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Eight new high-temperature superconductors with the 1:2:4 structure

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New high-temperature superconducting compounds RBa$_2$Cu$_4$O$_8$ (R =Nd, Sm, Eu, Gd, Dy, Ho, Er, and Tm) which share the 1:2:4 structure of YBa$_2$Cu$_4$O$_8$ are bulk synthesized using a new high-pressure oxygen technique. All compounds show substantial Meissner diamagnetism [$(3-25)\times10^{-4}$ emu/g at 20 K]. Critical temperatures (57–81 K) vary inversely with ion size (opposite to 1:2:3), and directly with orthorhombic distortion (which is much smaller than in corresponding 1:2:3 compounds). R_2Ba$_4$Cu$_7$O$_x$ compounds (with alternating blocks of 1:2:3 and 1:2:4) were also prepared. The variable oxygen stoichiometry of 1:2:3 is not shared by the 1:2:4 compounds.

The number of known high-temperature superconducting compounds is growing steadily,[1–4] yet there is no clear consensus on relationships among crystal structure, electronic configuration, and other key physical properties. We propose a new avenue to synthesis of additional high-temperature superconductors. It is well known that the superconducting cuprates are very highly oxidized compounds (the original La$_{1.85}$Sr$_{0.15}$CuO$_4$ superconductor has an average Cu valency of 2.15, while in YBa$_2$Cu$_3$O$_7$ the value is 2.33) and tend to lose oxygen when heated, e.g., during synthesis. Processing in concentrated oxygen (high-pressure oxygen gas) can prevent this oxygen loss, and will thermodynamically favor the formation of highly oxidized phases, which may be new superconductors.

To demonstrate this principle, we have synthesized the high-temperature superconductor YBa$_2$Cu$_4$O$_8$ and eight new rare-earth compounds RBa$_2$Cu$_4$O$_8$ (R =Nd, Sm, Eu, Gd, Dy, Ho, Er, and Tm). YBa$_2$Cu$_4$O$_8$ was sintered in high-pressure oxygen [$P(\text{O}_2)\approx120$ atm] for 8 h at 930 °C using a commercial high-pressure oxygen furnace.[5] Preparation of the rare-earth compounds required differing synthesis temperatures and pressures.[6] Bulk superconductivity was demonstrated by substantial Meissner diamagnetism, with $\chi\approx-25\times10^{-4}$ emu/g for YBa$_2$Cu$_4$O$_8$ at 20 K, corresponding to ~20% volume diamagnetism (see Table I and Fig. 1).

The 1:2:4 compounds are thermodynamically stable in high-P(O$_2$), because the alternative 1:2:3 phase (RBa$_2$Cu$_3$O$_{7-\delta}$) loses oxygen upon heating to processing temperature. These new compounds comprise the first set of isostructural, stoichiometric (i.e., with well-constrained oxygen content) superconductors, and thus they are an ideal system to study effects of small structural variations on superconducting properties. Their critical temperatures range from 57 to 81 K and vary with structural parameters (see Fig. 5). The oxygen high-pressure synthesis technique can also produce the 2:4:7 compounds R_2Ba$_4$Cu$_7$O$_{15-x}$ in which 1:2:3 and 1:2:4 layers alternate along the c axis. P-T-x phase-stability diagrams will be published elsewhere.[6]

The 1:2:4 structure had first been observed as intergrowth in YBa$_2$Cu$_3$O$_{7-\delta}$ (the 1:2:3 compound) as planar defects in which a second CuO layer is introduced between the BaO layers, increasing the Y-Y distance from 11.7 to 13.6 Å.[7,8] Because the positions of Cu in the Cu-O layers differ by $a/2$ along the a axis,[8] c is doubled to $2\times13.6=27.2$ Å.[9] Epitaxial thin films were made with

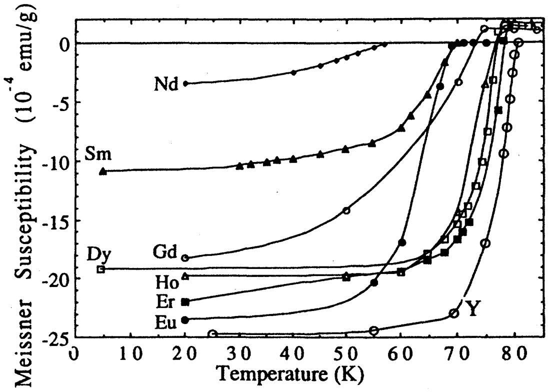

FIG. 1. Meissner susceptibility curves of superconducting compounds RBa$_2$Cu$_4$O$_8$ (R =Y, Nd, Sm, Eu, Gd, Dy, Ho, Er). The transitions are strong and sharp. T_c's differ and are correlated with ion size, lattice parameters, and orthorhombic distortion (see Fig. 5).

