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Structure of $CuZr_2(PO_4)_3$ by X-ray and Neutron Powder Diffraction

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Abstract. Copper(I) dizirconium monophosphate, $CuZr_2(PO_4)_3$, $M_r = 530.90$, trigonal, $R\bar{3}c$, $Z = 6$, structure refined with powder diffraction methods. X-ray diffraction: $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $F(000) = 1500$, room temperature, $a = 8.9018\,(2)$, $c = 22.2021\,(6)$ Å, $V = 1523.6\,(1)$ Å^3, $D_x = 3.47$ Mg m^{-3}, $R_p = 0.039$, $R_I = 0.047$, 231 reflections. Neutron diffraction: $\lambda = 1.594$ Å, $F(000) = 642.06$ fm, room temperature, $a = 8.892\,(1)$, $c = 22.190\,(1)$ Å, $V = 1519.5\,(3)$ Å^3, $D_x = 3.48$ Mg m^{-3}, $R_p = 0.056$, $R_I = 0.091$. The atomic arrangement is a three-dimensional skeleton involving ZrO_6 octahedra and PO_4 tetrahedra sharing common corners. The Cu environment is a compromise between the usual linear coordination of Cu^I and the antiprismatic surrounding of the $M(1)$ site within the three-dimensional $Zr_2(PO_4)_3$ framework. Existence of Cu^I–Cu^I pairs within $M(1)$ is discussed with respect to the luminescent properties. The JCPDS File No. for $CuZr_2(PO_4)_3$ is 43–1495.

Introduction. Several copper(I) Nasicon-type derived phosphates have been characterized with respective compositions $Cu_{1-x}Nb_xTi_{2-x}(PO_4)_3$, $Cu_{1+x}Ti_{2-x}Cr_x(PO_4)_3$, $CuZr_2(PO_4)_3$, $CuTi_2(PO_4)_3$ and $H_{0.5}Cu_{0.5}M_2(PO_4)_3$ (M = Ti, Zr) (Yao & Fray, 1983; El Jazouli, Serghini, Brochu, Dance & Le Flem, 1985; Le Polles, Parent, Olazcuaga, Le Flem & Hagenmuller, 1988; Le Polles, El Jazouli, Olazcuaga, Dance, Le Flem & Hagenmuller, 1987; McCarron, Calabrese & Subramanian, 1987). Among these phosphates $CuZr_2(PO_4)_3$ exhibits remarkable properties in two very different fields of material science. On the one hand it is an active catalyst of 2-butanol decomposition with aperiodic oscillatory behaviour (Serghini, Kacimi, Zyiad & Brochu, 1988); on the other hand this phosphate is the first example of a Cu-rich insulating phosphor: under UV excitation blue and green fluorescences are observed respectively at low and room temperatures (Le Polles *et al.*, 1988).

In order to interpret the mechanisms of both phenomena, it was of interest to investigate its crystal structure. In the absence of a suitable single crystal, the structure determination was carried out by applying the Rietveld profile analysis method to the X-ray and neutron diffraction diagrams of polycrystalline samples.

Experimental. $CuZr_2(PO_4)_3$ was obtained by the interaction of metallic Cu with a sample of $Cu_{0.5}Zr_2(PO_4)_3$, previously obtained by a sol–gel route. The starting compounds $ZrOCl_2.8H_2O$ and CuO are separately dissolved in a 2 *M* HNO_3 solution. These solutions are mixed in stoichiometric proportions. The addition of a solution of $NH_4H_2PO_4$ under constant stirring produces a white gel. This gel and the floating solution are maintained at 353 K for 24 h and then progressively heated to 473 and 673 K to allow both ammonia and nitrous vapours to evaporate. The crystallization of $Cu_{0.5}Zr_2(PO_4)_3$ begins at 873 K and is completely achieved at 1073 K. Metallic copper reacts at 1123 K with $Cu_{0.5}Zr_2(PO_4)_3$ in a vacuum-sealed tube leading

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Table 1. *Conditions used for data collection for both X-ray and neutron diffraction*

