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A New High-Temperature Superconductor: Bi$_2$Sr$_{3-x}$Ca$_x$Cu$_2$O$_{8+y}$

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A new superconductor that displays onset behavior near 120 K has been identified as Bi$_2$Sr$_{3-x}$Ca$_x$Cu$_2$O$_{8+y}$ with x ranging from about 0.4 to 0.9. Single crystal x-ray diffraction data were used to determine a pseudo-tetragonal structure based on an A-centered orthorhombic subcell with $a = 5.399$ Å, $b = 5.414$ Å, and $c = 30.904$ Å. The structure contains copper-oxygen sheets as in La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_7$, but the copper-oxygen chains present in YBa$_2$Cu$_3$O$_7$ do not occur in Bi$_2$Sr$_{3-x}$Ca$_x$Cu$_2$O$_{8+y}$. The structure is made up of alternating double copper-oxygen sheets and double bismuth-oxygen sheets. There are Ca^{2+} and Sr^{2+} cations between the adjacent Cu-O sheets; Sr^{2+} cations are also found between the Cu-O and Bi-O sheets. Electron microscopy studies show an incommensurate superstructure along the a axis that can be approximated by an increase of a factor of 5 over the subcell dimension. This superstructure is also observed by x-ray diffraction on single crystals, but twinning can make it appear that the superstructure is along both a and b axes. Flux exclusion begins in our samples at about 116 K and is very strong by 95 K. Electrical measurements on a single crystal of Bi$_2$Sr$_{3-x}$Ca$_x$Cu$_2$O$_{8+y}$ show a resistivity drop at about 116 K and apparent zero resistivity at 91 K.

MICHEL ET AL. (*1*) REPORTED superconductivity in the Bi/Sr/Cu/O system with a transition temperature (T_c) in the 7 to 20 K range. Although they presented some unit cell dimensions, they did not report a structure for the compound they designated as Bi$_2$Sr$_2$Cu$_2$O$_{7+y}$. On 22 January 1988, there was a report from Maeda *et al.* (*2*) that a T_c onset near 120 K can be obtained in the Bi/Sr/Ca/Cu/O system. This result was immediately reproduced by others (*2*). Chu and co-workers (*2*) subsequently announced superconductivity in the Bi/Sr/Ca/Cu/Al/O system but indicated that the Al was not important. Although some characterization of phases in the Bi/Sr/Ca/Cu/O system has been reported (*3*), none of the structures of the various phases in the system have been revealed. We have explored these systems and discovered a superconducting phase best described as Bi$_2$Sr$_{3-x}$Ca$_x$Cu$_2$O$_{8+y}$.

Many compositions (about 300) in the Bi/Sr/Ca/Cu/O system were prepared by re-acting Bi$_2$O$_3$, CaCO$_3$, SrO$_2$/Sr(NO$_3$)$_2$, and CuO in various proportions at 700° to 900°C in air for 12 to 36 hours. Black, plate-like, and needle-shaped crystals were found in many preparations. Flux exclusion measurements showed superconductivity around 85 to 95 K in many of the samples but never in samples prepared at 700°C. Most of our samples were slowly cooled. However, quenching the samples directly into liquid nitrogen did not lower the T_c

significantly. Powder x-ray diffraction revealed that most products were multiphase containing unreacted CuO, mixed oxides of Ca, Sr, and Cu, as well as a new phase having a characteristic reflection with a *d*-value of ~15.4 Å in the powder pattern. The Meissner effect was particularly strong whenever the 15.4 Å *d*-value in the x-ray pattern was predominant. Chemical analyses on samples showing the strongest flux exclusion indicated that of the total copper present about one-third is Cu^{3+} and two-thirds is Cu^{2+}.

