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Thermoelectric power and superconducting properties of $Y_1Ba_2Cu_3O_{7-\delta}$ and $R_1Ba_2Cu_3O_{7-\delta}$

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The high-T_c superconductors $R_1Ba_2Cu_3O_{7-\delta}$ (R denotes rare-earth elements) and $Y_1Ba_2Cu_3O_{7-\delta}$ are prepared in several different processes. $Y_1Ba_2Cu_3O_{7-\delta}$ prepared in flowing O_2 and slowly cooled shows $T_c=94$ K, a lattice parameter ratio $c/b=3.00$, and negative thermoelectric power S, while quench-cooled $Y_1Ba_2Cu_3O_{7-\delta}$ shows reduced T_c, an elongated structure along the c axis with $c/b=3.02$, and positive S. Most of the rare-earth-element superconductors show T_c near or higher than 90 K. Rare-earth-element superconductors with the rare-earth-element ionic radius larger than 0.92 Å show positive S, while those with the ionic radius smaller than 0.92 Å show negative S. These experimental results seem to indicate a close correlation between the structural strain and the superconducting properties.

Following the discovery of superconductivity in La-Ba-Cu-O by Bednorz and Müller,[1] superconductivity well above liquid-nitrogen temperature has been reported in $Y_1Ba_2Cu_3O_{7-\delta}$ (Refs. 2–5) as well as in compounds[6,7] which contain rare-earth elements with a strong magnetic moment. Thus, it is speculated that the element occupying the yttrium site in the "1:2:3" perovskite structure does not play any crucial role in the superconductivity.

Several models have been proposed to explain the unusually high transition temperatures of the high-T_c superconductors including the Peierl's-instability-related model,[8] the resonating-valence-bond model,[9] spin fluctuation[10,11] in antiferromagnetism in CuO_2, an excitonic model,[12] a two-band model,[13] and also conventional strong-coupling theory. There is not yet, however, any conclusive experimental evidence for any of the proposed models.

Recently, Khim *et al.*[14] reported an observation of a negative thermoelectric power S in single-phase $Y_1Ba_2Cu_3O_{7-\delta}$, contradictory to the reports of Cooper *et al.*,[15] Cheong *et al.*,[16] and Cava *et al.*,[4] who reported positive S in this material. Furthermore, the observation of the negative thermoelectric power implies that the majority carrier can be an electron if one admits that the sign of S is related to the majority charge carrier type.

In order to clarify these rather contradictory results, superconducting properties including the thermoelectric power were measured for $R_1Ba_2Cu_3O_{7-\delta}$ (R denotes the rare-earth elements Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu) and $Y_1Ba_2Cu_3O_{7-\delta}$ prepared in several different processes.

$Y_1Ba_2Cu_3O_{7-\delta}$ samples were prepared in four different processes. After mixing high-purity Y_2O_3, $BaCO_3$, and CuO according to the appropriate atomic ratios, the well-mixed powder was calcined at 930 °C for 12 h in flowing O_2. After cold pressing at 10 kbar to form a pellet of 1 cm diam., the sample was sintered at 960 °C in either flowing O_2 or air for 12 h. The sample was then either quench cooled or slowly cooled to room temperature. In the slow-cooling process, the sample was cooled to 700 °C in 4 h, held at 700 °C for 2 h more, and then furnace cooled to room temperature, which usually took 4 h. The rare-earth-element "1:2:3"-structure superconductor was prepared with almost the same process as for the slow-cooling process for $Y_1Ba_2Cu_3O_{7-\delta}$ except for the sintering temperature. Rare-earth-element superconductors prepared at sintering temperatures slightly below the melting temperature showed the highest T_c.

X-ray diffraction of the slowly cooled $Y_1Ba_2Cu_3O_{7-\delta}$ revealed an orthorhombically distorted perovskite structure with the lattice constants $a=3.815$ Å, $b=3.891$ Å, $c=11.673$ Å, and, thus, the lattice constant ratio $a/b=0.98$ and $c/b=3.00$. The quench-cooled sample also shows an orthorhombic perovskite structure. The resulting lattice constant ratio of c/b is, however, 3.02, implying elongation along the c axis, evidenced by the splitting of the (020) and (006) peaks as shown in Fig. 1. Table I

