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The Crystal Structure of $Ca_3Cu_3(PO_4)_4$

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Single crystals of $Ca_3Cu_3(PO_4)_4$ synthesized hydrothermally at 420°C and 55 kpsi (3.8 kbar) were found to occur in the space group $P2_1/a$ (No. 14) with a = 17.619(2), b = 4.8995(4), c = 8.917(1) Å, β = 124.08(1)°, and Z = 2. Full-matrix least-squares refinement of the structure using diffractometer data converged to a final anisotropic R = 0.037 (R_w = 0.046). The two calcium atoms are in six- and nine-coordination and the two copper-containing polyhedra (four- and five-coordinated) are similar to those previously found in $Cu_3(PO_4)_2$.

Introduction

Both divalent calcium and copper ions are known to exist in phosphates and other oxidic environments in sites of varied geometries. For example, in α-$Ca_3(PO_4)$, a total of 18 different calcium ions have coordination numbers ranging from five to nine (*1*). On the other hand, Cu(II) is found to occur characteristically in sites of four-, five-, and six-coordination (*2*) with a tendency to form four short and one or two longer bonds.

As part of our studies of the crystal chemistry of Cu(II) and during a successful attempt (*3*) to grow single crystals of a copper-containing whitlockite, $Ca_{18}Cu_2H_2(PO_4)_{14}$, a second phase was observed to form when the ratio of Ca to Cu in the nutrient material was less than ~9. This paper reports the crystal structure of this new phase which proved to have the composition $Ca_3Cu_3(PO_2)_4$.

Experimental

$Ca_3Cu_3(PO_4)_4$ was synthesized under hydrothermal conditions using a mixture of $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite) and $Cu_3(PO_4)_2$ as nutrient. The mixture, suspended in 0.3 ml of 0.1 M H_3PO_4 mineralizer solution, was sealed in a thin walled gold capsule and then subjected to a temperature of 420°C and pressure of 55 kpsi (3.8 kbar) for 2 weeks in a Tempress Model 112R bomb.

A sphere of this light blue material was ground to a diameter of 0.016(1) cm. Precession photographs identified the space group as $P2_1/a$.

The lattice parameters were determined in a PICK-II least-squares refinement program, using 30 reflections within the angular range $35 < 2\theta < -44°$; the reflections were automatically centered on a Picker

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FACS-I four-circle diffractometer using Mo$K\alpha_1$ radiation (λ = 0.70930 Å). At 22°C the lattice parameters were found to be a = 17.619(2), b = 4.8995(4), c = 8.917(1) Å, β = 124.08(1)°, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated volume is 637.6 Å, giving a calculated density, with Z = 2, of 3.598 g cm^{-3}.

Diffraction intensities were measured using Zr-filtered Mo$K\alpha$ radiation at a takeoff angle of 1.5° with the diffractometer operating in the ω scan mode. Ten-second background counts were taken at both ends of a 1.4° $\theta - 2\theta$ scan corrected for dispersion. Of the 1514 independent data investigated in the angular range $2\theta < 54°$, 1388 were considered observable according to the criterion $|F_o| > 3.0\sigma_F$, where σ_F is defined as $0.2|F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$; the total scan count is C, k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored; the maximum variation in intensity observed was never greater than ±3% over the data collection period.

Intensity data were corrected for Lorentz and polarization effects, and spherical absorption corrections (μ = 122 cm^{-1}, Mo$K\alpha$) were made. The maximum relative absorption correction was 1% of $|F_o|$.

The positions of the heavy atoms were determined by the program MULTAN (*4*). These positions were refined by least-squares methods and a difference Fourier map revealed all of the remaining oxygen atoms.

Full-matrix least-squares refinement (*5*) using the positional parameters for the seven atoms, a $1/\sigma^2$ weighting scheme, zerovalent scattering factors (*6*) for Cu, Ca, P, and O, isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, yielded a residual R = 0.052 and a weighted residual R_w = 0.071. The final anisotropic refinement, based on a data : parameter ratio of 12 with 188 inde-

TABLE I

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS FOR $Ca_3Cu_3(PO_4)_4$[a]