Single crystals of the superconducting phase were grown from a Bi:Sr:Ca:Cu = 2:2:1:3 oxide mixture in a gold crucible. The mixture was heated to 850° to 900°C, held for 36 hours and cooled at the rate of 1°C per minute. Plate-like crystals that exhibited cleavage in the basal plane were predominant in the melt. They were mechanically separated and used for further characterization and structure determination. Both flux exclusion and electrical resistivity measurements on the single crystals revealed a sharp superconducting transition at $T_c \sim 95$ K (Figs. 1 and 2). In these single crystals the T_c onset occurs at about 116 K. This suggests that it is unlikely that two distinctly different structures are responsible for T_c's near 116 K and 95 K.

Single crystal x-ray diffraction information is summarized in Table 1. Many crystals show superstructure along the a and b axes, characteristic of twinning. Axial oscillation photographs of a crystal showed a super-
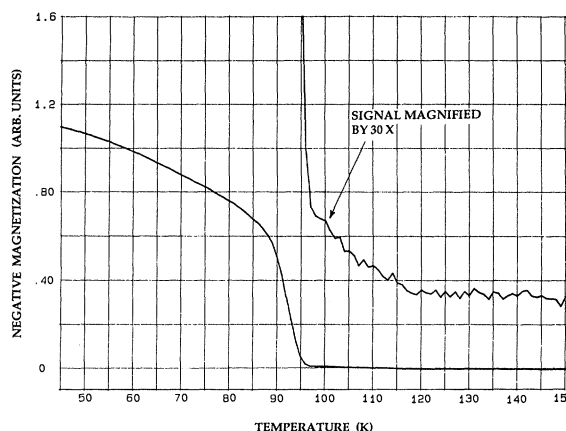
Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, DE 19898.

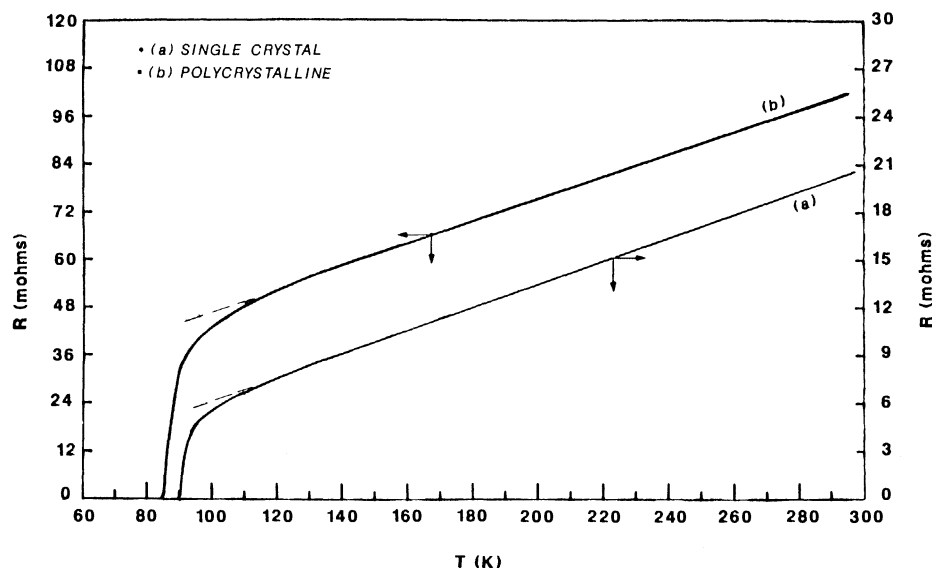**Fig. 1.** Magnetic flux exclusion of a few randomly oriented single crystals of Bi$_2$Sr$_{3-x}$Ca$_x$Cu$_2$O$_{8+y}$ superconductor measured by an ac susceptometer.

Fig. 2. Resistivity curves for $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ superconductor.

Fig. 3. Structure of $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ showing the CuO_2 layers. Metal atoms are shaded and only Cu-O bonds are shown. Oxygen atoms for the Bi layers are idealized.

