

Phosphates with Nasicon-derived structure: an extended X-ray absorption fine structure investigation

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Abstract

An extended X-ray absorption fine structure investigation of Nasicon-derived phosphates with different oxidation states (Cu^I , Cu^{II}) is reported. For the $\text{Cu}^{II}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s) phosphate obtained by solid state reaction, it is shown that Cu^{2+} ions are surrounded by four oxygen atoms. In contrast, for $\text{Cu}^I\text{Zr}_2(\text{PO}_4)_3$, copper pairs were found with small Cu^I - Cu^I distances (2.40 Å) at the M(1) site of the Nasicon structure, in agreement with a preliminary study by X-ray and neutron diffraction.

1. Introduction

The copper Nasicon-type phosphates have been extensively studied as a result of their catalytic and luminescent properties [1–4]. In these materials copper can exist with oxidation state (I) or (II), the skeleton structure not being destroyed by the redox reaction $\text{Cu}^{II} + e^- \rightarrow \text{Cu}^I$. The structure of $\text{Cu}^I\text{Zr}_2(\text{PO}_4)_3$ consists of a three-dimensional network formed by PO_4 tetrahedra sharing corners with ZrO_6 octahedra [5–7]. Copper is located in an oxygenated anti-prism, usually labelled M(1), elongated along the \bar{c} axis in an off-centred position [7]. An extended X-ray absorption fine structure (EXAFS) study at the copper K-edge of $\text{Cu}^I\text{Zr}_2(\text{PO}_4)_3$ and $\text{Cu}^{II}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s) will give local information around copper atoms in these materials.

2. Data collection

The X-ray absorption spectra of $\text{Cu}^I\text{Zr}_2(\text{PO}_4)_3$ and $\text{Cu}^{II}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s) were recorded on an EXAFS III spectrometer (LURE, DCI) in transmission mode at room temperature, over 8800–9800 eV. The monochromator was Si 311, the ring storage was 1.85 GeV and the intensity was about 250 mA. The EXAFS analysis was carried out as already described [8].

3. Results

The Fourier transforms for the two compounds $\text{Cu}^I\text{Zr}_2(\text{PO}_4)_3$ and $\text{Cu}^{II}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s) are given in Fig. 1. The back-transformed contribution of the first and second coordination shells were least-square fitted

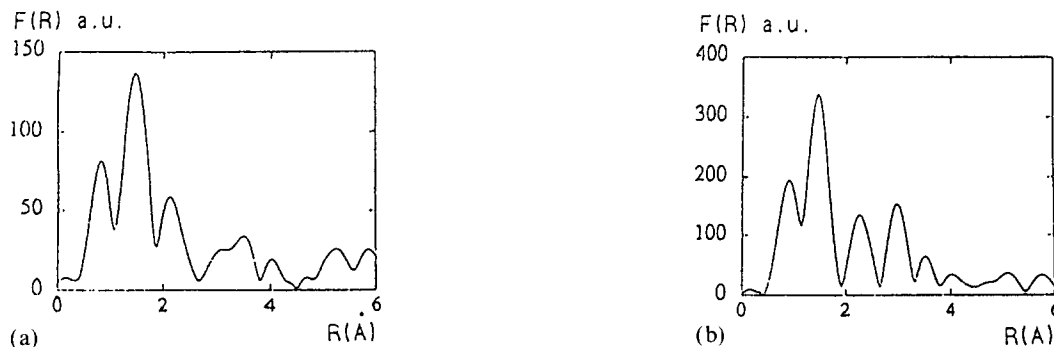


Fig. 1. Fourier transforms of (a) $\text{Cu}^I\text{Zr}_2(\text{PO}_4)_3$, and (b) $\text{Cu}^{II}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s).

