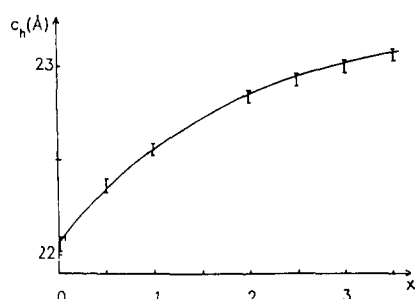
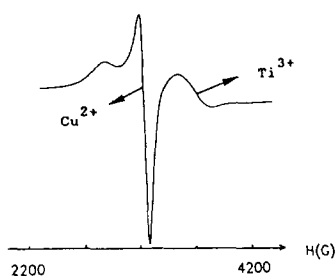
Fig. 1. Evolution of c_h intercalated $\text{Li}_x\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ ($0 \leq x \leq 3.5$) phases vs. lithium rate.

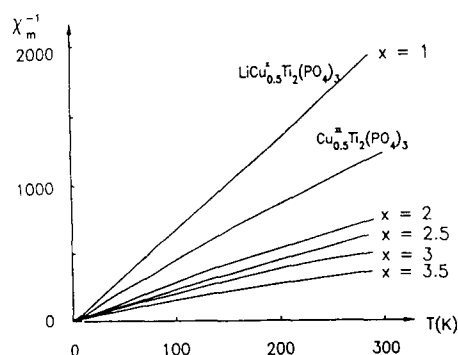
TABLE 2. EPR parameters vs. lithium rate

	$x = 0.5$	$1 \leq x \leq 2$	$2 < x \leq 3.5$
300 K	ϵCu^{2+} $g_{\parallel} = 2.44$ $g_{\perp} = 2.07$	ϵCu^{2+} $g_{\parallel} = 2.44$ $g_{\perp} = 2.07$	—
4 K	ϵCu^{2+}	ϵCu^{2+} + Ti^{3+} $g = 1.86$	Ti^{3+} $g = 1.86$

Fig. 2. EPR spectrum of $\text{LiCu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ at 4 K.

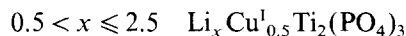
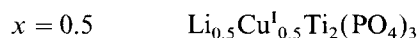
5. Magnetic properties

The magnetic susceptibility of $\text{Li}_x\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ ($0 \leq x \leq 3.5$) was measured between 4 K and 300 K (Fig. 3). In the range $1 < x < 3.5$ the curve $\chi_m^{-1} = f(T)$ of the different compositions is a straight line running through the origin, except for $x = 3.5$. In this case the linearity only appears at $T > 125$ K. The experimental

Fig. 3. Thermal variation of the reciprocal susceptibility of $\text{Li}_x\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ ($0 \leq x \leq 3.5$).

molar Curie constants rise with lithium rate while the effective magnetic moment, for Ti^{III} , decreases (Table 3).

This magnetic behaviour does not agree with that of $\text{Li}_3\text{Ti}_2(\text{PO}_4)_3$, obtained by lithium intercalation in $\text{LiTi}_2(\text{PO}_4)_3$, in the context of a localized electron model assuming a rising magnetic moment with temperature (Fig. 4) [9, 10]. The presence of Cu^{I} would cause this discrepancy by favouring $\text{Ti}^{\text{III}}-\text{Ti}^{\text{III}}$ interactions. According to the data obtained by EPR and magnetic investigations, we can propose these different formulae for the various steps of intercalation:



For $x > 2.5$ there are two possibilities: either reduction of Cu^{I} to Cu^0 which has been excluded by a nuclear magnetic resonance study [11], or the presence of Ti^{II} .

TABLE 3. Experimental molar Curie constants and magnetic moments for Ti^{III}

x	$C_{\text{mol.exp.}}$	$\mu_{\text{eff}}(1\text{Ti}^{3+})$
1	0.143	1.51
2	0.379	1.42
2.5	0.460	1.34
3	0.507	
3.5	0.914	

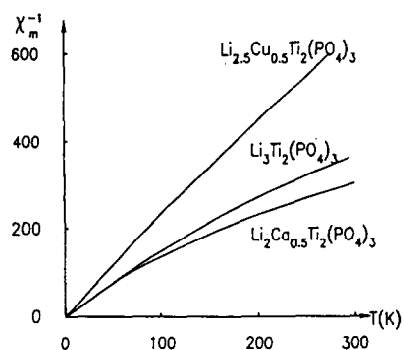


Fig. 4. Thermal variation of the reciprocal susceptibility of $\text{Li}_{2.5}\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$, $\text{Li}_3\text{Ti}_2(\text{PO}_4)_3$ and $\text{Li}_2\text{Ca}_{0.5}\text{Ti}_2(\text{PO}_4)_3$.

An electron spectroscopy for chemical analysis study, now in progress, seems indeed to confirm this last hypothesis.

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