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High-Pressure Synthesis and Bond Lengths of Calcium Copper Germanium Oxide $[CaCu_3](Ge_4)O_{12}$

BY Y. OZAKI,* M. GHEDIRA, J. CHENAVAS, J. C. JOUBERT AND M. MAREZIO

Laboratoire de Cristallographie, CNRS, 166*X*, 38042 *Grenoble CEDEX, France*

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Abstract. Single crystals of $[CaCu_3](Ge_4)O_{12}$ have been synthesized under high-pressure (50–70 kbar) and high-temperature (1000°C) conditions. It has the cubic perovskite-like $[NaMn_3](Mn_4)O_{12}$ structure, $a = 7{\cdot}202$ Å, space group $= Im3$, $Z = 2$. The structure has been refined from single-crystal X-ray data. The average cation–oxygen distances are: Ca–O = 2·549 (icosahedral coordination); Cu–O = 1·960, 2·677, 3·134 (three sets of four O neighbours); Ge–O = 1·895 Å (octahedral coordination).

Introduction. The three-cation mixed oxide $CaCu_3Ge_4O_{12}$ has been synthesized as part of a continuing program in this laboratory to investigate the series of compounds with the general formula $[AC_3](B_4)O_{12}$. These compounds have a perovskite-like arrangement and are usually cubic with a doubled lattice parameter with respect to the simple ABO_3 cubic perovskite. The brackets and the parentheses are used in order to show the relation between the two structures. The doubling of the unit cell is due to the order between the *A* and *C* cations and to a distortion of the O lattice consisting of a tilting of the O octahedra forming the three-dimensional corner-sharing network. This tilting distorts the 12-coordinated sites of the simple perovskite in such a way that the *A* cations are still surrounded by 12 equidistant O atoms arranged, however, as a slightly distorted icosahedron. On the other hand, the coordination polyhedra of the *C* cations consist of four close O atoms arranged as a square and four further away arranged as a rectangle perpendicular to the square. The other four O atoms around the *C* cations are arranged as a square perpendicular to the first two sets; however, these atoms are so far apart that they must be considered second nearest neighbours. The first two sets of O atoms form a polyhedron which can accommodate

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* Present address: College of Technology, Seikei University Kichijoji Kitamachi 3, Mushashino-shi, Tokyo 180, Japan.

Jahn–Teller cations. The *B* cations are octahedrally coordinated.

Two subseries have been prepared so far: $[A\mathrm{Cu}_3^{2+}](B_4)\mathrm{O}_{12}$ and $[A\mathrm{Mn}_3^{3+}](B_4)\mathrm{O}_{12}$. When the *B* cations of the Cu subseries are Mn^{3+} and/or Mn^{4+} cations then a serious problem arises during the synthesis; in fact, some Mn can take the place of the Cu cations on the *C* sites as Mn^{3+}. The difference in charge between Mn^{3+} and Cu^{2+} is compensated by a reduction of the Mn^{4+} cations occupying the *B* sites to Mn^{3+}. This substitution and consequent reduction cause a drastic variation in the magnetic properties of these compounds which are ferro- or ferrimagnetic with rather high Curie temperatures and large spontaneous magnetization.

It is important, therefore, to synthesize compounds in which the *C* sites are, definitely, occupied by the Cu^{2+} cations and the other sites are occupied by cations which are not easily oxidized or reduced. This paper reports the synthesis and the structural refinement of $[\mathrm{CaCu_3}](\mathrm{Ge_4})\mathrm{O_{12}}$.