Bi
Sr
Cu
Ca(Sr)
Cu
Sr
Bi
Bi
Sr
Cu
Ca(Sr)
Cu
Sr
Bi
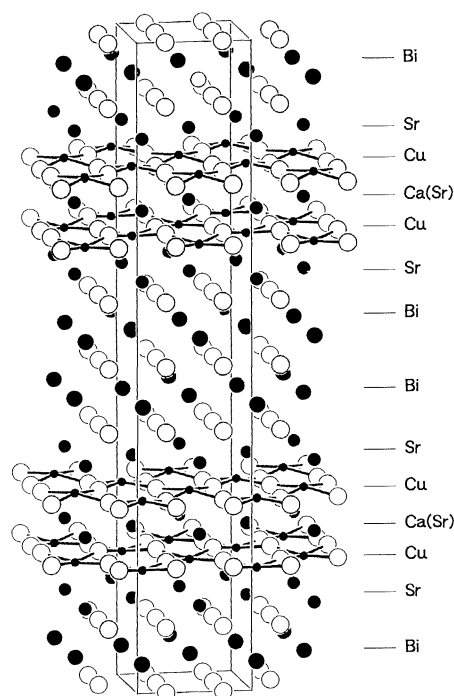
structure along the a axis only. An initial model for the 5.4 by 5.4 Å subcell data was obtained by the direct phasing method (4), and was further developed by Fourier and least-squares cycles to yield the gross Bi^{3+}, Sr^{2+}, Ca^{2+}, and copper-oxygen sheet coordinates (Table 2). The crystallographic repeat unit consists of one Bi, Sr, and Cu each on mirror-related sites, the Ca(Sr) on an inversion center, and two oxygens on twofold rotation axes. The resulting structure yields square-planar Cu, cubic Ca(Sr), and octahedral oxygen coordination geometries. A mixed stoichiometry of the "Ca layer" was approximated as Sr:Ca = 1:1 from an examination of the thermal coefficient of the Ca as a function of the ratio of the Sr and Ca

scattering factor curves. The oxygen atom structure of the bismuth bilayer could not, however, be completely determined with the subcell data. Presumably, the superstructure includes oxygen ordering within this region of the structure. Partially occupied oxygen atom coordinates obtained from difference maps lowered the agreement indices ($R = 0.071, R_w = 0.061$). Least-squares refinement on a large superstructure cell is in progress to obtain the ordered model which may be monoclinic. Elongation of the heavy-atom thermal ellipsoids along the a axis is also consistent with the superstructure in this direction.

The structure can be described as containing double sheets of corner-sharing approxi-

mately square-planar CuO_4 units oriented in the (001) plane (Fig. 3). The Cu-Cu separation between the sheets in the double layer is 3.25 Å. Calcium and strontium ions are located between the Cu-O sheets with Ca(Sr)-O bond lengths ranging between 2.45 and 2.55 Å. This structural feature also exists in the $RBa_2Cu_3O_7$ phases where the copper-oxygen sheets are separated by 3.3 Å with trivalent rare earth cations. Cu-O bond distances within the sheets of $Bi_2Sr_{3-x}Ca_x$ Cu_2O_{8+y} are 1.91 Å. Strontium cations reside just above and below the Cu-O double sheets. These Sr-Cu-Ca(Sr)-Cu-Sr slabs alternate with a double bismuth layer resulting in a layer repeat sequence of $\cdots$Bi-Bi-Sr-Cu-Ca(Sr)-Cu-Sr$\cdots$. This structure is related to that of $Bi_2Ba_{0.1}Sr_{0.9}Ta_2O_9$ (5), which has double layers of corner-sharing TaO_6 octahedra with Sr ions situated between the layers. However, the double layers in the tantalum compound connect directly to a double bismuth layer giving a layer repeat sequence of $\cdots$Bi-Bi-Ta-Sr-Ta$\cdots$. That is, the additional strontium layers present in the copper compound are missing in the tantalum phase. This explains the close relationship in the orthorhombic a and b lattice parameters [~5.4 Å (Cu) versus ~5.5 Å (Ta)] and the large difference in the c parameter [30.9 Å (Cu) versus 25.1 Å (Ta)] of the two compounds.