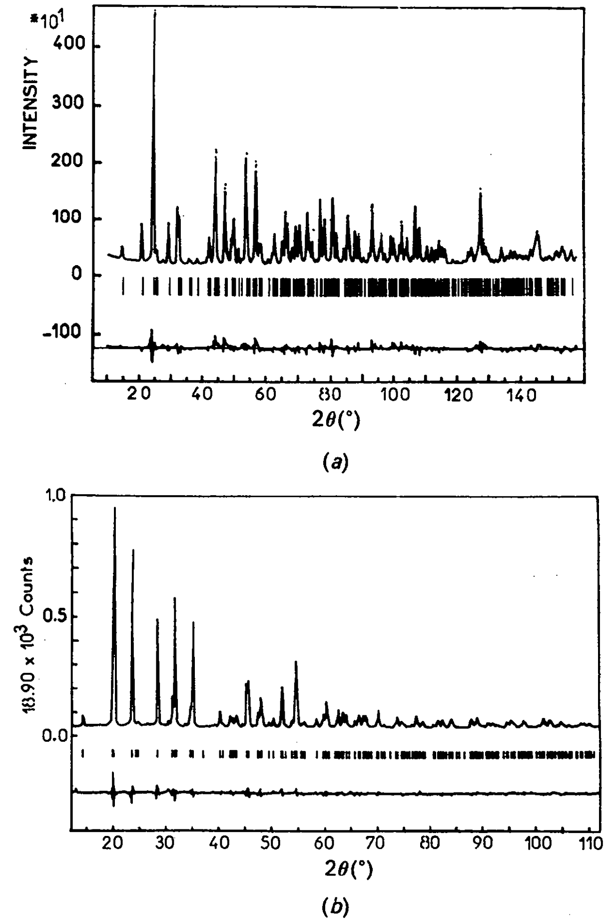
Space group $R\bar{3}c$ ($Z = 6$ in H cell).

	X-ray diffraction	Neutron diffraction
Sample container	Aluminium holder	Vanadium holder
Diffractometer	Philips PW 1050	D2B ILL Grenoble
Monochromator	Graphite	Germanium
Instrument geometry	Bragg–Brentano	Multidetector
Wavelength, λ (Å)	$K\alpha_{1-2}$Cu [$I(K\alpha_2/I(K\alpha_1) = 0.50$]	1.594 Å
Data collection range, 2θ (°)	12–112	5–165
2θ step (°), counting time (s)	0.02, 11.7	0.05, 32
Refinement program	*DBW* 3.2*S* (Wiles & Young, 1981)	*DBW* 3.2*S* (Wiles & Young, 1981)
Background	Points file	Polynomial function
Absorption correction	No	No
Preferred orientation	No	No
Law for full-width at half-maximum (FWHM)	$(\mathrm{FWHM})^2 = U\tan^2\theta + V\tan\theta + W$	$(\mathrm{FWHM})^2 = U\tan^2\theta + V\tan\theta + W$
Analytic function for profile shape	Pseudo-Voigt (*PV*), $PV = \eta L + (1-\eta)G$, $\eta = 0.341$ (6)	Gaussian
a (Å)	8.9018 (2)	8.892 (1)
c (Å)	22.2021 (6)	22.190 (1)
Number of reflections	231	337
$R_p = \Sigma\lvert y_i - y_{ci}\rvert\ \Sigma y_i$	0.039	0.056
$R_{WP} = [\Sigma w_i(y_i - y_{ci})^2/\Sigma w_i y_i\rvert^2]^{1/2}$	0.051	0.071
$R_I = \Sigma\lvert I_i - I_{ci}\rvert\Sigma\lvert I_i\rvert$	0.047	0.091

Table 2. *Final positional and thermal parameters and occupancy factors of* $CuZr_2(PO_4)_3$

XR = X-ray diffraction, N = neutron diffraction.