Single crystals of $\mathrm{CaCu_3Ge_4O_{12}}$ were prepared by subjecting a mixture of CaO + 3CuO + $4\mathrm{GeO_2}$ to a pressure of 50–70 kbar at 1000 °C and by quenching after 1 h to room pressure and temperature. $\mathrm{CaCu_3Ge_4O_{12}}$ must be prepared under high-pressure conditions in order to induce the octahedral coordination to the Ge cations. X-ray powder films showed that a complete reaction had been carried out and that the final product was a single phase and isostructural with $\mathrm{CaCu_3Mn_4O_{12}}$. The powders contained single cube-shaped crystals of edge ~0·3 mm. Precession photographs confirmed the space group *Im*3, a lattice parameter of ~7·2 Å and two molecules per unit cell. For the X-ray intensity-data collection one of the crystals was ground into a sphere 0·16 mm in diameter and placed on an automatic four-circle diffractometer equipped with Ag $K\alpha$ radiation. All possible reflections in the region $8° < \theta < 30°$ were measured by the ω-scan technique. The measuring procedure was that described in Chenavas, Joubert, Marezio & Bochu (1975). The Lorentz, polarization, and absorption (μR = 1·1) corrections were applied to the integrated intensities. The total number of independent reflections with $I > 0$ was 94. The structural refinements were carried out with the *LINEX* least-squares program. The atomic scattering factors for neutral atoms reported by Doyle & Turner (1968) were used. The anomalous dispersion correction was applied by using the f' and f'' values published by Cromer & Liberman (1970). The starting positional and thermal parameters and weighting scheme were those reported for $\mathrm{CaCu_3Mn_4O_{12}}$. The scale factor, the isotropic extinction coefficient, two positional and ten thermal parameters were varied. After convergence was attained the conventional *R* and *wR* factors were 0·011 and 0·011 respectively. The final positional and thermal parameters are reported in Table 1.* The lattice parameter, 7·202 ± 0·001 Å, was obtained by least-squares refinement on eight reflections, whose θ angles were obtained from the single crystal mounted on the automatic diffractometer for the intensity-data collection. The zero of the θ circle was obtained by measuring the θ and $-\theta$ values for each reflection.

Table 1. *Positional and thermal parameters of* $[\mathrm{CaCu_3}](\mathrm{Ge_4})\mathrm{O_{12}}$

By symmetry: $\beta_{11}=\beta_{22}=\beta_{33}$ and $\beta_{12}=\beta_{13}=\beta_{23}=0$ for Ca; $\beta_{12}=\beta_{13}=\beta_{23}=0$ for Cu; $\beta_{11}=\beta_{22}=\beta_{33}$ and $\beta_{12}=\beta_{13}=\beta_{23}$ for Ge; $\beta_{12}=\beta_{23}=0$ for O. Temperature factor = $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	Ca	Cu	Ge	O
x	0	0	0·25	0·3012 (5)
y	0	0·5	0·25	0·1859 (5)
z	0	0·5	0·25	0
β_{11}	0·0024 (4)	0·0015 (3)	0·00150 (6)	0·0025 (4)
β_{22}	0·0024	0·0019 (4)	0·00150	0·0020 (4)
β_{33}	0·0024	0·0027 (4)	0·00150	0·0014 (4)
β_{12}	0	0	−0·00008 (10)	0·0006 (4)
β_{13}	0	0	−0·00008	0
β_{23}	0	0	−0·00008	0

Discussion. The interatomic distances and angles with their standard deviations are reported in Table 2. The roman numerals indicate the position of the atom in the unit cell which is represented in Deschizeaux, Joubert, Vegas, Collomb, Chenavas & Marezio (1976).

As can be seen from the O—O distances and O—Ca—O angles, the O icosahedra around the Ca cations are almost perfect. The 20 triangles forming the icosahedron are equilateral within less than the standard deviation. The Ca—O distance (2·549 Å) is shorter than that found in $\mathrm{CaCu_3Mn_4O_{12}}$ (2·562 Å). This is because the size of the icosahedral site is determined by the size of the octahedra surrounding the *B* cations. In fact, each octahedron shares two of its faces with two icosahedra. In the present compound the octahedra are occupied by the Ge cations, which are smaller than the manganese cations occupying the octahedral sites in $\mathrm{CaCu_3Mn_4O_{12}}$. The octahedral Ge—O distance is 1·895 Å whereas the corresponding Mn—O distance in $\mathrm{CaCu_3Mn_4O_{12}}$ is 1·915 Å. As for the icosahedra, the octahedra are almost undistorted; for instance, all 12 O—Ge—O angles are equal to 90°.