Atom	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	0	0	0	0.62(5)	0.47(4)	0.86(4)	0	0.28(4)	0
Cu(2)	1199(1)	4754(1)	9431(1)	0.59(3)	0.95(3)	0.78(3)	0.07(2)	0.38(3)	−0.10(2)
Ca(1)	1/2	0	1/2	0.76(7)	1.26(6)	0.61(6)	0	0.41(6)	0
Ca(2)	2645(1)	4621(2)	7244(2)	0.77(5)	1.03(4)	0.89(5)	0.07(4)	0.47(5)	0.25(4)
P(1)	5939(1)	−83(3)	2498(2)	0.60(6)	0.54(5)	0.66(6)	0.06(4)	0.43(5)	0.04(4)
P(2)	8406(1)	148(3)	2158(1)	0.62(6)	0.46(5)	0.76(6)	−0.01(4)	0.43(6)	−0.01(4)
O(1)	6799(3)	−946(8)	4234(6)	0.76(19)	1.00(15)	0.98(17)	0.04(13)	0.52(17)	0.09(13)
O(2)	87(3)	5496(9)	2531(6)	0.61(18)	1.27(16)	0.78(16)	0.13(13)	0.47(16)	0.07(13)
O(3)	6001(3)	2883(8)	1993(6)	0.82(18)	0.52(14)	1.06(18)	0.01(12)	0.59(16)	0.07(12)
O(4)	5824(3)	−1926(8)	935(5)	0.68(18)	0.82(15)	0.79(17)	−0.18(13)	0.56(16)	−0.11(12)
O(5)	8983(3)	−1449(9)	3888(6)	1.47(21)	1.14(16)	1.00(18)	0.67(14)	0.65(18)	0.36(14)
O(6)	8543(3)	−725(8)	660(6)	1.02(19)	0.72(14)	1.10(17)	0.17(13)	0.71(17)	0.00(13)
O(7)	3571(3)	1733(8)	2458(6)	0.89(19)	0.57(14)	1.16(18)	0.16(12)	0.66(17)	0.07(12)
O(8)	7399(3)	−380(9)	1529(6)	0.41(18)	1.37(16)	1.14(17)	−0.24(14)	0.33(16)	0.24(14)

[a] Numbers in parentheses are estimated standard deviations in the last significant figures. The B's are defined by the general temperature factor $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE II

BOND DISTANCES (Å), POLYHEDRAL EDGE LENGTHS (Å), AND BOND ANGLES (°) FOR THE METAL POLYHEDRA[a]