TABLE I. Superconducting and structural parameters of RBa$_2$Cu$_4$O$_8$ compounds. Parentheses denote uncertainties indicated by Rietveld refinement. Square brackets are values for the 2:4:7 phase.

	Superconducting parameters[a]			Phases present[d]			Lattice parameters[e] of 1:2:4 phase (2:4:7 phase)				
R	T_c (K)	$\chi_{20\,\mathrm{K}}$[b]	$4\pi\rho\chi_{20\,\mathrm{K}}$[c]	1:2:3	2:4:7	1:2:4	a (Å)	b (Å)	c (Å)	V (Å^3)	b/a
Y	80.4 ± 0.2	−25	20%	no	no	all	3.8395(2)	3.8703(2)	27.231(1)	404.7	1.0080
Nd	~57	−3.5	3%	trace	no	minor			~27.3		
Sm	69.3 ± 0.4	−11	10%	70%	no	30%	3.872(1)	3.886(1)	27.308(5)	410.9	1.0036
Eu	68.9 ± 0.4	−24	21%	no	40%	60%	3.8650(6)	3.8837(5)	27.279(4)	409.5	1.0048
							[3.879(2)]	[3.886(1)]	[50.39(3)]	[759.6]	[1.0018]
Gd	73.4 ± 1.2	−18	16%	no	60%	40%	3.863(1)	3.881(7)	27.259(5)	408.7	1.0047
							[3.872(1)]	[3.879(1)]	[50.36(2)]	[756.4]	[1.0018]
Dy	77.2 ± 0.1	−19	17%	no	no	all	3.8463(3)	3.8726(3)	27.237(1)	405.7	1.0068
Ho	77.4 ± 0.6	−20	18%	no	no	all	3.8404(6)	3.8704(6)	27.221(5)	404.6	1.0078
Er	78.3 ± 0.2	−22	20%	no	no	all	3.8366(5)	3.8685(5)	27.230(4)	404.1	1.0083
Tm	78.6 ± 0.3	−11	10%	no	no	all	3.827(1)	3.864(1)	27.18(1)	401.9	1.0097

[a] By observation of bulk diamagnetism. The T_c's correlate with lattice parameters a and b, and with orthorhombic distortion (see Fig. 5).

[b] Flux expulsion on cooling to 20 K in a constant 6-Oe field, in units of 10^{-4} emu/g.

[c] Diamagnetic volume fraction, neglecting expelled flux trapped in pores. The density ρ is calculated from the unit-cell volume.

[d] Relative amounts estimated from x-ray powder-diffraction patterns and Reitveld refinements.

[e] The Rietveld procedure was used and a sample displacement correction was refined along with the unit-cell parameters. The refinement included 1:2:3 or 2:4:7 phases when present. The unit-cell parameters found for the Dy compound did not differ significantly from those determined using a Cr$_2$O$_3$ internal standard.

1:2:4 as a distinct,[9] or majority phase[10,11] with $T_c \sim 80$ K, but bulk 1:2:4 material could not be prepared. X-ray diffraction on films[11] gave approximate lattice parameters, but orthorhombic distortion, oxygen locations, and fractional site occupation could not be determined in the absence of bulk specimens.

Our bulk samples, prepared in high-P(O$_2$), were confirmed as 1:2:4 by electron diffraction (Fig. 2), transmission electron microscopy (TEM) (Fig. 3), and x-ray powder diffraction (XPD) (Fig. 4). The lattice parameters of YBa$_2$Cu$_4$O$_8$ are $a = 3.8395(2)$ Å, $b = 3.8703(2)$ Å, $c = 27.231(1)$ Å, in general agreement with Ref. 11 but with higher precision. The average value of the a and b crystallographic axes (3.855 Å) is close to that of 1:2:3 in both its orthorhombic (3.853 Å) and tetragonal (3.857 Å) variants,[12] but the axial ratio $b/a = 1.008$ corresponds to distortion less than half that in fully oxidized YBa$_2$Cu$_3$O$_7$ ($b/a = 1.017$).