As we have stated above, in the compounds containing Cu and Mn there exists the problem of the occupancy of the *C* Jahn–Teller sites. In the present compound these sites are occupied only by the Cu^{2+} cations; therefore, the three sets of Cu—O distances,

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32879 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Ca polyhedron		
Ca–O	×12	2·549 (4)
O(XXI)–O(XVII)	×24	2·681 (5)
O(XXI)–O(XVIII)	×6	2·678 (5)
O(XV)–Ca(II)–O(XVIII)	×6	116·63 (12)
O(XVI)–Ca(II)–O(XVIII)	×24	63·45 (07)
O(XXI)–Ca(II)–O(XVIII)	×6	63·37 (12)
Cu polyhedron		
Cu(I)–O(XXII)	×4	1·960 (4)
Cu(I)–O(V)	×4	2·677 (4)
Cu(I)–O(XXI)	×4	3·134 (4)
O(XIX)–O(XXII)	×4	2·678 (5)
O(XIII)–O(XXII)	×2	2·864 (5)
O(V)–O(XXII)	×8	2·679 (4)
O(XI)–Cu(I)–O(V)	×2	115·3 (1)
O(VIII)–Cu(I)–O(V)	×2	64·7 (1)
O(XIX)–Cu(I)–O(XXII)	×2	87·6 (1)
O(XIII)–Cu(I)–O(XXII)	×2	92·4 (1)
O(V)–Cu(I)–O(XXII)	×2	68·6 (1)
Ge octahedron		
Ge–O	×6	1·895 (1)
O(I)–O(XVII)	×6	2·679 (4)
O(I)–O(II)	×6	2·681 (4)
O(I)–Ge(I)–O(II)	×6	90·0 (1)
O(I)–Ge(I)–O(XVII)	×6	90·0 (1)
Important angles		
Cu(I)–O(XIX)–Ge(I)		108·0 (1)
Cu(I)–O(II)–Ge(I)		84·2 (1)
Cu(I)–O(XXI)–Ge(I)		79·1 (1)
Cu(I)–O(XIX)–Ca(I)		105·2 (1)
Cu(I)–O(II)–Ca(I)		154·0 (1)
Cu(I)–O(XXI)–Ca(II)		77·9 (1)
Ge(I)–O(I)–Ca(I)		87·8 (1)
Cu(I)–O(XIX)–Cu(II)		100·7 (1)
Cu(I)–O(XIX)–Cu(IV)		176·9 (2)
Cu(I)–O(VIII)–Cu(II)		76·1 (1)
Ge(I)–O(XXI)–Ge(II)		143·7 (2)

Table 3. *Thermal data*

		Angle (°) with		
	R.m.s. (Å)	*x*	*y*	*z*
Ca	0·079 (3)	–	–	–
Cu(1)	0·071 (2)	90	0	90
(2)	0·063 (2)	0	90	90
(3)	0·084 (3)	90	90	0
Ge(1)	0·059 (2)	55 (5)	55	55
(2)	0·064 (2)	45	135	90
(3)	0·064 (2)	114	114	35
O(1)	0·061 (4)	90	90	0
(2)	0·065 (4)	125 (25)	35	90
(3)	0·087 (4)	35	55	90

1·960, 2·677 and 3·134 Å, represent the values corresponding to the sites fully occupied by Cu^{2+}. The values corresponding to the *C* sites fully occupied by Mn^{3+} can be taken from $NaMn_3Mn_4O_{12}$. They are 1·910 2·690 and 3·258 Å respectively.

The thermal data for $CaCu_3Ge_4O_{12}$ are reported in Table 3. It can be seen that all atoms have normal thermal vibrations when compared with the data reported for $NaMn_3Mn_4O_{12}$, $CaCu_3Mn_4O_{12}$ and $ThCu_3Mn_4O_{12}$. The only difference is that in the present compound the Cu cations do not vibrate as anisotropically as in the other compounds. This is because the O atoms corresponding to the second set of Cu—O distances (2·677 Å), forming the rectangle perpendicular to the small square, are closer to the Cu cations than in the other compounds.

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