Electron microscopy of $Bi_2Sr_{3-x}Ca_x$ Cu_2O_{8+y} shows platy crystals with diameters ranging from a few micrometers up to 30 μm and thickness less than 0.5 μm. The lamellar structure of these plates is shown in Fig. 4. The tendency of these micaceous crystals to delaminate can easily be appreciated from Fig. 4 (bottom). Microanalysis of these plates indicates that the value of x in $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ ranges from about 0.4 to 0.9. Elongated needle-like crystals up to 50 μm in length are also present in this sample but constitute a small fraction of the total volume. Microanalysis of the needles indicates that they are poor in bismuth (6). Some micrometer-sized equiaxed particles were also evident in the sample. These have been identified by microprobe analysis to be unreacted copper oxide.

Because the platy crystals were found to be high T_c superconductors, they were picked out with the aid of an optical microscope for further examination. The (001) plane of the plates was observed in samples prepared by mounting crystal fragments on carbon grids. To observe (100) and (010) planes, samples were microtomed. Both a Philips CM12 and JEOL 2000EX were used in this study. Electron diffraction from the face of the plate (Fig. 5) indicates a 5.4 by 5.4 Å subcell with a superstructure along one axis. This superstructure may be ap-

proximated with cell dimensions $a = 27.0$ Å and $b = 5.4$ Å in reasonable agreement with those from Michel et al. (1) for "$Bi_2Sr_2Cu_2O_{7+y}$". The c axis of 31.0 Å was also confirmed by means of electron diffraction.

The compound $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ is fairly stable in the presence of the electron beam. Its lamellar nature and tendency for the thin sheets to bend complicates both electron diffraction and structure imaging. Our examination of several crystallites thus far indicates a propensity for twinning, stacking faults, and dislocations in this material.

There are now three copper-oxygen–based structures that exhibit high-temperature superconductivity: $La_{2-x}A_x^{2+}CuO_4$ where A^{2+} is Ba, Sr, or Ca; $RBa_2Cu_3O_7$ where R is nearly any rare earth; and $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$. In all three cases, there are copper-oxygen sheets where the copper is in essentially square-planar coordination. In La_2CuO_4, there are, in addition, two more oxygens bound to copper to form a highly distorted octahedron. The sheet copper in the $YBa_2Cu_3O_7$ structure has a fifth oxygen with a longer Cu-O distance to form a square pyramidal coordination for copper. In $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$, there are no oxygens between the adjacent sheets;

thus, the copper coordination is four or five. A common feature of all copper oxide–based superconductors is the mixed oxidation states Cu^{II}-Cu^{III}.

There has been considerable speculation about the role of copper-oxygen chains in the $YBa_2Cu_3O_7$ structure because such chains are apparently required to achieve high-temperature superconductivity in this structure. One consequence of the chains is that they lower the symmetry of the structure from tetragonal to orthorhombic. For the La_2CuO_4 structure, distortion of the copper-oxygen sheets also seems to be essential for superconductivity. Again for $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$, we find an orthorhombic distortion of the pseudo-tetragonal sheets. It is therefore tempting to conclude that lowering the symmetry of the copper-oxygen sheets is essential for high T_c. Furthermore, it appears that the bismuth-oxygen sheets may play a role in this distortion. In fact, there could well be chain-like character to the Bi-O structure.

There is an even greater separation between certain copper-oxygen layers in the $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ structure than in ei-

ther the La_2CuO_4 structure or the $RBa_2Cu_3O_7$ structure. Thus we might expect even more anisotropic properties in this lamellar structure. This expectation is further supported by the extreme tendency of this platy material to delaminate. This delamination behavior makes it very difficult to obtain reliable electrical data perpendicular to the sheets.

Unlike the crystals of the $RBa_2Cu_3O_7$ materials, crystals of $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ readily exhibit strong flux exclusion behavior without the need for extensive annealing in oxygen. Either the crystals form initially with adequate oxygen, or the oxygen is very rapidly absorbed on cooling in air. Thus, we expect much easier ceramic processing of this material because a final oxygen anneal may be unnecessary. A difficulty with both $La_{2-x}A_x^{2+}CuO_4$ and $RBa_2Cu_3O_7$ is their reactivity with humid air. Preliminary observations on the $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ phases indicate a much greater stability in this regard.

