Crystal structure of the oxides BaCuGd$_2$O$_5$ and Ba$_2$Cu$_3$GdO$_{7-x}$

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We have grown crystals of BaCuGd$_2$O$_5$ and Ba$_2$Cu$_3$GdO$_{7-x}$ and determined their structures by single-crystal x-ray diffraction. Green and black BaCuGd$_2$O$_5$ are roughly identical. In the refinement of Ba$_2$Cu$_3$GdO$_{7-x}$ a value of $x = 0.5$ is obtained. The existence of oxygen vacancies is compatible with an incommensurable system and also with high-order superstructures.

The high T_c's in the Ln-Ba-Cu superconductors were first obtained in polycrystalline material with nominal composition Ba$_{0.8}$Y$_{1.2}$CuO$_{4-y}$, which was a mixture of several phases, the most abundant a green semiconductor, BaCuY$_2$O$_5$, and a superconducting phase, Ba$_2$Cu$_3$Y-O$_{7-x}$. Polycrystalline BaCuGd$_2$O$_5$ is[1] orthorhombic, $a = 12.321(2)$, $b = 7.226(2)$, $c = 5.724(1)$ Å, and probable space groups *Pnma* (no. 62) and *Pna2$_1$* (no. 33). The structure of Ba$_2$Cu$_3$GdO$_{7-x}$ has not been solved (to our knowledge), but it is known that this oxide is isomorphic with orthorhombic Ba$_2$Cu$_3$YO$_{7-x}$, whose structure has been refined[2] from high-resolution neutron powder diffraction data in the space group *Pmmm*. In this

Brief Report we present the results of a study in which we have grown crystals of BaCuGd$_2$O$_5$ and Ba$_2$Cu$_3$GdO$_{7-x}$, and have established both structures from single-crystal x-ray diffraction data.

The samples were prepared by our mixing stoichiometric amounts of analytical grade BaCO$_3$, Co(NO$_3$)$_2$·6H$_2$O, CuO, and Gd$_2$O$_3$ for compositions Ba$_2$CoCu$_2$GdO$_{6.5}$ (sample A), and Ba$_2$Cu$_3$GdO$_{6.5}$ (sample B), grinding, and heating in a Pt crucible at 890 °C in air for one day. After being annealed, the materials were pelletized, sintered at 1000 °C for one day, and slowly reannealed in air. When observed through a magnifying glass, sample A contained a mixture of black and light green prismatic

TABLE I. Crystal data for the oxides BaCuGdO$_5$ and Ba$_2$Cu$_3$GdO$_{7-x}$.

	BaCuGd$_2$O$_5$	Ba$_2$Cu$_3$GdO$_{7-x}$
M (formula weight)	595.4	734.6
Crystal size (mm^3)	0.012×0.012×0.032	0.106×0.106×0.025
System	Orthorhombic	Orthorhombic
a (Å)	12.339(2)	3.859(1)
b (Å)	7.2065(9)	3.885(2)
c (Å)	5.7296(7)	11.759(3)
V (Å^3)	509.5(1)	176.3(1)
Formulas per unit cell	4	1
Calculated density (gcm^{-3})	7.76	6.92
Structure factor for reflection (000)	1012	319-311
μ(Mo $K\alpha$) (linear absorption coefficient for $K\alpha$ wavelength of molibdenum radiation, cm^{-1})	375.5	292.3
Space group	*Pnma* (no. 62)[a]	*Pmmm* (no. 47)[a]
Measured reflections	800	349
Observed reflections	539	272
R	2.5	4.0
$R_w = (\sum(|F_0| - |F_c|)^2)^{1/2}$	2.8	4.5
Average shift-to-error ratio	0.003	0.002

[a]Reference 4.

TABLE II. Atomic parameters for $BaCuGd_2O_5$ and Ba_2Cu_3-GdO_{7-x}.

Atom	x/a	y/b	z/c
		$BaCuGd_2O_5$	
Ba	0.9046(1)	0.25	0.9302(1)
Cu	0.6580(2)	0.25	0.7101(3)
Gd(1)	0.2892(1)	0.25	0.1158(1)
Gd(2)	0.0741(1)	0.25	0.3954(1)
O(1)	0.4334(6)	−0.0107(14)	0.1689(10)
O(2)	0.2279(6)	0.5058(16)	0.3543(11)
O(3)	0.0995(10)	0.25	0.0752(16)
		$Ba_2Cu_3GdO_{7-x}$	
Ba	0.50	0.50	0.1886(1)
Cu(1)	0	0	0
Cu(2)	0	0	0.3557(3)
Gd	0.50	0.50	0.50
O(1)	0	0.50	0
O(2)	0.50	0	0.3744(14)
O(3)	0	0.50	0.3757(14)
O(4)	0	0	0.1563(17)

TABLE III. Interatomic distances d (Å), the number of equal metal-oxygen distances (n), and principal angles (deg) for $BaCuGd_2O_5$ and $Ba_2Cu_3GdO_{7-x}$, and estimated standard deviations (σ) in distances and angles.

