

Structure of $\text{Cu}^{\text{I}}_2\text{CrZr}(\text{PO}_4)_3$ by powder neutron diffraction

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Abstract

The crystal structure of the copper-rich Nasicon-type phosphate $\text{Cu}^{\text{I}}_2\text{CrZr}(\text{PO}_4)_3$ was solved from neutron diffraction data by the Rietveld profile method. It consists of a three-dimensional framework made of $[\text{PO}_4]$ and $[(\text{Zr}, \text{Cr})\text{O}_6]$ octahedra sharing common corners. The copper arrangement in both M(1) and M(2) sites (triangular coordination) confirms the pairing tendency as already observed from an extended X-ray absorption fine structure analysis of $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$.

1. Introduction

Cations with closed d^{10} configuration are subject to aggregate [1]. For monovalent copper, cluster-like assembly has been observed mainly in coordination compounds. Nevertheless $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ pairs were found recently in inorganic materials. In $\text{Cu}_{2x}\text{Cr}_{2x}\text{Sn}_{2-2x}\text{S}_4$ ($0 \leq 2x \leq 1$) the $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ shortest distance is 2.35 Å whereas in $\text{Cu}_6\text{Mo}_5\text{O}_{18}$, the $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ distance is 2.77 Å, i.e. 0.2 Å larger than the copper–copper distance in metal [2, 3]. A detailed investigation of the structure of the Nasicon-type phosphate $\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ by various techniques such as X-ray and neutron diffraction and X-ray absorption revealed the formation of copper pairs where the metallic ions are 2.4 Å apart [4, 5].

The present paper describes the structure of a copper-rich Nasicon-type phosphate $\text{Cu}^{\text{I}}_2\text{CrZr}(\text{PO}_4)_3$ obtained previously [6, 7].

2. Experimental details

A preliminary X-ray investigation was carried out using a Philips PW 1050 diffractometer with a Bragg–Brentano geometry. For neutron diffraction the data were collected at room temperature using the high flux beam reactor of the Institute Laue Langevin. The conditions of the data collected are given in Table 1.

3. Structure analysis

The refinement process was first developed by X-ray diffraction. The initial coordinates were those of

TABLE 1. Conditions used for data collection for neutron diffraction

| | |
|---|---|
| Diffractometer | D1A |
| Wavelength (Å) | 1.909 |
| Data collection range (2θ) (deg) | 15–50 |
| Step (2θ) (deg) | 0.05 |
| Refinement program | DBW 3.2 S (13) |
| Law for full-width at half-maximum | $(\text{FWHM})^2 = U\lg^2\theta + V\lg\theta + W$ |
| Analytic function for profile shape | Gaussian |
| a (Å) | 8.7449(3) |
| c (Å) | 21.819(1) |
| Number of reflections | 187 |
| $R_p = \sum y_i - y_{ci} / \sum y_i$ | 0.042 |
| $R_{wp} = [\sum w_i (y_i - y_{ci})^2 / \sum w_i y_i^2]^{1/2}$ | 0.053 |
| $R_1 = \sum I_i - I_{ci} / \sum I_i $ | 0.039 |

$\text{Cu}^{\text{I}}\text{Zr}_2(\text{PO}_4)_3$ in the $R\bar{3}c$ space group assuming statistical distribution of chromium and zirconium at the zirconium sites of the phosphate. The occupancy factor of copper at the M(1) site was found to be about 3/2. A second position for copper was detected at the M(2) site from a Fourier difference synthesis. Nevertheless, the X-ray refinement results were not completely satisfying, giving high Debye–Waller values for the copper atoms. Therefore, more information was obtained by neutron diffraction since copper atoms are better localized by their relative high scattering length.

As expected, the refinement converges to atomic parameters close to those found by X-ray diffraction but with more realistic Debye–Waller factors (Table 2). The agreement between observed and calculated neutron profiles is illustrated in Fig. 1.