	Distance	Angle	Edge
Cu(1) polyhedron			
Cu(1)–O(4)	2x 1.927(3)		
Cu(1)–O(3)	2x 1.958(3)		
O(4)–Cu(1)–O(3)		2x 86.8(1)	2.669(4)
O(4)–Cu(1)–O(3′)		2x 93.2(1)	2.822(5)
O(4)–Cu(1)–O(4′)		179.9(1)	3.853(6)
O(3)–Cu(1)–O(3′)		179.9(1)	3.915(6)
Cu(2) polyhedron			
Cu(2)–O(8)	1.906(4)		
Cu(2)–O(2)	1.941(4)		
Cu(2)–O(6)	2.038(3)		
Cu(2)–O(4)	2.090(3)		
Cu(2)–O(7)	2.169(3)		
O(8)–Cu(2)–O(2)		171.0(1)	3.835(5)
O(8)–Cu(2)–O(6)		92.6(1)	2.853(5)
O(8)–Cu(2)–O(4)		82.2(1)	2.630(5)
O(8)–Cu(2)–O(7)		95.9(1)	3.031(5)
O(2)–Cu(2)–O(6)		94.4(1)	2.920(5)
O(2)–Cu(2)–O(4)		88.9(1)	2.824(5)
O(2)–Cu(2)–O(7)		87.7(1)	2.853(5)
O(6)–Cu(2)–O(4)		132.6(1)	3.779(6)
O(6)–Cu(2)–O(7)		105.0(1)	3.339(6)
O(4)–Cu(2)–O(7)		122.4(1)	3.731(5)
Ca(1) polyhedron			
Ca(1)–O(5)	2x 2.287(3)		
Ca(1)–O(2)	2x 2.304(3)		
Ca(1)–O(7)	2x 2.409(3)		
O(5)–Ca(1)–O(2)		2x 87.8(1)	3.182(5)
O(5)–Ca(1)–O(2′)		2x 92.3(1)	3.309(5)
O(5)–Ca(1)–O(7′)		2x 73.0(1)	2.796(5)
O(5)–Ca(1)–O(7)		2x 107.0(1)	3.775(6)
O(2′)–Ca(1)–O(7)		2x 74.5(1)	2.853(5)
O(2′)–Ca(1)–O(7′)		2x 105.5(1)	3.753(6)
Ca(2) polyhedron			
Ca(2)–O(1)	2.316(4)		
Ca(2)–O(8)	2.370(4)		
Ca(2)–O(3)	2.414(3)		
Ca(2)–O(7)	2.524(3)		
Ca(2)–O(6)	2.583(3)		
Ca(2)–O(4)	2.598(3)		
Ca(2)–O(1′)	2.717(3)		
Ca(2)–O(5)	2.901(4)		
Ca(2)–O(8′)	3.043(3)		
O(1)–Ca(2)–O(3)		94.4(1)	3.472(6)
O(1)–Ca(2)–O(7)		88.5(1)	3.381(6)
O(1)–Ca(2)–O(1′)		78.3(1)	3.192(5)
O(1)–Ca(2)–O(5)		83.0(1)	3.485(6)
O(1)–Ca(2)–O(8′)		91.6(1)	3.874(6)
O(8)–Ca(2)–O(7)		93.5(1)	3.566(6)
O(8)–Ca(2)–O(6)		78.2(1)	3.129(6)
O(8)–Ca(2)–O(4)		63.7(1)	2.630(6)
O(8)–Ca(2)–O(1′)		76.0(1)	3.142(6)
O(8)–Ca(2)–O(5)		53.8(1)	2.430(6)
O(3)–Ca(2)–O(6)		72.9(1)	2.973(6)
O(3)–Ca(2)–O(4)		64.2(1)	2.669(6)
O(3)–Ca(2)–O(1′)		84.5(1)	3.459(6)
O(3)–Ca(2)–O(8′)		69.5(1)	3.152(6)
O(7)–Ca(2)–O(6)		77.6(1)	3.199(7)
O(7)–Ca(2)–O(5)		61.6(1)	2.786(6)
O(7)–Ca(2)–O(8′)		52.2(1)	2.494(6)
O(6)–Ca(2)–O(4)		68.6(1)	2.918(6)
O(6)–Ca(2)–O(8′)		60.3(1)	2.853(6)
O(4)–Ca(2)–O(1′)		55.7(1)	2.484(6)
O(1′)–Ca(2)–O(5)		91.8(1)	4.037(6)

[a] Numbers in parentheses are estimated standard deviations in the last significant figures.

pendently varied parameters, yielded $R = 0.037$ and $R_w = 0.046$ for the observed data.[1] The maximum extinction correction (*7*) was 15% of $|F_o|$ for the 020 reflection.

Discussion

Table I presents the final atomic coordinates and anisotropic thermal parameters for $Ca_3Cu_3(PO_4)_4$. There are two copper and two calcium atoms in the structure. A copper atom lies on the origin with a square planar arrangement of coordinating oxygens while the other copper atom lies near the center of a distorted square pyramid. One of the calcium atoms lies on a center of symmetry at $\frac{1}{2}$, 0, $\frac{1}{2}$ and is coordinated by six oxygen atoms in a fairly regular octahedral arrangement. The second calcium atom lies in a large cavity surrounded by nine oxygen atoms.

The two copper-containing polyhedra in this structure are very similar to those

[1] See NAPS document No. 03841 for 8 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

found in $Cu_3(PO_4)_2$ (*8*). The average bond length for the square planar polyhedron in this structure is 1.943 Å as compared to 1.953 Å in the orthophosphate. The irregular five-coordinated polyhedron has four oxygens at an average length of 1.994 Å and a fifth at 2.169 Å. In the orthophosphate these four bonds have an average length of 1.965 Å and the fifth is at 2.265 Å. More interestingly, all of the corresponding bond angles in both polyhedra vary by no more than 4°. This same irregular polyhedron is also found in $Cu_3(AsO_4)_2$ (*9*) and $Cu_4(PO_4)_2O$ (*10*).