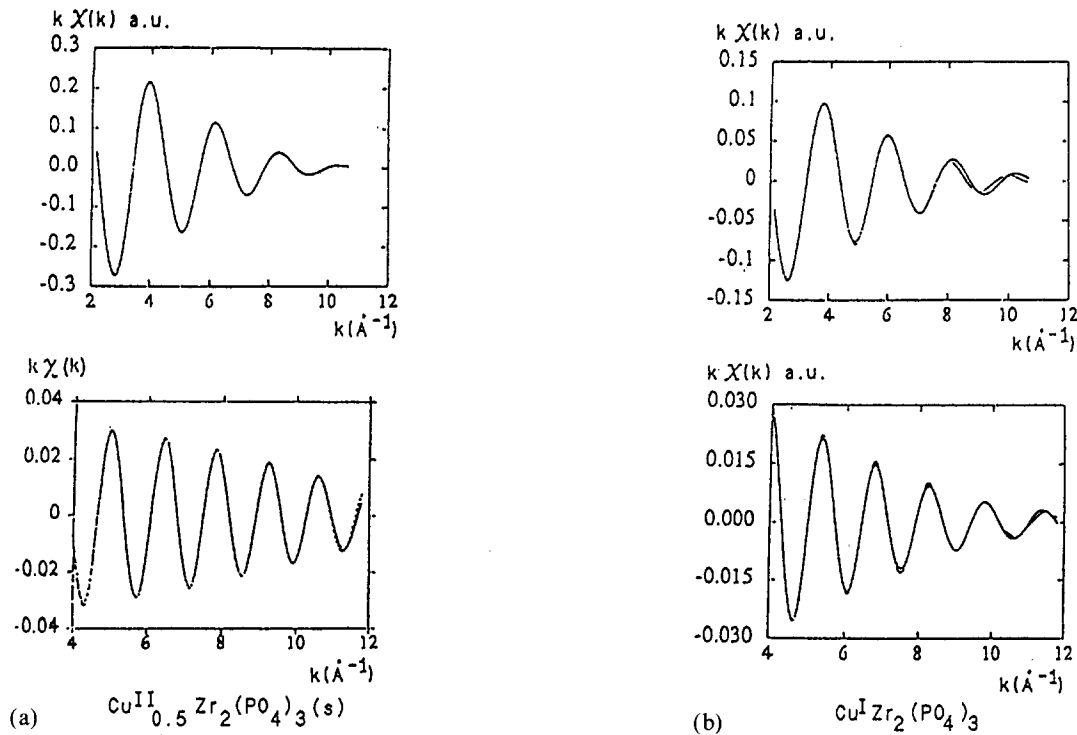


Fig. 2. Experimental (dotted line) and calculated (solid line) EXAFS spectra of the first (a) and second (b) coordination shells of copper in $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ and $\text{Cu}^{\text{II}}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s).

in both cases (Figs. 2(a) and 2(b)). The results of the simulations are reported in Table 1. For $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ we show that in agreement with neutron diffraction results, Cu^{I} atoms are located near an edge of the elongated CuO_6 octahedra, called M(1) sites, having only two nearest neighbour oxygen atoms [7]. This non-central position explains why Cu^{I} atoms can pair in the M(1) site, as shown by our EXAFS second shell results. We effectively show that $20\% \pm 4\%$ of M(1) sites contain copper pairs with $\text{Cu}^{\text{I}}\text{--Cu}^{\text{I}}$ distances of $2.40 \pm 0.04 \text{ \AA}$, $20\% \pm 4\%$ remain empty and $60\% \pm 4\%$ of them contain only one copper atom.

For $\text{Cu}^{\text{II}}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s) we find that the first shell of copper is composed of four oxygen atoms (1.95 \AA). Then each copper atom has about another copper atom in its second coordination shell and we found that the

distances between copper atoms are equal to $2.76 \pm 0.02 \text{ \AA}$. The third shell (approximately 3.5 \AA) is constituted probably of heavy atoms such as zirconium and phosphorus atoms.

4. Conclusion

These EXAFS experiments provide interesting structural information about $\text{Cu}^{\text{II}}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s) and $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$. In the former case the first shell of copper atoms involves four oxygen atoms at 1.95 \AA . For $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ the results confirm the presence of two different types of copper atoms. A neutron diffraction study of this compound had shown a statistical distribution of Cu^{I} atoms in an off-centred position

TABLE 1. Structural information for $\text{Cu}^{\text{II}}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s) and $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$

	Type of neighbour	Number of neighbours	Interatomic distance (\AA)	Debye–Waller factor (\AA^2)
$\text{Cu}^{\text{II}}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (s)				
First shell	oxygen	4.0 ± 0.6	1.95 ± 0.01	0.0036
Second shell	copper	0.92 ± 0.18	2.76 ± 0.02	0.0001
	oxygen	0.70 ± 0.14	2.82 ± 0.02	0.0001
$\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$				
First shell	oxygen	2.0 ± 0.3	1.99 ± 0.01	0.0001
Second shell	copper	0.4 ± 0.08	2.40 ± 0.02	0.0039
	oxygen	1.63 ± 0.32	2.73 ± 0.02	0.0056

with six equivalent positions for the same M(1) site. The EXAFS study shows the existence of monovalent copper pairs which is in agreement with the observed luminescent properties [4]. Such short Cu^I-Cu^I distances have been found in one inorganic material (Cu_{2x}Cr_{2x}S_{2-2x}S₄, 2.35 Å) and in numerous organo-metallic compounds (2.60–2.80 Å) exhibiting a low energy emission at room temperature [9, 10].

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