TABLE 2. Structural parameters of $\text{Cu}^I_2\text{CrZr}(\text{PO}_4)_3$

| Atom | Site | x | y | z | B_{iso} (\AA^2) | Occupancy |
|-------|------|-----------|------------|-----------|-------------------------------------|-----------|
| Cu(1) | 36f | 0.039(2) | 0.156(2) | 0.0046(2) | 4.6(2) | 1.56(2) |
| Cu(2) | 36f | 0.650(4) | 0.074(5) | 0.295(1) | 4.6(2) | 0.44(2) |
| Zr | 12c | 0 | 0 | 0.1413(2) | 1.16(7) | 1 |
| Cr | 12c | 0 | 0 | 0.1413(2) | 1.16(7) | 1 |
| P | 18e | 0.2884(3) | 0 | 1/4 | 1.25(7) | 3 |
| O(1) | 36f | 0.1830(3) | -0.0113(3) | 0.1931(1) | 2.87 ^a | 6 |
| O(2) | 36f | 0.1959(3) | 0.1697(3) | 0.0849(1) | 1.82(5) | 6 |

^aEquivalent isotropic thermal parameter as calculated from the refined anisotropic thermal parameters

| Atom | $B_{11} \times 10^4$ | $B_{22} \times 10^4$ | $B_{33} \times 10^4$ | $B_{12} \times 10^4$ | $B_{13} \times 10^4$ | $B_{23} \times 10^4$ |
|------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| O(1) | 140(6) | 225(7) | 8.4(2) | 136(6) | -23(2) | -12(2) |

