

Ca polyhedra connect together along both the [100] and [010] directions, and build up a relatively dense Ca polyhedral sheet parallel to {001}. This polyhedral sheet is waved compared to the flat octahedral sheet observed in Ca(OH)₂. As shown in Fig. 2, SiO₃OH tetrahedra and hydrogen bonds bridge the Ca polyhedral sheets lying along the {001} plane. Between the polyhedral sheets, there are oval-shaped hollow spaces.

References

- ALBERTI, A. & GALLI, E. (1980). *Am. Mineral.* **65**, 1270–1276.
 COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 DONNAY, G. & ALLMANN, R. (1970). *Am. Mineral.* **55**, 1003–1015.
 HAMID, S. G. (1981). *Z. Kristallogr.* **154**, 189–198.
 HELLER, H. (1952). *Acta Cryst.* **5**, 724–728.
 HELLER, H. (1954). *Proc. 3rd Int. Symp. Chem. Cem.* pp. 237–244, London.
 INGRAM, L. & TAYLOR, H. F. W. (1977). Grant-in-Aid Report to JCPDS.
 MALIK, K. M. A. & JEFFERY, J. W. (1976). *Acta Cryst.* **B32**, 475–480.
 NOBUGAI, G., TOKONAMI, M., TAKAHASHI, K. & MITSUDA, T. (1980). *J. Mineral. Soc. Jpn.* **14** (special issue 2), 172–180.
 RYSKIN, YA. I. & STAVITSKAYA, G. P. (1961). *Opt. Spectrosc.* **9**, 320–324.
 SAKURAI, T. (1967). Editor. *Universal Crystallographic Computation Program System*. The Crystallographic Society of Japan, Tokyo, Japan.
 TAYLOR, H. F. W. (1964). *The Chemistry of Cement*. London: Academic Press.
 TAYLOR, H. F. W. (1971). *Mineral. Mag.* **38**, 26–31.
 UDAGAWA, S., URABE, K., NATSUME, M. & YANO, T. (1980). *Cem. Concr. Res.* **10**, 139–144.
 WAN, C. & GHOSE, S. (1977). *Am. Mineral.* **62**, 503–512.

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Structure of Ag₃Cu₁₂Y₅, a New Ternary Compound

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Abstract. Dodecacopper trisilver pentayttrium, Ag₃Cu₁₂Y₅, $M_r = 1530.62$, cubic, $P4_132 (O^7)$, $a = 7.127 (4) \text{ \AA}$, $V = 362.0 (7) \text{ \AA}^3$, $Z = 1$, $D_m = 7.09$, $D_x = 7.02 \text{ Mg m}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.54178 \text{ \AA}$, $\mu = 76.31 \text{ mm}^{-1}$, $F(000) = 684$, $T = 298 \text{ K}$. The new cubic phase is of the $\beta\text{-Mn}(A13)$ type. The three Ag atoms and five Y atoms occupy 8(c) positions with $x = 0$ and the 12 Cu atoms occupy 12(d) positions with $x = 0.135$.

Introduction. A new ternary compound has been found in our recent investigation of the 773 K isothermal section of the Ag–Cu–Y system (Li, Zeng & Zhuang, 1993). The new phase, which is Ag₃Cu₁₂Y₅, has a limited solid solubility. The compositional range is 23–27% Y, 9–19% Ag and 68–54% Cu. We have therefore determined its crystal structure.

Experimental. The alloy sample of 15 g was prepared in a high-frequency induction furnace. Stoichiometric quantities of high-purity component materials, 99.98% silver, 99.99% copper and 99.9% yttrium, were melted in a MgO crucible under a pure argon atmosphere. The weight loss during melting was 0.2%. The ingot was annealed at 1123 K for four weeks in a quartz tube under vacuum, then

cooled at a rate of 10 K h⁻¹ to room temperature. Samples for X-ray diffraction analysis were powdered and annealed at 773 K for five days under vacuum.

The X-ray powder diffraction data were collected at 298 K on a Rigaku (3015) X-ray diffractometer. Cu $K\alpha$ radiation was employed and 5N purity Si powder was used as an internal standard. The scanning rate was 0.5° min⁻¹ and the data were taken over the 2 θ Bragg angle range 15–140°. The pattern lines were assigned using a computer program and were indexed successfully according to cubic structure. The lattice constant was calculated by least-squares methods.