	Site	x	y	z	B_{iso}(Å^2)	Occupancy
Cu(*XR*)	36(*f*)	0.0454 (13)	−0.0977 (6)	0.0007 (4)	2.5 (2)	0.166
Cu(*N*)	36(*f*)	0.046 (2)	−0.093 (2)	0	3.41 (3)	0.162 (4)
Zr(*XR*)	12(*c*)	0	0	0.1419 (1)	0.62 (2)	0.333
Zr(*N*)	12(*c*)	0	0	0.142 (1)	0.87 (4)	0.333
P(*XR*)	18(*e*)	0.2861 (3)	0	0.2500	1.20 (6)	0.500
P(*N*)	18(*e*)	0.286 (1)	0	0.2500	1.10 (5)	0.500
O_I(*XR*)	36(*f*)	0.1839 (4)	−0.0082 (5)	0.1915 (2)	1.8 (1)	1.000
O_I(*N*)	36(*f*)	0.187 (1)	−0.009 (1)	0.194 (1)	1.78 (3)	1.000
O_{II}(*XR*)	36(*f*)	0.1949 (4)	0.1667 (4)	0.0832 (2)	1.3 (1)	1.000
O_{II}(*N*)	36(*f*)	0.198 (1)	0.171 (1)	0.085 (1)	1.26 (3)	1.000



(*a*)

(*b*)

Fig. 1. Diffractometer patterns of $CuZr_2(PO_4)_3$, showing comparisons between experimental and calculated data from (*a*) X-ray diffraction and (*b*) neutron diffraction experiments.

to $CuZr_2(PO_4)_3$ according to the reduction reaction:

$$Cu + 2Cu_{0.5}Zr_2(PO_4)_3 \rightarrow 2CuZr_2(PO_4)_3.$$

The absence of copper(II) in the white powder obtained was confirmed by EPR spectroscopy. Details of the data collection and of the Rietveld refinements for both X-ray and neutron diffraction methods are given in Table 1.*

X-ray diffraction. The refinement process was developed in the following steps:

(i) The initial atomic coordinates were those proposed for $NaZr_2(PO_4)_3$ by Hagman & Kierkegaard (1968). The R factors were $R_p = 0.0575$, $R_{wp} = 0.0756$ and $R_I = 0.0976$. Under these conditions the Cu isotropic thermal parameter is anomalously large.

(ii) The introduction of Cu into the usual labelled $M(2)$ sites results in an increase of all R factors.

(iii) Final atomic parameters were in fact satisfactorily obtained as Cu atoms were delocalized within the $M(1)$ antiprism with a statistical occupancy ($\frac{1}{6}$) of a general site (0.0454, 0.0977, −0.0007). The final refinement factors were $R_p = 0.0393$, $R_{wp} = 0.0507$ and $R_I = 0.0470$. The resulting atomic coordinates and their e.s.d.'s are listed in Table 2. In Fig. 1, a comparison of the experimental and calculated X-ray diffraction data is presented.

Neutron diffraction. Neutron powder diffraction data were collected at room temperature using the high-resolution powder diffractometer D2B at the high-flux beam reactor of the Institute Laue–Langevin (Grenoble). The experimental conditions are reported in Table 1. The structural scattering lengths used in the refinement were $b_{Cu} = 0.0077$, $b_{Zr} = 0.00716$, $b_P = 0.00513$ and $b_O = 0.00580$ Å. The refinement of the atomic parameters converges to values very close to those obtained from X-ray data.

Table 2 compares the final X-ray and neutron parameters of $CuZr_2(PO_4)_3$. The agreement between

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* Lists of structure factors and Rietveld-analysis data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55189 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected bond lengths* (Å) *and angles* (°) *for* $CuZr_2(PO_4)_3$

	X-ray	Neutron
Cu—O_{II}[*M*(1)]	1.98 (1)	2.06 (3)
	2.09 (1)	2.12 (3)
	2.66 (1)	2.69 (3)
	2.74 (1)	2.78 (3)
	3.20 (1)	3.24 (3)
	3.27 (1)	3.27 (3)
Cu—Cu*	2.25 (1)	2.18 (2)
Zr—O_I	2.004 (5)	2.06 (2)
Zr—O_{II}	2.082 (5)	2.08 (2)
P—O_I	1.566 (5)	1.50 (2)
P—O_{II}	1.575 (4)	1.54 (2)
O_{II}—Cu—O_{II}	163.6 (2)	162.0 (2)
O_I—P—O_I	112.2 (2)	111.5 (2)
O_{II}—P—O_{II}	109.3 (2)	108.6 (2)
O_I—Zr—O_I	92.7 (2)	91.6 (2)
O_I—Zr—O_{II}	173.0 (2)	175.0 (2)

* Symmetric position about the *M*(1) centre.