All phases in the polycrystalline samples appear black and optically opaque, with average grain sizes $\lesssim 1$ μm. Electron microanalyses of samples in the Y-Ba-Cu-O system were obtained on a JSM model 35 scanning electron microscope (SEM), (20 kV, 0.01-μA beam current, 2.5-μm spot size). Standards include pure Cu metal, NBS microprobe standard K253 for Ba, and Y standard REE3 as described in Ref. 13. Portions of ceramic-disk samples were embedded in epoxy cement and polished for microprobe analysis. SEM of the polished surface revealed smooth areas suited for electron microanalysis, as well as considerable intergranular porosity characteristic of ceramic superconductors.

The predominant phase is a ternary oxide with cation ratios of Y:Ba:Cu close to 1:2:4. Though a few analyses yielded only 3.7 to 3.8 Cu per three Y+Ba, no analyses close to a 1:2:3 stoichiometry were obtained. Occasional grains of a yttrium cuprate and a barium cuprate, both with 1:1 cation ratios, were observed. The powder-diffraction pattern for YBa$_2$Cu$_4$O$_8$ shows minor amounts of Ba cuprate and an unidentified phase (peaks at 7.49, 3.09, and 3.00 Å), but no evidence of a 1:2:3 component. Thus, we conclude that the 1:2:4 compound is the predominant bulk superconductor in these samples. However, the calculated intensity of the diagnostic 11.7-Å line for the Y-bearing 1:2:3 compound is relatively weak (4.2%), so trace amounts of it cannot be ruled out.

Calculated powder patterns for 1:2:3 phases show that the intensity of the 11.7-Å peak increases with increasing atomic number from a relative intensity 4.2% for Y to 33% for Eu and Gd. Therefore, even very minor quanti-

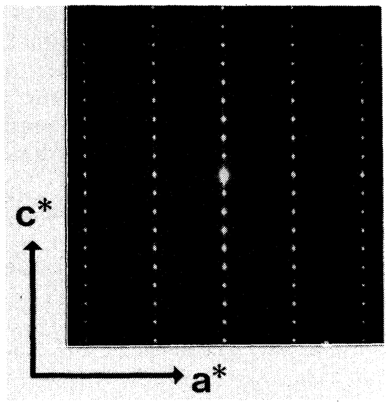

FIG. 2. A **b**-axis selected-area electron diffraction pattern of YBa$_2$Cu$_4$O$_8$, indicating that most of this phase is well ordered. Minor diffuse streaking parallel to **c*** indicates that some crystals possess some structural disorder affecting the periodicity of the (00$\bar{1}$) planes (see Fig. 3).

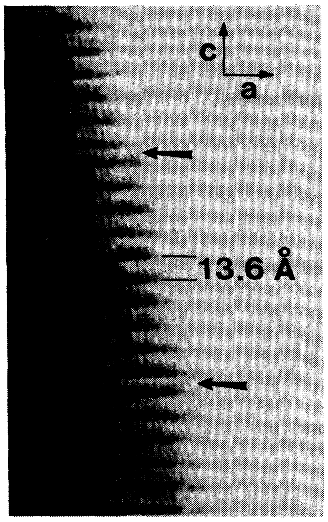

FIG. 3. A **b**-axis lattice image of the bulk 1:2:4 structure. In this image, planar defects corresponding to (002) layers with spacing smaller than 13.6 Å are seen (arrows), but most grains are perfect 1:2:4 structure without these defects.

ties of a 1:2:3 phase would be apparent in powder-diffraction patterns of the rare-earth-substituted samples. The 1:2:3 peak was seen only in the Sm and Nd patterns. All of the samples, with the exception of Nd, contained minor amounts of an unknown phase that has a characteristic diffraction peak at about 7.5 Å. Microanalyses of phases in the R-substituted systems are in progress.

Electron diffraction, TEM, and x-ray analytical electron microscopy (AEM) were performed with a Philips 420ST microscope equipped with an EDAX energy-dispersive detector and a PGT 4000 analyzer.[14] Selected-area electron-diffraction patterns and AEM analyses from numerous grains of crushed sample confirm that most of the material is well-crystallized, bulk 1:2:4 structure. The data are consistent with the x-ray unit-cell parameters and space group *Ammm*. Single crystals of the yttrium 1:2:4 phase were observed up to several tens of μm across. Electron diffraction patterns (Fig. 2) indicate that most of this phase is rather well-ordered, though streaking parallel to $\mathbf{c}^*$ shows that some crystals possess some structural disorder affecting the periodicity of the $(00\bar{1})$ planes.