$BaCuGd_2O_5$			$Ba_2Cu_3GdO_{7-x}$		
	d (Å)	n		d (Å)	n
Ba-O(1)	3.069	4	Ba-O(1)	2.940	2
-O(1)	3.272	2	-O(2)	2.924	2
-O(2)	2.972	2	-O(3)	2.926	2
-O(2)	3.053	2	-O(4)	2.764	4
-O(3)	2.621	1			
-O(3)	2.866	2			
Cu-O(1)	1.978	2	Cu(1)-O(1)	1.943	2
-O(2)	2.039	2	-O(4)	1.838	2
-O(3)	2.179	1			
Gd(1)-O(1)	2.355	2	Cu(2)-O(2)	1.942	2
-O(2)	2.382	2	-O(3)	1.957	2
-O(2)	2.357	2	-O(4)	2.344	1
-O(3)	2.359	1			
Gd(2)-O(1)	2.337	2	Gd-O(2)	2.440	4
-O(1)	2.403	2	-O(3)	2.421	4
-O(2)	2.416	2			
-O(3)	2.329	1			

Configuration	Angle (deg)	Configuration	Angle (deg)
∠O(1)-Cu-O(2)	165.9	∠O(1)-Cu(1)-O(1)	180.0
∠O(1)-Cu-O(3)	103.1	∠O(1)-Cu(1)-O(4)	90.0
∠O(2)-Cu-O(3)	90.8	∠O(2)-Cu(2)-O(3)	89.2
		∠O(2)-Cu(2)-O(4)	96.5
		∠O(3)-Cu(2)-O(4)	96.9

Involved atom	σ (Å)	σ (deg)	Involved atom	σ (Å)	σ (deg)
Gd	0.009		Gd	0.009	
Ba	0.007		Ba	0.007	
Cu	0.009	0.3	Cu	0.007	0.3

crystals lying on a polycrystalline dark substratum, whereas sample B contained reflecting prismatic, quasicubic, crystals of metallic luster. Sample A crystals did not contain cobalt, not even traces.

The three crystals were mounted in an Enraf-Nonius CAD-4F diffractometer. Intensities within $1° < \theta < 30°$ were measured at 295 K, considering as observed those of $I > 2\sigma(I)$. Additional details on data collection and structure determination can be found elsewhere.[3] Green crystal of sample A was anisotropically refined within space groups $Pnma$ and $Pna2_1$, up to final R values of 2.5 and 3.0 where $R = \sum |F_0| - |F_c| / \sum |F_0|$, and F_0 and F_c are the observed and calculated structure factors, respectively. In $Pnma$ all the anisotropic thermal parameters determinants were positive; in $Pna2_1$ some of them became negative, and the standard deviations were larger. Hence, the space group $Pnma$ was retained. Black A crystal led to $R = 2.8$ in space group $Pnma$; and to $R = 3.1$ with all determinants negative in $Pna2_1$. Both A crystals are roughly identical. The structure of $Ba_2Cu_3GdO_{7-x}$ was anisotropically refined, excluding Ga, Cu(2), and O(4) atoms, in the $Pmmm$ space group (no. 47). Crystal data for both oxides are included in Table I. Atomic positions and standard deviations are shown in Table II. Main interatomic distances and angles can be seen in Table III.

The structure determined for $CuBaGd_2O_5$ confirms that previously established,[1] but there are relatively large differences in three Cu-O distances: two of 2.34 Å and one of 2.49 Å first reported,[1] against two of 2.039 Å and one of 2.179 Å in our case. A stereoscopic projection of the unit-cell of $CuBaGd_2O_5$ is shown in Fig. 1. In the CuO_5 tetragonal pyramid Cu is situated at 0.249(2) Å on the basal plane, and the angle formed by CuO(3) and a perpendicular to the same basal plane equals 8.3(3)°. On the other hand, in Gd_2BaCuO_5 some metal-metal dis-

tances are shorter than those expected; for instance, the $Gd(1)-Gd(2)$ is 0.25 Å shorter than the same distance in Gd metal.[4]

Crystal data determined for $Ba_2Cu_3GdO_{7-x}$ are similar to those established for the Y compound from neutron powder diffraction data,[2] but some difference was observed during the isotropic refinement of the O(1) atom. After obtaining a temperature factor about ten times the average thermal parameter of the other oxygen atoms, this average value was fixed for O(1), and the population factor was refined. After several cycles of refinement this factor fell to 0.44(7) and remained unchanged. Then, this population factor was fixed, and the refined temperature factor obtained for O(1) was not so large as David et al.[2] report, but equal to that of O(4), that is, slightly higher than the average for oxygen atoms.
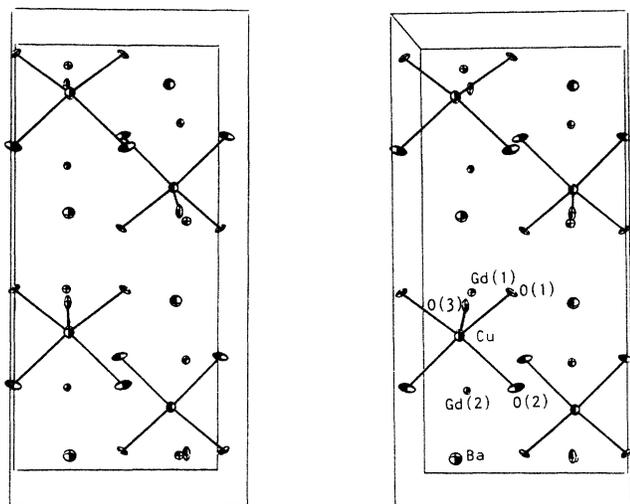
The structure of $Ba_2Cu_3GdO_{7-x}$ is the same as that of