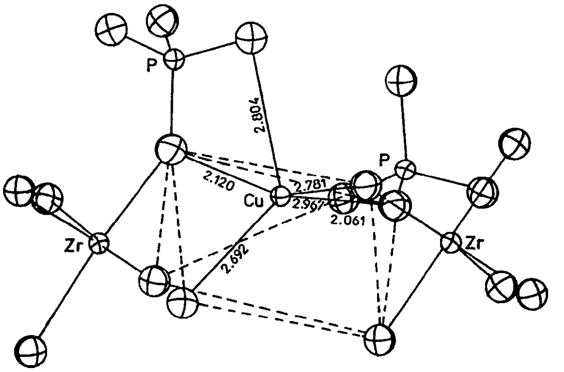

Fig. 2. O-atom environment of Cu in $CuZr_2(PO_4)_3$. Distances in Å.

observed and calculated neutron profile diagrams is illustrated in Fig. 1.

Table 3 compares selected bond distances and angles deduced from both investigations. The final calculated positions are almost identical within the limit of the e.s.d.'s. This point will be discussed below.

Discussion. The copper(I) zirconium monophosphate belongs to the Nasicon family. The three-dimensional framework is made up of PO_4 tetrahedra and ZrO_6 octahedra sharing common corners. The cation–anion distances of this skeleton can be compared with those previously reported for other $MZr_2(PO_4)_3$ (M = Li, Na, K, NH_4, H_3O) (Petit, Colomban, Collin & Boileau, 1986; Hagman & Kierkegaard, 1968; Sljukic, Matkovic, Prodic & Anderson, 1969; Rudolf, Subramanian, Clearfield & Jorgensen, 1985). For all these compounds the ZrO_6 octahedra are slightly distorted with two different Zr—O distances, such as Zr—O_{II} > Zr—O_I. The PO_4 tetrahedra are almost regular with a small dispersion of the O—P—O angles which are included between 106.5 and 112.3° in $CuZr_2(PO_4)_3$. In conclusion, the difference between the positional parameters obtained by X-ray and neutron diffraction leads to slight but significant changes in the interatomic distances only when O_I is involved.

The Cu atoms are displaced from the centre position (0,0,0) of the *M*(1) site occupied by the Na atoms in the prototype $NaZr_2(PO_4)_3$ (Fig. 2). In this site it results in two short Cu—O distances (2.05 Å) and four longer distances at about 2.70 Å. Such an environment is identical to that reported for $CuTi_2(PO_4)_3$, in which the corresponding short Cu—O distances are 2.01 and 2.06 Å, and longer distances are between 2.40 and 2.85 Å (McCarron *et al.*, 1987; Mbandza, Bordes, Courtine, El Jazouli, Soubeyroux, Le Flem & Hagenmuller, 1988). For both phosphates the Cu coordination appears to be a compromise between the usual linear coordination and the geometry of the *M*(1) site created by the covalent framework.

For cuprous oxides exhibiting linear bonds with O atoms, Cu—O distances are shortened, *e.g.* in Cu_2O (Cu—O = 1.849 Å) and in the delafossite-type structure the Cu—O distances are between 1.798 ($CuScO_2$) and 1.861 Å ($CuAlO_2$) (Swanson & Fuyat, 1953; Ishiguro, Kitazawa, Mituzani & Kato, 1981). In the case of Cu^INbO_3, which has a structure with stepped NbO_3 layers, the coordination around Cu is almost linear and the ⟨Cu—O⟩ distance is 1.85 Å. In this niobate the deviation from linearity in the O—Cu—O bonding is less than 5° (Marinder & Wahlström, 1984).