Superconductivity is also known in the bismuth based oxide system $Ba(Pb,Bi)O_3$ (7). Furthermore, the T_c of 13 K observed for this phase is higher than expected based on traditional Bardeen-Cooper-Schrieffer (BCS) theory; thus, this oxide has also been regarded as a high-temperature superconductor. However, it is unlikely that bismuth plays a direct role in any conduction mechanism for $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ phases unless some of the bismuth is oxidized to Bi^V. Our chemical analysis indicates that this is very unlikely. Furthermore, the structural analogy between $Bi_2^{III}Ba_{0.1}Sr_{0.9}Ta_2O_9$ (5) and $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ indicates that Bi^{III} rather than Bi^V predominates in both phases. Further speculation on this question must await the detailed structural analysis that is in progress.

Noted added in proof: Further refinement of the subcell structure has improved the agreement factor to $R = 0.055$ and indicates $x = 0.67$ in the formula.

Table 1. Summary of crystallographic information for the compound $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ (for $x = 0.5$). The data were taken with an Enraf-Nonius CAD4 diffractometer that used Mo-Kα monochromatic radiation. The instrument was operated in the ω scan mode over a 2θ range of 0 to 50 degrees. The absorption correction was determined analytically.

Dimensions (mm)	$0.10 \times 0.07 \times 0.01$
Formula weight	912.1
Crystal system	Orthorhombic
Space group	Amaa (no. 66 − Cccm)
Cell constants	$a = 5.399(2)$ (Å)
	$b = 5.414(1)$ (Å)
	$c = 30.904(16)$ (Å)
Calculated density	6.70 g/cm^3
Octants	HKL, HKL̄
Absorption coefficient	578.5 cm^{-1}
Total reflections	2064
Independent reflections	231 ($I > 3\sigma$)
Data/parameters	8.00
R (data merge)	0.031 (185 duplicates)
R	0.099
R_w	0.088

Table 2. Positional (x, y, z) and thermal (B) parameters for the atoms of $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$.

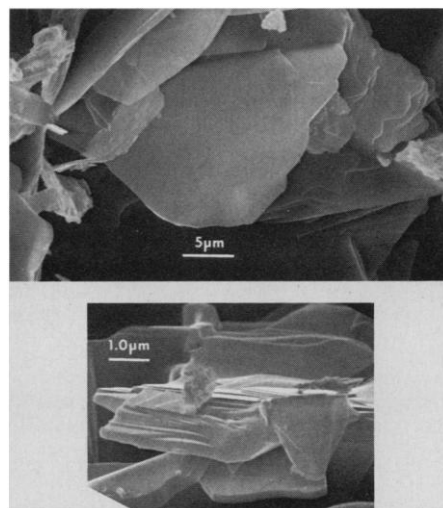| Atom	x	y	z	B (Å^2)
Bi(1)	0.50	0.2278(5)	0.0523(1)	5.4(1)
Sr(1)	0.00	0.2523(12)	0.1408(3)	3.4(2)
Cu(1)	0.50	0.2501(15)	0.1974(3)	2.5(2)
Ca(1)	0.00	0.25	0.25	2.1(4)
O(1)	0.75	0.00	0.2005(15)	1.0(9)
O(2)	0.25	0.50	0.1953(19)	2.7(13)

Fig. 4. Electron micrographs of crystallites of $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ showing platy morphology and tendency to delaminate.
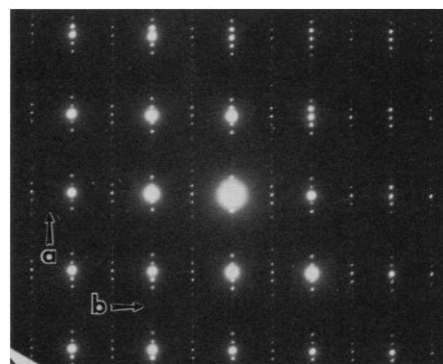

Fig. 5. Electron diffraction pattern of the basal plane of a platy crystal.

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