The two unique calcium atoms are found in six- and nine-coordination. The six-coordinated Ca lies on a center of symmetry with an average bond length of 2.333 Å. The nine-coordinated Ca atom

TABLE III

BOND DISTANCES (Å), POLYHEDRA EDGE LENGTHS (Å), AND BOND ANGLES (°) FOR THE PHOSPHATE TETRAHEDRA[a]

	Distance	Angle	Edge
P(1) tetrahedron			
P(1)–O(1)	1.497(4)		
P(1)–O(2)	1.532(3)		
P(1)–O(3)	1.543(3)		
P(1)–O(4)	1.575(3)		
O(1)–P(1)–O(2)		112.2(1)	2.514(6)
O(1)–P(1)–O(3)		111.8(1)	2.518(6)
O(1)–P(1)–O(4)		107.9(1)	2.484(6)
O(2)–P(1)–O(3)		111.1(1)	2.536(6)
O(2)–P(1)–O(4)		107.4(1)	2.504(6)
O(3)–P(1)–O(4)		106.1(1)	2.492(6)
P(2) tetrahedron			
P(2)–O(5)	1.506(4)		
P(2)–O(6)	1.544(3)		
P(2)–O(7)	1.551(3)		
P(2)–O(8)	1.553(3)		
O(5)–P(2)–O(6)		113.6(1)	2.551(6)
O(5)–P(2)–O(7)		112.4(1)	2.540(6)
O(5)–P(2)–O(8)		105.2(1)	2.430(6)
O(6)–P(2)–O(7)		108.5(1)	2.512(6)
O(6)–P(2)–O(8)		110.0(1)	2.537(6)
O(7)–P(2)–O(8)		106.9(1)	2.494(6)

* Numbers in parentheses are estimated standard deviations in the last significant figures.

TABLE IV

BOND DISTANCES (Å), POLYHEDRA EDGE LENGTHS (Å), AND BOND ANGLES (°) FOR THE OXYGEN POLYHEDRA[a]

	Distance	Angle	Edge
O(1) polyhedron			
O(1)–P(1)	1.497(4)		
O(1)–Ca(2)	2.316(4)		
O(1)–Ca(2′)	2.717(3)		
P(1)–O(1)–Ca(2)		137.8(3)	3.570(2)
P(1)–O(1)–Ca(2′)		96.7(2)	3.252(2)
Ca(2)–O(1)–Ca(2′)		125.1(2)	4.471(2)
O(2) polyhedron			
O(2)–P(1)	1.532(3)		
O(2)–Cu(2)	1.941(4)		
O(2)–Ca(1)	2.304(3)		
P(1)–O(2)–Cu(2)		129.5(3)	3.146(2)
P(1)–O(2)–Ca(1)		126.5(2)	3.443(2)
Cu(2)–O(2)–Ca(1)		100.7(2)	3.276(1)
O(3) polyhedron			
O(3)–P(1)	1.543(3)		
O(3)–Cu(1)	1.958(3)		
O(3)–Ca(2)	2.414(3)		
P(1)–O(3)–Cu(1)		126.1(3)	3.126(2)
P(1)–O(3)–Ca(2)		128.0(2)	3.577(2)
Cu(1)–O(3)–Ca(2)		103.4(2)	3.444(1)
O(4) polyhedron			
O(4)–P(1)	1.575(3)		
O(4)–Cu(1)	1.927(3)		
O(4)–Cu(2)	2.090(3)		
O(4)–Ca(2)	2.598(3)		
P(1)–O(4)–Cu(1)		121.6(2)	3.061(2)
P(1)–O(4)–Cu(2)		110.2(2)	3.020(2)
P(1)–O(4)–Ca(2)		99.5(2)	3.252(2)
Cu(1)–O(4)–Cu(2)		123.6(2)	3.540(1)
Cu(1)–O(4)–Ca(2)		98.0(2)	3.444(1)
Cu(2)–O(4)–Ca(2)		93.9(1)	3.443(1)
O(5) polyhedron			
O(5)–P(2)	1.506(4)		
O(5)–Ca(1)	2.287(3)		
O(5)–Ca(2)	2.901(4)		
P(2)–O(5)–Ca(1)		139.0(3)	3.563(2)
P(2)–O(5)–Ca(2)		87.4(2)	3.206(2)
Ca(1)–O(5)–Ca(2)		97.2(2)	3.912(2)
O(6) polyhedron			
O(6)–P(2)	1.544(3)		
O(6)–Cu(2)	2.038(3)		
O(6)–Ca(2)	2.583(3)		
P(2)–O(6)–Cu(2)		116.7(2)	3.059(2)
P(2)–O(6)–Ca(2)		132.3(2)	3.798(2)
Cu(2)–O(6)–Ca(2)		99.1(2)	3.535(2)