Decreasing the O—Cu—O angle leads to an increase in the Cu—O distances as can be deduced from several recent investigations, *e.g.*:

(i) In $Cu^INb_3O_8$, where Cu is located in a very distorted tetrahedron, the Cu^I—O distances range from 2.08 to 2.25 Å (Marinder, Werner, Wahlström & Malmros, 1980).

(ii) For $Cu_4^IMo_5O_{17}$, where the Cu atom can also be described as tetrahedrally coordinated, the shortest Cu—O distances range from 1.93 to 2.25 Å (McCarron & Calabrese, 1986).

It is of interest to compare the interatomic angles and distances of $CuTi_2(PO_4)_3$ and $CuZr_2(PO_4)_3$ within the *M*(1) site. In the titanium phosphate the O—O distances are shorter, involving a shrinkage of the O-atom antiprism along the *c* axis, but the mean values of the two shortest Cu—O distances are of the same order of magnitude (2.06 Å). It results in a large decrease of the O—Cu—O angles of 163.6 (Zr) and 141.8° (Ti). Accordingly, the distances between the possible Cu positions within *M*(1) are strongly reduced, *e.g.* the distance between the symmetrical positions about the $M(1)$ centre is 1.59 Å for $CuTi_2(PO_4)_3$ and 2.18 (neutron), 2.25 Å (X-ray) for $CuZr_2(PO_4)_3$. The small discrepancy between these last values is probably a result of the experimental conditions. In both cases the refinement procedures were complete and it would not be meaningfull to try to refine more detailed structural models. Actually, the least-squares deviations are usually an underestimation of the real e.s.d. and the Cu positions within $M(1)$ are probably subjected to greater uncertainties than the non-Cu atoms.

At first sight coexistence of two Cu atoms within the same $M(1)$ site seems to be unrealistic. Nevertheless, the two reported fluorescence bands of $CuZr_2(PO_4)_3$ arise clearly from two distinct excitation centres (Le Polles *et al.*, 1988). The present investigation, however, cannot relate these emissions to the existence of two crystallographic sites of the Cu ion.

As was described in detail by Rath, Holt & Tanimura (1985) various fluorescent Cu^I complexes show low-energy emissions with their maximum located between 550 and 628 nm as $Cu^I—Cu^I$ distances are less than 2.8 Å. The question of interaction between metal–metal centres in d^{10} systems is then raised. Previous calculations of Mehotra & Hoffmann (1978) do not exclude soft attractive $Cu^I—Cu^I$ interactions and the creation of such pairs could explain the room-temperature luminescence of $CuZr_2(PO_4)_3$. The occurrence of such pairs with a more precise determination of the $Cu^I—Cu^I$ nearest neighbours is presently under examination by an EXAFS investigation.

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A Niobium Silicophosphate Belonging to the Niobium Phosphate Bronze Series: $K_4Nb_8P_4SiO_{34}$

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Abstract. Niobium potassium silicophosphate, $K_4Nb_8P_4SiO_{34}$, $M_r = 1595.6$, tetragonal $P\bar{4}m2$, $a = 10.6050$ (9), $c = 6.4099$ (5) Å, $V = 720.9$ (1) Å^3, $Z = 1$, $D_x = 3.67$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 3.90$ mm^{-1}, $F(000) = 750$, $T = 294$ K, $R = 0.030$, $wR = 0.028$ for 793 reflections with $I > 3\sigma(I)$ out of 3355 unique reflections measured. This oxide is isotypic with $Na_{2-x}K_2Nb_8P_5O_{34}$, *i.e.* its structure consists of similar $[Nb_6P_4O_{26}]_\infty$ double layers related to the hexagonal tungsten bronzes which are linked through $[Nb_2SiO_8]_\infty$ chains instead of $[Nb_2PO_8]_\infty$ chains. It represents the first member of the niobium phosphate bronze series $(K_3Nb_6P_4O_{26})_n(KNb_2MO_8)$ with M = P, Si. The stability of the structure is discussed in terms of the size of the cages where K atoms are located.

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