Superconductivity of the single-phase compound $Er_1Ba_2Cu_3O_{9-\delta}$: Transport and structural properties

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We report electrical and structural measurements on the high-T_c single-phase superconductor $Er_1Ba_2Cu_3O_{9-\delta}$. Our best samples have a relatively low room-temperature resistance and a superconducting onset temperature of 94 K. The structure of the single phase is found to be an orthorhombic perovskite similar to the one reported for the $Y_1Ba_2Cu_3O_{9-\delta}$ compound, but different from the K_2NiF_4 perovskite structure found in the earlier high-T_c compounds. The calculated effect of possible oxygen deficiencies in several of the crystal planes will be discussed. The x-ray diffraction spectrum shows that there could be more than one phase present, depending on the preparation conditions.

The recent discovery of superconductivity above the boiling point of liquid nitrogen has stirred interest in both the scientific and general communities. Due to the numerous possible applications of this new superconducting material, there has been an unprecedented rush to understand the underlying physical mechanism and to find new high-T_c materials. Much is already known about the Y-Ba-Cu-O system.[1,2] The magnetic susceptibility measurements made by several groups have established definitively the superconductivity for this material.[3] Although the first reported compound by Chu *et al.* was multiphase, its transition temperature was still around 90 K.[1,2] Later, the black "1-2-3" phase was singled out over the green phase as being responsible for the superconductivity. Detailed x-ray analyses by Cava *et al.*[4] and by Le Page *et al.*[5] have determined the structure of this phase to be an oxygen-deficient perovskite, though the exact positions of the oxygen deficiencies differ in their two accounts.

In this paper, we report electrical and structural measurements of the 1-2-3 compound $Er_1Ba_2Cu_3O_{9-\delta}$. Like the $Y_1Ba_2Cu_3O_{9-\delta}$ compound which preceded it, this compound exhibits an onset T_c above liquid-nitrogen temperature at 94 K with a 90%-10% transition width of 1 K. The structure of this superconducting phase was determined by x-ray diffraction to be an orthorhombic perovskite similar to $Y_1Ba_2Cu_3O_{9-\delta}$. We could not distinguish the K_2NiF_4 perovskite phase which is believed to be the superconducting phase for the $La_{2(1-x)}Ba_{2x}CuO_{4-\delta}$ type-2 system.[6,7]

In analogy with the Y-based 1-2-3 superconducting phase, we inferred the same stoichiometry for the Er system. With the belief that this system would also be single phase, we proceeded to prepare our samples by the method of coprecipitation to insure a mixing of the constituents on the atomic scale. The success of such a mixing process seemed to be at least that afforded by many mortar and pestle grindings. In the coprecipitation method, the nitrated forms of Er, Ba, and Cu were mixed in solution in the proper stoichiometric amounts. Sodium carbonate was then added to precipitate the carbonated form of these materials. The precipitate was washed with distilled water continuously until a neutral pH was observed in the rinse, indicating that the sample was not contaminated by lingering basic ions. The precipitate was dried at 140 °C for 12 h to remove water, and then heated to 900 °C for 6 h to remove carbon dioxide. The remaining porous clump was then pulverized and reheated to 900 °C several times. The final black oxide powder was then pressed into pellet form and sintered at temperatures ranging from 800 °C to 925 °C for a period of 12 h. All samples were annealed in the presence of oxygen at 500 °C for 12 h. Finally, the samples were cooled slowly toward room temperature in the oxygen atmosphere.

The sample resistances were measured using a four-lead connection by locking in on a selected ac current input. Plots of the resistance versus temperature are given in Fig. 1. For the sample fired at 900 °C the superconductive onset is 94 K, with a midpoint at 93.5 K and a resistance below the instrument resolution at 93 K. As the firing temperature was lowered the transition temperature was reduced slightly and the transition region broadened (i.e., the "quality" of the transition decreased). Firing at 850 °C, for example, lowered the T_c by 2 K and broadened the 90%-10% resistive width from 1 to 5 K. Moreover, the room-temperature resistance was increased by a factor of 4. The change in the sample resistance was even more dramatic when the firing condition was lowered to 800 °C (Fig. 2). Here the room-temperature value was several orders of magnitude greater than the other samples. This sample does not show the superconducting behavior.