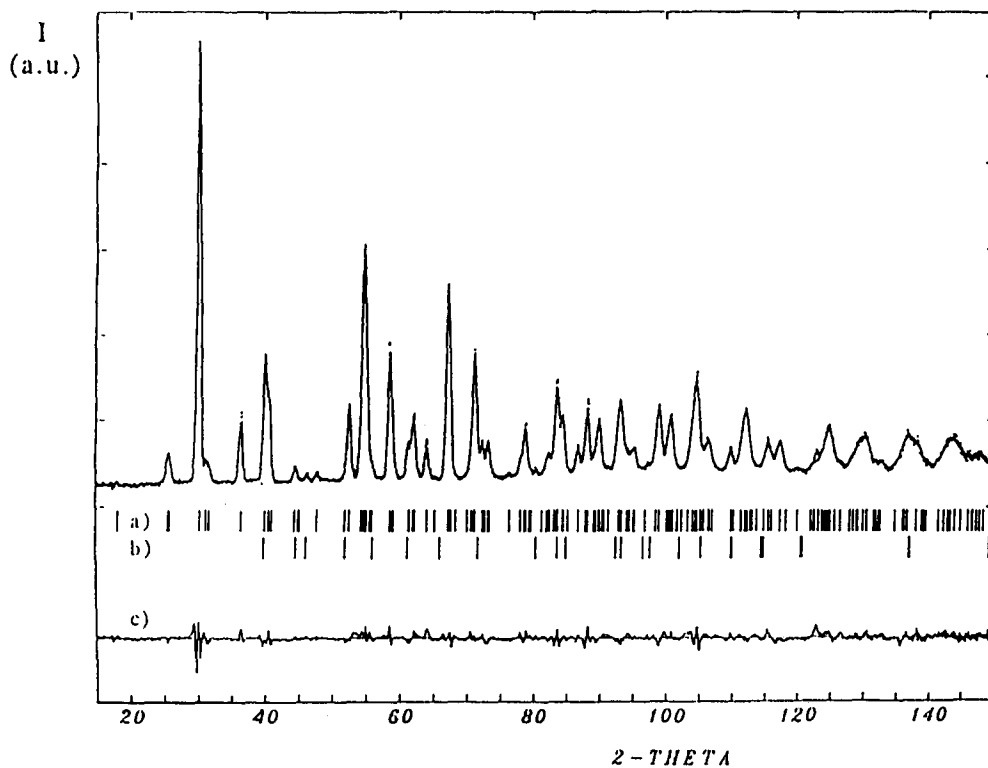


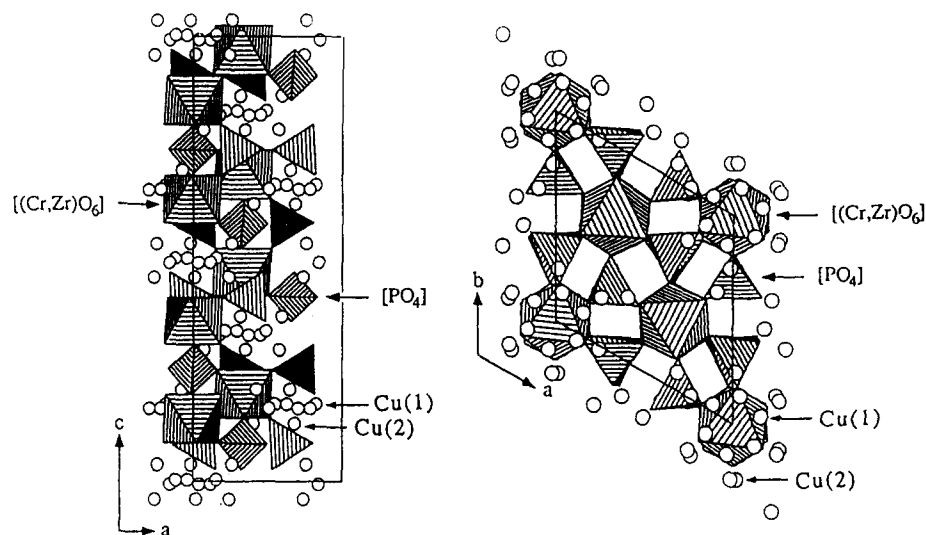
Fig. 1. Neutron diffractogram of $\text{Cu}^I_2\text{CrZr}(\text{PO}_4)_3$: comparison between experimental and calculated data.

4. Discussion

$\text{Cu}^I_2\text{CrZr}(\text{PO}_4)_3$ belongs to the Nasicon family with a three-dimensional framework of $[\text{PO}_4]$ tetrahedra and $[(\text{Zr}, \text{Cr})\text{O}_6]$ octahedra sharing common corners (Fig. 2). Table 3 gives the selected bond lengths and angles of $\text{Cu}^I_2\text{CrZr}(\text{PO}_4)_3$. The copper atoms in M(1) are located in an off-centred position. This results in copper pairing about the M(1) centre with a $\text{Cu}^I\text{-Cu}^I$ distance of 2.47 \AA . In this geometry copper atoms are three-fold

coordinated (2.00, 2.19 and 2.37 \AA) and they are located near the bottleneck in the diffusion path between the M(1) and M(2) sites (Fig. 3).

An almost identical anionic arrangement is found for Cu^I at the M(2) site, (2.13, 2.16 and 2.3 \AA) (Fig. 4). The two cationic positions in M(1) and M(2) are almost symmetrical about the common edge $\text{O}_2^1\text{-O}_2^2$ of the two sites. Copper atoms are statistically distributed in two equivalent positions at M(2) with an occupancy factor of about 1/2.

Fig. 2. Perspective views of the structure of $\text{Cu}^1_2\text{CrZr}(\text{PO}_4)_3$.TABLE 3. Selected bond lengths and angles of $\text{Cu}^1_2\text{CrZr}(\text{PO}_4)_3$.