FIG. 1. From Ref. 5. Stereoscopic pair of the cell of $BaCuGd_2\text{-}O_5$ viewed from [100]. Ellipsoid probability, 70%.

the compound of yttrium.[2] $a\text{-}b$ and $b\text{-}c$ perspectives of the unit-cell are shown in Fig. 2. Ba is located at 0.127(2) Å above the $a\text{-}b$ plane of O(4) atoms. The Cu cations are of two kinds: Cu(1), with a square planar oxygen coordination; and Cu(2) coordinated to five oxygens at the vertexes of a square pyramid. The number of Cu(2) is twice that of Cu(1). Two-thirds of the $a\text{-}b$ planes containing copper consist of pyramidal, quasiplanar, corner-linked $Cu(2)O_4$ groups, with the Cu atom at 0.227(3) Å from the oxygen plane and towards the apical oxygen. There are two different distances of Cu(2) to basal oxygens, 1.94 and 1.96 Å, being 2.34 Å the distance to the apical oxygen. Oxygen atoms O(2) and O(3) lie upon the $a\text{-}b$ planes defined by Cu(2) atoms, at 0.2187(2) and 0.2328(2) Å, respectively. The quasiplanar CuO_4 groups form two-dimensional $a\text{-}b$ sheets slightly puckered. In addition, there are one-dimensional chains of planar $Cu(1)O_4$ units in the $b\text{-}c$ plane, linked parallel to the b direction, and weakly bound to the quasiplanar $Cu(2)O_4$ pyramids by the apical bond of 2.344 Å. Some metal-metal distances are shorter than those expected: for instance, two Ba-Ba distances of 3.859 and 3.885 Å, shorter than this distance in Ba metal,[4] 4.34 Å.

We have also tried the refinement performed for the yttrium compound by David et al.,[2] obtaining an identical population factor, 0.92(3), for O(2). This factor would imply for our crystal: the formula $Ba_2Cu_3GdO_{6.85}$; bond valences[2,6] 2.29 and 2.51 for Cu^{2+} and Cu^{3+} respectively at Cu(1) sites, and 2.03 and 2.07 for Cu^{2+} and Cu^{3+} respectively at Cu(2) positions; and, hence, Cu^{2+} at pyramidal Cu(2) positions, and a $Cu^{3+}:Cu^{2+}$ distribution at the planar positions of 70:15. Nevertheless, we retain our
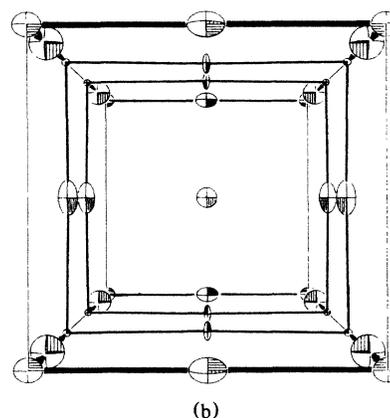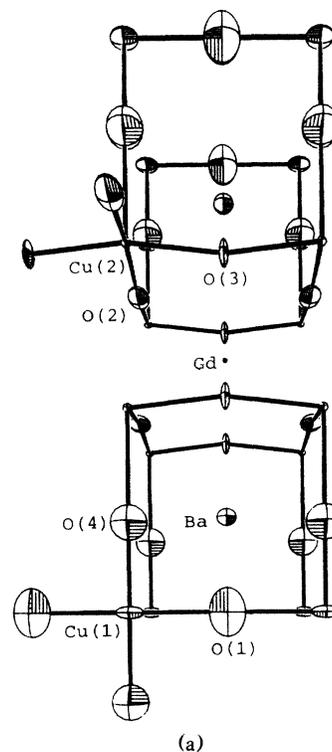

FIG. 2. From Ref. 5. Perspectives of the cell of Ba_2Cu_3Gd-O_{7-x} viewed at 7.5 inches from: (a) [100]; (b) [001]. Ellipsoid probability, 90%.

refinement by the reasons above mentioned. On the other hand, extremely wider $0k0$ reflections, for instance 2.3° instead of 1.0° for reflection 040, have been observed, denoting disorder in the b direction. This observation is compatible with the existence in this direction either of an incommensurable system, or of high-order superstructures.

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