We have also identified the principal phase responsible for the superconductivity. Our results show a similarity

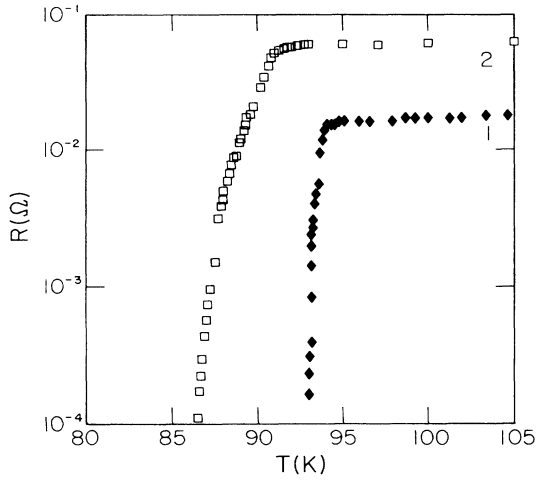

FIG. 1. The resistive transition of $Er_1Ba_2Cu_3O_{9-\delta}$ at different sintering temperatures. Plot 1 is sintered at 900 °C and plot 2 at 850 °C. The resistance above the transition, the onset temperature T_c, and the transition width all depend on the sintering temperature.

with the x-ray diffraction results of $Y_1Ba_2Cu_3O_{9-\delta}$ by Grant *et al.*[8] They identified the black single phase as one consisting of a tetragonal crystal with lattice parameters $a=3.89$ Å, $b=11.65$ Å, and $b/a=3.00$. The proposed unit cell was an oxygen-deficient perovskite structure with a sandwiched ordering of Ba, Y, and Ba. Since the peak positions and relative intensities of our Y and Er 1-2-3 samples matched well, we could qualitatively assume the above structure for the Er sample as a starting point for a more detailed analysis. What was clear now was that the substitution of the larger Er atom for the Y atom did not affect the high-T_c transition or the crystal structure significantly, lessening the importance of the rare-earth

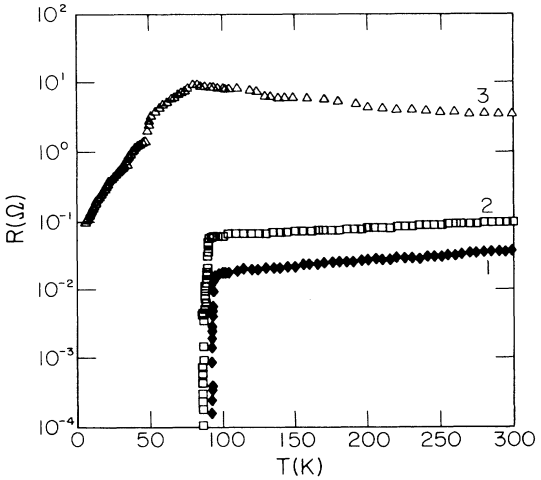

FIG. 2. The resistive transition of $Er_1Ba_2Cu_3O_{9-\delta}$ at different sintering temperatures. Plot 1 is sintered at 900 °C, plot 2 at 850 °C, and plot 3 at 800 °C. The best procedure is to sinter at as high a temperature as possible without melting the sample.

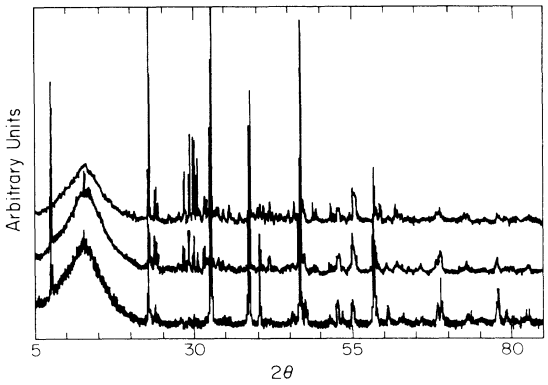

FIG. 3. The x-ray measurement of $Er_1Ba_2Cu_3O_{9-\delta}$ at different sintering temperatures. In succession from the bottom, the sintering temperatures are 900, 850, and 800 °C, respectively. As the sintering temperature is lowered, impurity phases are more evident, especially near $2\theta=30$.

metal's contribution to the superconducting mechanism itself.

A more detailed analysis concludes that the erbium compound is an orthorhombic perovskite structure with the Er atom sandwiched between the Ba atoms. A least-squares fit of the d spacings from the x-ray diffraction pattern (Fig. 3) subsequently gives us the lattice spacings $a=3.8152\pm0.0013$ Å, $b=11.6502\pm0.0037$ Å, and $c=3.8822\pm0.0013$ Å. As shown in Table I, we found very good agreement between the measured and calculated d spacings assuming this structure, with some minor differences occurring at small 2θ values where the error is expected to be larger.