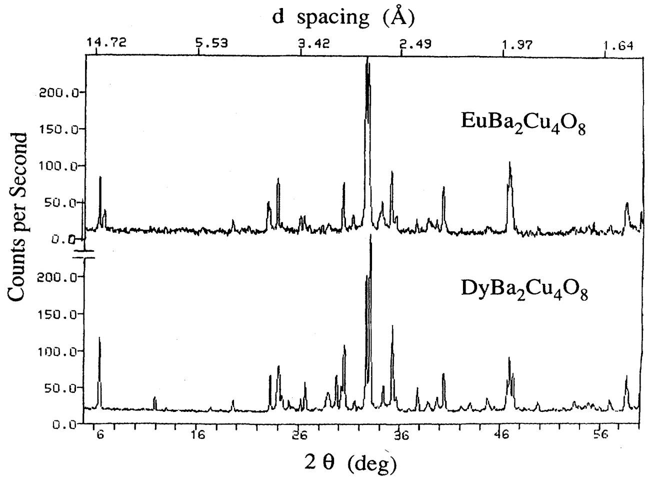

FIG. 4. X-ray powder diffraction patterns of $\mathrm{EuBa_2Cu_4O_8}$ and $\mathrm{DyBa_2Cu_4O_8}$. Note the (002) peak near $2\theta = 6.5°$ (d spacing ≈ 13.6 Å) in both patterns, and the (004) peak of $\mathrm{Eu_2Ba_4Cu_7O_x}$ near 7° (d spacing ≈ 12.55 Å).

High-resolution lattice images (Fig. 3) show that at least part of the disorder results from the insertion of occasional layers that are either smaller or larger than the 13.6-Å (002) layers of the ideal 1:2:4 structure. Similar intergrowth defects have been observed in Bi and Tl based high-T_c superconductors, as well as in $\mathrm{YBa_2Cu_3O_{7-\delta}}$.[2,15] In the present material, a few ordered crystals of an additional pure Y-Ba-Cu phase with layer spacing of approximately 15.2 Å also were found. In addition to these complications related to layer spacing, electron-diffraction patterns and lattice images from 1:2:4 indicate that many crystals are ordered parallel to the **a** axis, producing modulations and superstructures in this direction having multiples of the 3.84-Å **a** axis repeat; the resulting microstructures will be described elsewhere.

X-ray-powder diffraction was performed on a Scintag automated powder diffraction using Cu $K\alpha$ radiation. Diffraction patterns of the samples were examined for evidence of the superconducting phases 1:2:4 and/or 1:2:3, as indicated by the presence of peaks at approximately 13.6 or 11.7 Å, respectively. For each sample that showed the 1:2:4 structure as the major phase, unit-cell parameters

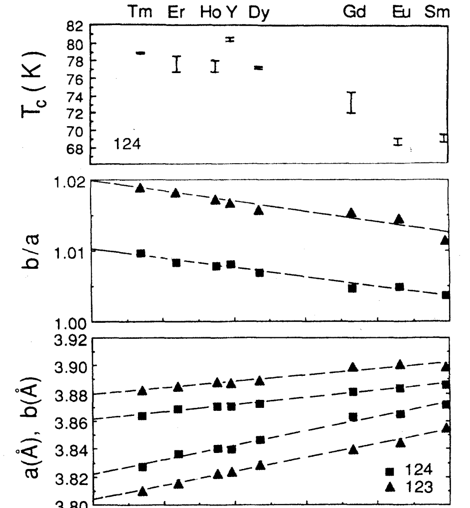

FIG. 5. T_c vs ion size, lattice parameters a and b, and orthorhombic distortion for 1:2:4 compounds (■) from Table I. Values for 1:2:3 compounds (▲) from Ref. 12. Ionic radii from Ref. 17; other data from Table I. In the 1:2:4 series T_c *decreases* with axial ratio b/a as ion size and a and b increase. In contrast, the 1:2:3 compounds show T_c's *increasing* with ion size (Ref. 18) while distortion decreases. T_c of $\mathrm{YBa_2CuO_8}$ is ~3 K higher than HoBa- $\mathrm{Cu_4O_8}$, although lattice parameters are nearly identical (see text).

were refined by the Rietveld method, assuming space group *Ammm* and the model structure reported in Ref. 11. (In the cases of samples which also contained 1:2:3 or 2:4:7 phases, they were included in the refinement.) Our preliminary Rietveld studies indicate that the atomic structure of our 1:2:4 phases are consistent with that given in Ref. 11. Our lattice parameters are given in Table I. A detailed structural study giving atomic positions, lattice distortions, and anisotropic atomic vibrations has been performed on a single crystal of $DyBa_2Cu_4O_8$ (Ref. 16).