Each unit cell contains 20 atoms based on the lattice parameter ($a = 7.127 \text{ \AA}$) and density ($D_m = 7.09 \text{ g cm}^{-3}$) measured by the specific gravity bottle method. In agreement with the formula Ag₃Cu₁₂Y₅, three atoms are silver, five atoms are yttrium and 12 atoms are copper. The employed atomic scattering factors and Lorentz–polarization factors are those listed in *International Tables for X-ray Crystallography* (1974, Vol. IV). The absorption factor and Debye–Waller temperature factor are neglected in the intensity calculation. The quantity $R = \sum |I_o - I_c| / \sum I_o = 0.14$ shows that the reflections (Table 1) are

Table 1. $\text{Ag}_3\text{Cu}_{12}\text{Y}_5$ powder pattern at 298 K ($2\theta = 15\text{--}90^\circ$)

Intensity				Intensity					
<i>hkl</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>I</i> _{obs}	<i>I</i> _{calc}	<i>hkl</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>I</i> _{obs}	<i>I</i> _{calc}
100		7.127	0.0	0.3	{ 510		1.398	0.0	0.0
110	5.043	5.040	5.0	7.5	{ 431		1.398	0.0	1.1
111	4.119	4.115	6.0	5.7	{ 511	1.372	1.372	32.0	7.4
200		3.564	0.0	0.4	{ 333	1.372	1.372		22.1
210	3.182	3.187	9.0	12.0	{ 520		1.324	0.0	0.5
211		2.910	0.0	4.0	{ 432		1.324	0.0	1.1
220	2.519	2.520	47.0	54.7	{ 521		1.301	0.0	1.6
{ 300		2.376	0.0	0.0	{ 440	1.260	1.260	23.0	22.5
{ 221		2.376	0.0	0.3	{ 522		1.241	0.0	0.0
310		2.254	0.0	2.8	{ 441		1.241	0.0	0.1
311	2.149	2.149	100.0	100.0	{ 530		1.222	0.0	0.2
222	2.059	2.058	24.0	20.0	{ 433		1.222	0.0	0.5
320		1.977	0.0	3.5	{ 531		1.205	0.0	1.1
321		1.905	0.0	2.7	{ 600		1.188	0.0	0.0
400		1.782	0.0	0.0	{ 442		1.188	0.0	0.0
{ 410		1.729	0.0	0.1	{ 610		1.172	0.0	0.5
{ 322		1.729	0.0	0.1	{ 611		1.156	0.0	0.4
{ 411		1.680	0.0	0.6	{ 532		1.156	0.0	0.4
{ 330		1.680	0.0	0.8	{ 620	1.127	1.127	6.6	8.6
331		1.635	0.0	1.4	{ 621		1.113	0.0	0.0
420		1.594	0.0	0.0	{ 540		1.113	0.0	0.0
421		1.555	0.0	2.5	{ 443		1.113	0.0	0.0
332		1.520	0.0	0.3	{ 541		1.010	0.0	0.0
422	1.456	1.455	16.0	19.2					
{ 500		1.425	0.0	0.0					
{ 430		1.425	0.0	0.0					

Table 2. Interatomic distances (Å) in $\text{Ag}_3\text{Cu}_{12}\text{Y}_5$

Atom	Neighbour	Distance (Å)
Y (Ag) (<i>c</i> ₁)	Cu (<i>d</i> ₁)	2.96
		3.04
Y (Ag) (<i>c</i> ₂)	Cu (<i>d</i> ₁)	2.87
		3.04
Y (Ag) (<i>c</i> ₂)	Cu (<i>d</i> ₂)	2.87
		2.96
Y (Ag) (<i>c</i> ₃)	Cu (<i>d</i> ₂)	2.87
		2.96
Y (Ag) (<i>c</i> ₃)	Cu (<i>d</i> ₃)	3.04
		2.87
Y (Ag) (<i>c</i> ₄)	Cu (<i>d</i> ₃)	2.87
		2.96
Y (Ag) (<i>c</i> ₄)	Cu (<i>d</i> ₄)	2.96
		3.04
Cu	Cu	2.57
Ag (Y)	Y (Ag)	3.09

consistent with the space group $P4_132 (O^7)$. This is a structure of the $\beta\text{-Mn}(A13)$ type (Smithells, 1976). The positions of the 20 atoms are as follows:

3 Ag and 5 Y atoms random in 8(*c*): (*c*₁) $x, x, x; \frac{1}{2} + x, \frac{1}{2} - x, -x$; (*c*₂) $\frac{1}{4} - x, \frac{3}{4} + x, \frac{1}{4} + x; \frac{3}{4} + x, \frac{1}{4} + x, \frac{1}{4} - x$; (*c*₃) $-x, \frac{1}{2} + x, \frac{1}{2} - x; \frac{1}{2} - x, -x, \frac{1}{2} + x$; (*c*₄) $\frac{3}{4} - x, \frac{3}{4} - x, \frac{3}{4} - x; \frac{1}{4} + x, \frac{1}{4} - x, \frac{3}{4} + x$; with $x_c = 0$.