In order to confirm the assumed structure we have to take into account the peak intensities in addition to the d spacings. We calculated an x-ray spectrum based on the constituents, their crystal positions, and the assumed lattice constants. The results appear in Table I. Though the finite values of the calculated peak intensities strengthen the assumption that the crystal framework is orthorhombic, there are large discrepancies in several peak intensities. To try to account for these differences, we recalculated the intensity spectrum for the cases of oxygen deficiencies on various crystal planes within the unit cell. We first assumed that there were oxygen vacancies in the outer copper planes, i.e., the planes that lie between the barium planes. However, except for small improvements along the course of the spectrum, these calculated intensities still differ significantly from the measured intensities. The calculations for oxygen vacancies in other planes are also included. For example, we considered oxygen deficiencies in the Ba and Er planes. None of these assumptions can account for the noted discrepancies, though the assumption of oxygen vacancies on the copper plane fares slightly better than the assumption of 100% occupancy. All of these cases show a pronounced discrepancy in the doublet (041) and (050) line which also appears in the data for the x-ray measurement of $Y_1Ba_2Cu_3O_{9-\delta}$ by Beyers *et al.*[9] Again, such a difference is much too large to be accounted for by these oxygen manipulations. We

TABLE I. Calculated x-ray spectrum. I(1), experimentally measured intensity; I(2), calculated intensity by assuming 100% oxygen site occupation; I(3), calculated intensity by assuming a total oxygen deficiency on the outer copper planes (i.e., between the Ba planes of adjacent unit cells); I(4), calculated intensity by assuming a total oxygen deficiency on the Ba plane; I(5), calculated intensity by assuming a total oxygen deficiency on the Er plane.

(hkl)	2θ	d(obs)	d(calc)	I(1)	I(2)	I(3)	I(4)	I(5)
(010)	7.643	11.5570	11.6502	40	0.5	6	2	0.6
(030)/(001)	22.913	3.8780	3.8834	73	11	13	16	11
(100)	23.347	3.8070	3.8152	4	5	5	0.1	6
(031)	32.618	2.7430	2.7456	54	51	48	58	54
(130)/(101)	32.902	2.7200	2.7215	100	100	100	100	100
(050)/(041)	38.952	2.3310	2.3300	70	0.1	0.2	0.1	0.1
(140)	38.835	2.3170	2.3151	11	0.0	0	0.0	0.1
(131)	40.452	2.2280	2.2285	21	24	19	20	22
(002)/(060)	46.750	1.9430	1.9411	99	32	28	29	31
(200)	47.621	1.9080	1.9076	7	15	13	14	14
(061)/(032)	52.680	1.7350	1.7360	12	3	3	3	3
(160)/(102)	52.850	1.7300	1.7330	10	3	2	4	3
(230)/(201)	53.500	1.7110	1.7120	6	3	3	3	3
(070)/(122)	55.150	1.6640	1.6660	13	0.0	0.1	0.0	0.0
(161)	58.315	1.5810	1.5806	30	18	18	16	17
(132)	58.436	1.5780	1.5803	17	18	17	19	19
(231)	58.928	1.5660	1.5666	9	17	16	19	18
(062)	68.253	1.3730	1.3728	6	9	7	8	8
(260)/(180) /(202)	68.881	1.3620	1.3607	15	17	14	15	16
(091)/(033)	77.772	1.2270	1.2278	9	7	6	8	7
(190)/(103)	77.923	1.2250	1.2255	11	7	7	7	7
(330)/(301)	79.234	1.2080	1.2085	4	7	6	7	7

can conclude, however, that the orthorhombic structure appears to be valid based on the peak positions and the general trend of the peak intensities. This strengthens the definition of another high-T_c superconducting phase different from the K_2NiF_4 perovskite phase which was responsible for the superconductivity in the now relatively-low-T_c La-(Ba,Sr) type-2 compounds.[6,7]

The x-ray spectra of the samples fired at 850 °C and 800 °C show the emergence of other phases. The structure near $2\theta = 30°$ is severe. As these other structures crept in, the "quality" of the superconducting transition was reduced. Significant changes in T_c, the room-temperature resistance, and the width of the superconducting transition were mentioned earlier in this paper. These changes can be explained by the fact that the composite nature of these samples tend to suffocate the superconducting phase. This is in addition to the fact that the percolating path of the superconducting phase is already limited by the considerable porosity of the material, as can be seen from scanning-electron microscopy (SEM) photographs. The sample fired at 800 °C illustrates this point well. The superconducting phase still dominates the x-ray spectrum and the decrease in resistance below 90 K shows that there is extensive superconductive shorting within the sample, but a percolating path is not formed and the net resistance remains relatively high.

In summary, we have prepared and identified the single phase of the superconducting material $Er_1Ba_2Cu_3O_{9-\delta}$ and found it to be dependent upon the firing conditions. The onset temperature for the samples fired at 900 °C is 94 K with complete zero resistance at 93 K. It was found that the structure of the superconducting phase is similar to that of $Y_1Ba_2Cu_3O_{9-\delta}$, i.e., a perovskite structure with a stacked Ba-Er-Ba ordering. The assumption of oxygen deficiencies on the various crystal planes could account for only a small portion of the discrepancy in the measured and calculated peak intensities. Using lower firing temperatures, the transition temperature was lowered and other phases appeared.

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