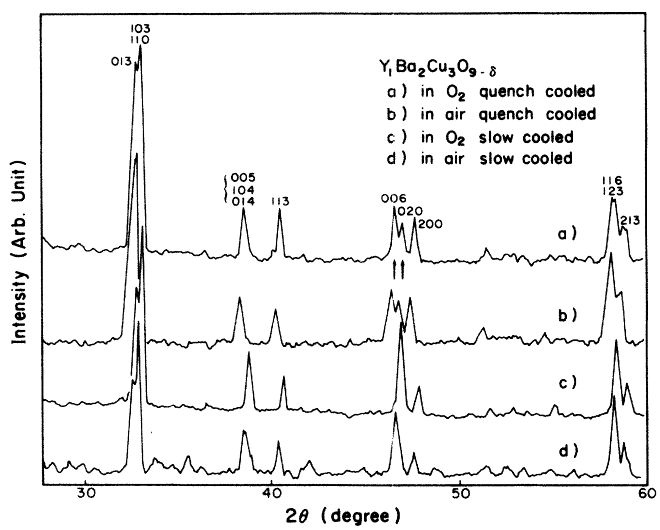

FIG. 1. X-ray (Cu $K\alpha$) diffraction patterns of $Y_1Ba_2Cu_3O_{7-\delta}$ prepared in four different processes. Quench-cooled samples show splitting of (020) and (006) peaks indicated by arrows. Splitting manifests the lattice parameter ratio $c/b\neq3.00$.

TABLE I. Effects of preparation method for $Y_1Ba_2Cu_3O_{7-\delta}$.

Preparation method	c	c/b	a/b	T_c Onset	Mid	Zero	ΔT_c [a]	S (μV/K) [b]
In O_2 and slow cooled	11.673	3.000	0.984	95.5	94.0	92.2	2.0	−2.7
In O_2 and quench cooled	11.772	3.021	0.986	80.3	71.8	67.3	7.6	18.0
In air and slow cooled	11.720	3.000	0.981	94.9	91.3	57.2	17.0	5.4
In air and quench cooled	11.770	3.010	0.986	67.2	59.5	50.3	18.3	56.0

[a] $\Delta T_c = T_c(90\%) - T_c(10\%)$.
[b] Thermoelectric power at room temperature.

shows the effect of the preparation method for $Y_1Ba_2Cu_3O_{7-\delta}$.

The resistivity was measured by the conventional four-points method with contact made by In soldering. The typical sample size was $1\times1\times8$ mm^3 cut from the sintered pellet. To overcome the small resistivity of the sample, a rather high current density was employed for the resistivity measurements with the current density ranging from 0.1 to 0.5 A/cm^2. The effect of the test current density on the transition temperature was unnoticeable for the above current density range. Figure 2 shows the temperature-dependent resistivity of $Y_1Ba_2Cu_3O_{7-\delta}$ prepared in four different processes.

Superconducting transition temperatures, defined as the midpoint of the transition, are 94.0, 71.8, 91.3, and 59.5 K for samples prepared in O_2 and slowly cooled, in O_2 and quench cooled, in air and slowly cooled, and in air and quench cooled, respectively. The zero-resistance temperatures for the above-mentioned samples are 92.2, 67.3, 57.2, and 50.2 K, respectively. Compared to the slow-cooled sample, the quench-cooled sample showed a drastic reduction in the transition temperature, accompanied by structural elongation along the c axis as shown in the x-ray diffraction measurement. The effect of O_2 gas during the sintering process seemed to enhance homogeneous oxygen distribution for the single-phase superconductor as evidenced by the narrow transition width [$\Delta T_c = T_c(90\%) - T_c(10\%)$] compared to the sample prepared in air. Above T_c, samples prepared in O_2 show a metallic behavior with an almost linear temperature dependence in the resistivity. The linearities $d\rho/dT$ for the sample prepared in O_2 and slowly cooled and quench cooled are 4.1 and 7.0 $\mu\Omega$ cm/K, respectively. On the other hand, samples prepared in air show a rather complex semiconductorlike behavior. $Y_1Ba_2Cu_3O_{7-\delta}$ prepared in air and slowly cooled shows an onset T_c almost equal to that of $Y_1Ba_2Cu_3O_{7-\delta}$ prepared in O_2 and slowly cooled. It shows, however, the zero-resistance temperature $T_0 = 57.2$ K. This, together with the semiconductorlike behavior above T_c, is interpreted as a result of the percolating behavior for the mixture of the superconducting phase and nonsuperconducting phase due to the excessive deficiency of oxygen. Superconductivity is also confirmed by the ac susceptibility measurement. The onset T_c from the susceptibility measurement was in good agreement with the result of resistivity measurement. The quench-cooled $Y_1Ba_2Cu_3O_{7-\delta}$ showed a diamagnetic behavior at 80 K without any appreciable susceptibility jump near 90 K. This again supports, together with the narrow transition width shown in the resistivity measurement and x-ray diffraction result, that the quench-cooled sample is of the single phase with a homogeneous oxygen distribution.

Thermoelectric power measurement for the samples shows a quite unexpected result. Figure 3 shows the result of the thermoelectric power measurements for $Gd_1Ba_2Cu_3O_{7-\delta}$, $Yb_1Ba_2Cu_3O_{7-\delta}$, and two $Y_1Ba_2Cu_3O_{7-\delta}$, one prepared in O_2 and slowly cooled and the other one also prepared in O_2 and slowly cooled but slightly off-stoichiometric. Clearly the abrupt and complete disappearance of S below T_c within the experimental error indicates that the transition is of superconductive transition.