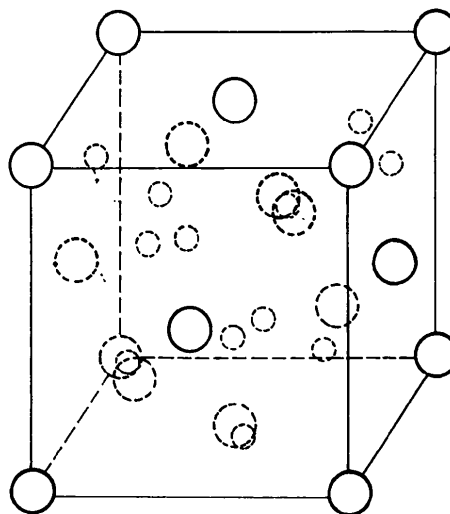
12 Cu atoms in 12(*d*): (*d*₁) $x, \frac{1}{4} + x, \frac{1}{8}; \frac{7}{8}, \frac{1}{2} + x, \frac{1}{4} - x; \frac{1}{4} + x, \frac{1}{8}, x$; (*d*₂) $\frac{1}{8}, x, \frac{1}{4} + x; \frac{3}{4} - x, \frac{5}{8}, \frac{1}{2} - x; -x, \frac{3}{4} + x, \frac{3}{8}$; (*d*₃) $\frac{5}{8}, \frac{1}{2} - x, \frac{3}{4} - x; \frac{1}{4} - x, \frac{7}{8}, \frac{1}{2} + x; \frac{1}{2} - x, \frac{3}{4} - x, \frac{5}{8}$; (*d*₄) $\frac{5}{8}, -x, \frac{3}{4} + x; \frac{3}{4} + x, \frac{5}{8}, -x; \frac{1}{2} + x, \frac{1}{4} - x, \frac{7}{8}$; with $x_d = 0.135$.

Discussion. The structure is shown in Figs. 1 and 2. Fig. 2 is a projection in the [100] direction. Fig. 1 shows that the structure consists of eight layers of atoms. Each layer of atoms is of the same kind, and different kinds of atoms from different layers pack alternately. For copper, each layer has three atoms

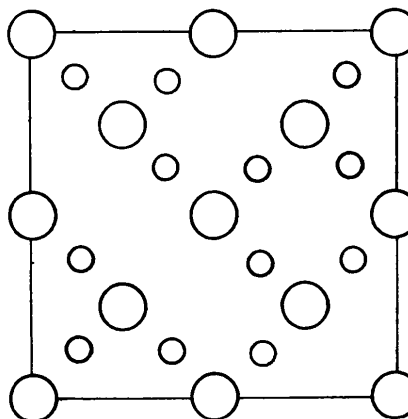
and for yttrium (or silver) each layer has two. The interatomic distances are listed in Table 2. The nearest distances between Cu and Y (or Ag), and Y and Ag are 2.87 and 3.09 Å, respectively. The nearest distance between Cu and Cu is 2.57 Å, which is very near the value (2.56 Å) of the interatomic distances in pure copper.

Ag and Y atoms are bigger than Cu atoms ($r_{\text{Ag}} = 1.44$, $r_{\text{Y}} = 1.78$, $r_{\text{Cu}} = 1.28$ Å), so it is reasonable to assume that three Ag and five Y atoms will have statistical distribution in 8(*c*). This conjecture was verified by the intensity calculation.

According to the model of hard spheres, the efficiency (η) of space filling of $\text{Ag}_3\text{Cu}_{12}\text{Y}_5$ is 0.72. When $\eta = 0.74$, the composition of the compound is 13%Ag–60%Cu–27%Y, which is in agreement with the maximum solubility for Y determined by Li, Zeng & Zhuang (1993).



○ Cu ● Y or Ag

Fig. 1. Unit cell of $\text{Ag}_3\text{Cu}_{12}\text{Y}_5$.Fig. 2. The projection of the $\text{Ag}_3\text{Cu}_{12}\text{Y}_5$ structure in the [100] direction.

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References

- LI, D., ZENG, L. & ZHUANG, Y. (1993). To be published.
SMITHELLS, C. J. (1976). *Metals Reference Book*. London/Boston: Butterworth.