| Distances (Å) and angles (deg) | |
|--------------------------------|----------------------|
| <i>M(1) site</i> | |
| Cu(1)–O(2) | 2.00(1) |
| | 2.19(1) |
| | 2.37(1) |
| | 3.08(1) |
| | 3.21(1) |
| | 3.33(1) |
| Cu(1)–O(1) | 2.52(1) |
| | 3.17(1) |
| O(2)–Cu–O(2) | 149(2) |
| | 135(1) |
| | 75.3(4) |
| Cu(1)–Cu(1) ^a | 2.47(2) |
| <i>M(2) site</i> | |
| Cu(2)–O(1) | 2.16(3) |
| | 2.63(4) |
| | 3.34(4) |
| | 3.42(3) |
| | 3.57(4) |
| | 3.75(4) |
| Cu(2)–O(2) | 2.13(3) |
| | 2.31(4) |
| | 2.63(4) |
| | 2.75(3) |
| | 2.82(4) |
| | 3.10(3) |
| O(1)–Cu(2)–O(2) | 165(9) |
| | 114(2) |
| O(2)–Cu(2)–O(2) | 78(1) |
| Cu(2)–Cu(1) | 1.25(4) |
| | 1.92(3) |
| | 2.33(4) |
| Cu(2)–Cu(2) | 2.26(4) |
| | 2.76(5) ^b |

TABLE 3

| Distances (Å) and angles (deg) | |
|--------------------------------|----------|
| (Zr, Cr)–O(1) | 2.002(4) |
| (Zr, Cr)–O(2) | 2.027(4) |
| O(1)–(Zr, Cr)–O(1) | 91.2(2) |
| O(1)–(Zr, Cr)–O(2) | 88.6(2) |
| | 93.2(2) |
| O(2)–(Zr, Cr)–O(2) | 87.0(2) |
| P–O(1) | 1.520(3) |
| P–O(2) | 1.520(3) |
| O(1)–P–O(1) | 109.9(3) |
| O(1)–P–O(2) | 107.7(3) |
| | 111.1(3) |
| O(2)–P–O(2) | 109.3(3) |

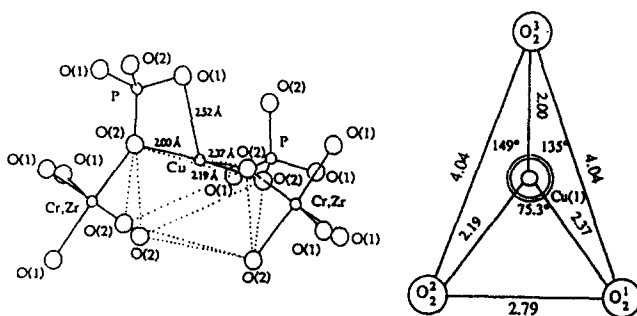
^aSymmetric position about the M(1) centre.^bBetween two M(2) sites.

Fig. 3. Oxygen surrounding copper at the M(1) site.

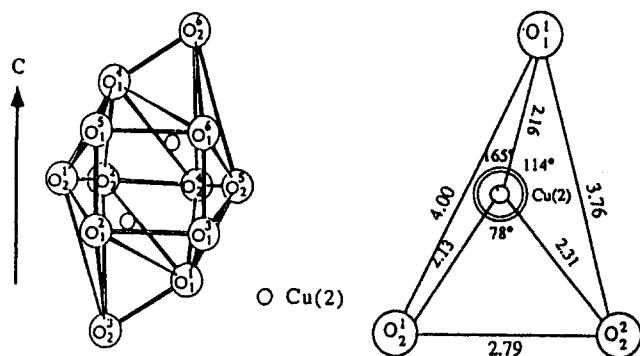


Fig. 4. Oxygen surrounding copper at the M(2) site.

5. Conclusion

A remarkable feature of the crystal structure of $\text{Cu}^{\text{I}}_2\text{CrZr}(\text{PO}_4)_3$ is the triangular coordination of Cu^{I} , whatever its location in M(1) or M(2). The total num-

ber of copper atoms at M(1) confirms strongly the copper tendency at this large site. In the Nasicon-type structure the copper pairing environment differs from those usually observed in organometallic compounds or in $\text{Cu}_6\text{Mo}_5\text{O}_{18}$ in the lack of a ligand bridge between the two metallic ions.

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