TABLE IV—*Continued*

	Distance	Angle	Edge
O(7) polyhedron			
O(7)–P(2)	1.551(3)		
O(7)–Cu(2)	2.169(3)		
O(7)–Ca(1)	2.409(3)		
O(7)–Ca(2)	2.524(3)		
P(2)–O(7)–Cu(2)		113.9(2)	3.136(2)
P(2)–O(7)–Ca(1)		120.4(2)	3.462(1)
P(2)–O(7)–Ca(2)		109.6(2)	3.375(2)
Cu(2)–O(7)–Ca(1)		91.2(2)	3.276(1)
Cu(2)–O(7)–Ca(2)		115.9(2)	3.983(2)
Ca(1)–O(7)–Ca(2)		104.9(2)	3.912(2)
O(8) polyhedron			
O(8)–P(2)	1.553(4)		
O(8)–Cu(2)	1.906(4)		
O(8)–Ca(2)	2.370(4)		
O(8)–Ca(2′)	3.043(3)		
P(2)–O(8)–Cu(2)		137.9(3)	3.230(2)
P(2)–O(8)–Ca(2)		107.8(2)	3.206(2)
P(2)–O(8)–Ca(2′)		88.3(2)	3.375(2)
Cu(2)–O(8)–Ca(2)		106.8(2)	3.443(1)
Cu(2)–O(8)–Ca(2′)		88.0(2)	3.535(2)
Ca(2)–O(8)–Ca(2′)		129.2(2)	4.899(1)

[a] Numbers in parentheses are estimated standard deviations in the last significant figures.

has an average bond length of 2.607 Å. These distances should be compared to the average Ca–O distances in the two forms of $CaCO_3$—2.356 Å in calcite (*11*) and 2.528 Å in aragonite (*12*), six- and nine-coordinated, respectively—and to 2.321 Å in six-coordinated $CaNa(H_2PO_2)_3$ (*13*) and 2.556 Å for the nine-coordinated site in $Ca_{10}(PO_4)_5(OH)_2$ (*14*). The choice of nine-coordination for Ca(2) is straightforward since there is a continuous increase in the Ca–O distance to 3.043 Å for the ninth ligand; the tenth oxygen lies at 3.71 Å. Furthermore, the valence requirements of Ca(2) are well-satisfied by nine oxygens with a sum of 1.9 v.u. (*15*). Table II lists the pertinent bond distances and angles as well as the polyhedral edge lengths for the copper and calcium. The standard deviations for all distances and angles were computed by the function and error program ORFFE (*16*).

The two phosphate tetrahedra have average bond lengths of 1.538 Å (−0.041,

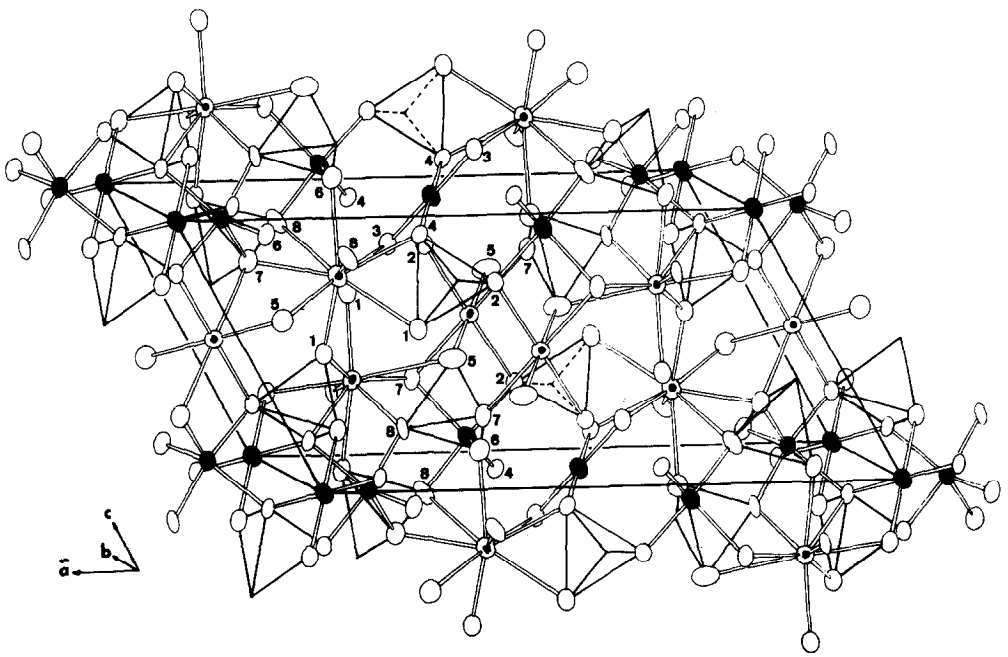

FIG. 1. The unit cell contents of $Ca_3Cu_3(PO_4)_4$ projected onto the *ac* plane but rotated 6° in two directions for clarity. The solid ellipsoids represent copper atoms and those centered with a solid dot represent calcium atoms. The phosphate tetrahedra are located but phosphorous atoms are not included.