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Isostructural Trigonal-Bipyramidal Cu^{II} and Nominally 1% Cu^{II}-Doped Zn^{II} Complexes with N₅ Ligand

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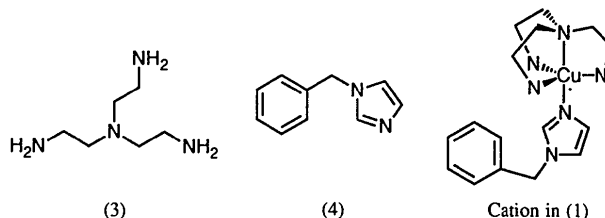
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Abstract. [Cu(C₆H₁₈N₄)(C₁₀H₁₀N₂)](ClO₄)₂, (1-benzylimidazole)[*N,N*-bis(2-aminoethyl)-1,2-ethanediamine]copper(II) diperchlorate (1), *M_r* = 566.88, monoclinic, *P*2₁/*c*, *a* = 10.549 (1), *b* = 9.2465 (9), *c* = 25.256 (2) Å, β = 101.42 (1)°, *V* = 2415 (1) Å³, *Z* = 4, *D_m* = 1.54 (1), *D_x* = 1.559 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 1.18 mm⁻¹, *F*(000) = 1172, *T* = 296 (1) K, *R* = 0.048, *wR* = 0.069 for 3063 reflections. [Zn_{0.99}Cu_{0.01}(C₆H₁₈N₄)(C₁₀H₁₀N₂)](ClO₄)₂, 1% Cu^{II}-doped (1-benzylimidazole)[*N,N*-bis(2-aminoethyl)-1,2-ethanediamine]zinc(II) diperchlorate (2), *M_r* = 568.72, monoclinic, *P*2₁/*c*, *a* = 10.708 (1), *b* = 9.229 (2), *c* = 25.205 (2) Å, β = 101.867 (8)°, *V* = 2438 (1) Å³, *Z* = 4, *D_m* = 1.54 (1), *D_x* = 1.549, λ(Mo *K*α) = 0.71073 Å, μ = 1.30 mm⁻¹, *F*(000) = 1176, *T* = 295 (1) K, *R* = 0.041, *wR* = 0.055 for 3282 reflections. The isostructural distorted trigonal-bipyramidal MN₅ cations are separated by perchlorate anions. Equatorial *M*—N distances are similar in both cations [range 2.083 (3) to 2.105 (3) Å for (1); 2.073 (3) to 2.084 (3) Å for (2)]. In contrast, the axial *M*—N distances differ substantially [2.043 (3) and 1.971 (3) Å for (1); 2.255 (4) and 2.054 (3) Å for (2)]. Axial contraction in the copper complex (1) is consistent with a *d*₂ ground state.

Introduction. As part of a long-term project designed to help understand the structural and spectroscopic properties of the active sites of selected metalloproteins, we have prepared and characterized numerous low molecular-weight analogues (Bharadwaj, Schugar & Potenza, 1991). The goal in the present study was to prepare both a distorted trigonal-bipyramidal CuN₅ complex having apical imidazole

ligation and a magnetically dilute Cu^{II}-doped Zn^{II} analogue. We report here the preparation and crystal structure of Cu(3)(4).2ClO₄ (1), and its isostructural Cu^{II}-doped Zn^{II} analogue, Zn_{0.99}Cu_{0.01}(3)(4).2ClO₄ (2).



The tetradentate ligand tris(2-aminoethyl)amine (3) is well suited to impose trigonal-bipyramidal geometry, allowing molecules such as 1-benzylimidazole (4) to bind at the open site. Both amine oxidases and galactose oxidase are thought to be five-coordinate around the active Cu site, though the donors are mixed nitrogen and oxygen (Lontie, 1984).

Experimental. An acetonitrile solution of 230 mg (1.57 mmol) of (3), 580 mg (1.57 mmol) of [Cu(ClO₄)₂].6H₂O, and 250 mg (1.58 mmol) of (4) was filtered and placed in a desiccator containing tetrahydrofuran. Vapor diffusion afforded large bright-blue crystals of (1). Nominally 1% doped (2) was prepared in a similar way using a 1:99 mol % ratio of [Cu(ClO₄)₂].6H₂O and [Zn(ClO₄)₂].6H₂O.

Details of the structure solution have values for (2) in parentheses. *D_m* was measured by flotation using a hexane/carbon tetrachloride/1,2-dibromoethane mixture for (1) and (2); bright-blue prism, 0.19 × 0.32 ×

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