In the compounds containing larger[17] (lighter) rare-earth ions, as a and b increase, T_c and orthorhombic distortion *decrease* (Fig. 5). In contrast, the 1:2:3 compound show T_c's *increasing* with ion size[18] and distortion decreasing.[12] This difference in behavior of T_c in closely related structures may provide a sensitive test of theoretical models. We also note that although the Ho and Y 1:2:4 compounds have nearly identical lattice parameters, the T_c of $HoBa_2Cu_4O_8$ is ~3 K lower. This may indicate that the large magnetic moment of Ho suppresses the coupling between the CuO_2 planes.

In the Eu and Gd systems, an additional 2:4:7 phase was found, with alternating 1:2:3 and 1:2:4 blocks joined at the R layers, analogous to $Y_2Ba_4Cu_7O_x$ (Ref. 19). Surprisingly, the T_c (~40–50 K) of this phase is much lower than the 70–90-K range of 1:2:3 and 1:2:4. It may be relevant that axial ratios ($b/a \approx 1.002$) are even smaller than in the corresponding 1:2:4 compounds. Diffraction peaks were found at about 12.6 Å (see Fig. 4) which we interpret to be the 004 reflection of compounds with 2:4:7 structure. The lattice parameters of the 2:4:7 phase were determined by refining together with the 1:2:4: phase; results are given in Table I. The c axes of the 2:4:7 compounds are shorter than the sum of those of the corresponding 1:2:4 and 1:2:3 compounds. We prepared the 2:4:7 phase in the Y, Dy, Ho, and Er systems as well, by varying the synthesis conditions.[6]

A unique feature of the 1:2:3 compound is the variable oxygen stoichiometry, and rapid and reversible oxidation-reduction above 400 °C.[20] Varying the oxygen content changes T_c and the normal-state resistivity. An absence of variable oxygen stoichiometry in 1:2:4: was conjectured by Marsh *et al.*,[11] on the basis that each oxygen in the two CuO layers of 1:2:4 is bonded to three Cu ions, in contrast to 1:2:3 where the O is bonded to only two Cu ions. Preliminary thermogravimetric studies indicate that $YBa_2Cu_4O_8$ indeed lacks the variable oxygen stoichiometry of $YBa_2Cu_3O_{7-\delta}$. Structural studies[16] indicate that the oxygen double-chain sites are fully occupied. The consistent oxygen content should permit precise determination of differences of T_c caused by varying rare-earth magnetic moment as well as ion size. The twinning caused by the tetragonal-orthorhombic transition during cooling of 1:2:3 should be absent, so 1:2:4 may be technologically useful.

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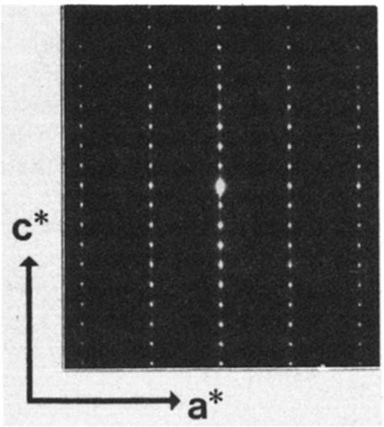

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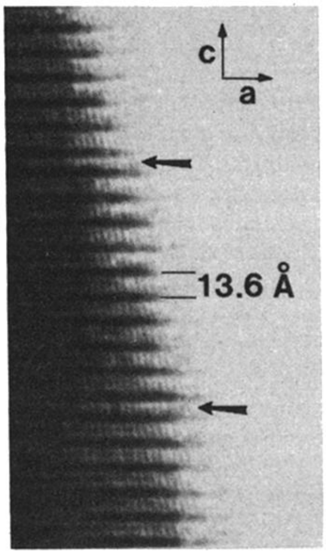

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