+0.037) and 1.539 Å (−0.033, +0.014), respectively, and average bond angles of 109.4° (−3.3, +2.8; −2.5, +4.2, respectively). Three of the four shortest edges in the phosphate tetrahedra (<2.5 Å) are involved in edge-sharing with the Ca(2)-containing polyhedron; O(5)–O(8) and O(7)–O(8) from P(2) and O(1)–O(4) from P(1). Phosphate groups only corner-share with the copper-containing polyhedra. Each of the eight oxygen atoms belong to a phosphate tetrahedron and have a total of either three- or four-coordination. Table III presents the relevant distances and angles for the phosphate tetrahedra while Table IV describes the environment about each of the oxygen atoms.

Although the short lattice parameter of 4.9 Å suggests that this compound might be a layer structure on the a–c plane, this does not prove to be the case. The cation polyhedra do link together via a number of shared edges, but there are no planes of linked polyhedra that can be used to define a particular stacking arrangement for this structure. Nevertheless, the divalent cations are arranged in separate planes. All of the copper atoms are found in a layer on or near the a–b plane close to the edge of the cell. The phosphate tetrahedra as well as the Ca(2) polyhedron lie roughly parallel to this plane at c approximately $\frac{1}{4}$ and $\frac{3}{4}$ as shown in Fig. 1. Note that Cu(1) bridges to opposite Ca(2) polyhedra by sharing the O(3)–O(4) edge while Ca(1) (on a center of symmetry) edge-shares [O(5)–O(7)] with the Ca(2) polyhedra forming a Ca(2)–Ca(1)–Cu(1)–Ca(1)–. . . chain through the face centers in the [101] direction.

Acknowledgments

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References

1. M. MATHEW, L. W. SCHROEDER, B. DICKENS, AND W. E. BROWN, *Acta Crystallogr. Sect. B* **33**, 1325 (1977).
2. A. F. WELLS, "Structural Inorganic Chemistry," 4th ed., p. 887. Clarendon Press, Oxford (1975).
3. F. A. RUSZALA AND E. KOSTINER, *J. Cryst. Growth* **48**, 473 (1980).
4. G. GERMAIN, P. MAIN, AND M. N. WOOLFSON, *Acta Crystallogr. Sect. A* **27**, 368 (1971).
5. W. R. BUSING, K. O. MARTIN, AND H. A. LEVY, ORNL-TM-305 (1962).
6. "International Tables for X-Ray Crystallography," Vol. IV, p. 99. Kynoch Press, Birmingham, (1974).
7. W. H. ZACHARIASEN, *Acta Crystallogr. Sect A* **23**, 558 (1968).
8. G. L. SHOEMAKER, J. B. ANDERSON, AND E. KOSTINER, *Acta Crystallogr. Sect. B* **33**, 2969 (1977).
9. S. J. POULSEN AND C. CALVO, *Canad. J. Chem.* **46**, 917 (1968).
10. J. B. ANDERSON, G. L. SHOEMAKER, AND E. KOSTINER, *J. Solid State Chem.* **25**, 49 (1978).
11. H. CHESSIN, W. C. HAMILTON, AND B. POST, *Acta Crystallogr.* **18**, 689 (1965).
12. J. P. R. DEVILLERS, *Amer. Mineral.* **56**, 758 (1971).
13. T. MATSUZAKI AND Y. IITAKI, *Acta Crystallogr. Sect. B* **25**, 1933 (1969).
14. A. S. POSNER, A. PERLOFF, AND A. DIORIO, *Acta Crystallogr.* **11**, 308 (1958).
15. I. D. BROWN AND R. D. SHANNON, *Acta Crystallogr. Sect. A* **29**, 266 (1973).
16. W. R. BUSING, K. O. MARTIN, AND H. A. LEVY, ORNL-TM-306 (1962).