Magnitude of S above T_c indicates that these high-T_c superconductors are of a metallic nature. Thermoelectric power S of $Y_1Ba_2Cu_3O_{7-\delta}$ prepared in O_2 and slowly cooled shows a negative sign with the magnitude ~4

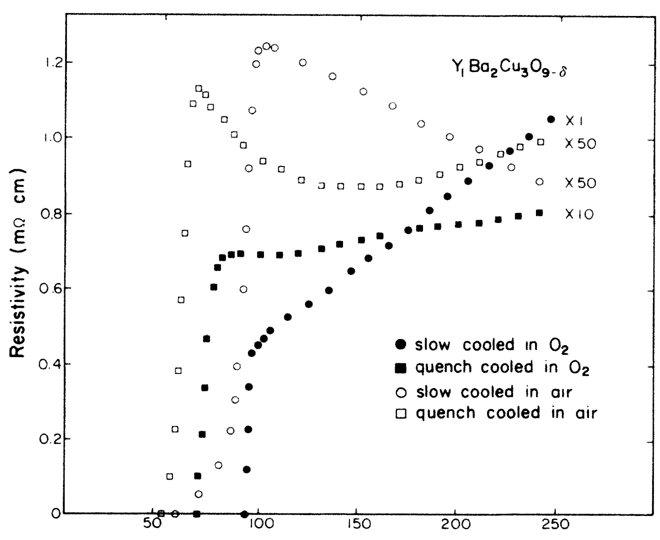

FIG. 2. Temperature dependence of the resistivity. The onset T_c of $Y_1Ba_2Cu_3O_{7-\delta}$ prepared in O_2 and slowly cooled and in air and slowly cooled is almost identical.

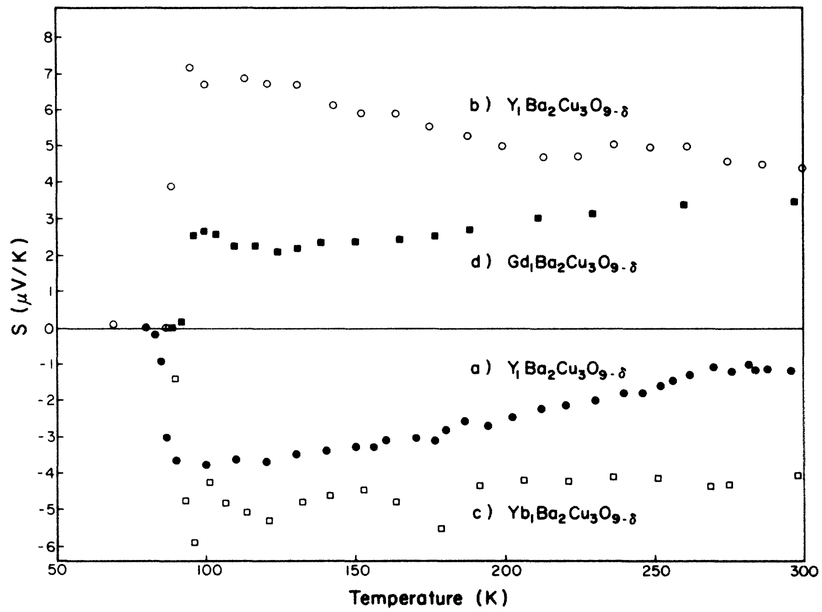

FIG. 3. Typical thermoelectric power of the high-T_c superconductors, which were prepared in O_2 and slowly cooled. $Y_1Ba_2Cu_3O_{7-\delta}$, which shows positive S, was made slightly off-stoichiometric by mixing less CuO.

μV/K similar to our earlier report.[14] Samples prepared in air and O_2 and quench cooled show, however, positive S. Furthermore, $Y_1Ba_2Cu_3O_{7-\delta}$ prepared slightly off the stoichiometry by mixing slightly less amounts of CuO also shows positive S, although the superconductive transition temperature is still ~90 K. In addition, the thermoelectric power S of the rare-earth-element superconductors which have T_c at ~90 K or above 90 K shows a close relation between the ionic size of the rare-earth element and the sign of S. Superconductors with the rare-earth ionic radius larger than 0.92 Å show positive S, while those with the rare-earth ionic radius smaller than 0.92 Å show negative S. For example, $Gd_1Ba_2Cu_3O_{7-\delta}$, which has the Gd ionic radius of 0.98 Å, shows a positive S, while $Yb_1Ba_2Cu_3O_{7-\delta}$, which has the Yb ionic radius of 0.86 Å, shows a negative S. Table II shows the resulting superconducting properties including the thermoelectric power at room temperature for the $R_1Ba_2Cu_3O_{7-\delta}$.

This observation indicates that the excessive oxygen deficiency realized through sintering in air, structural deformation by quench cooling, or possible internal strain in rare-earth-element superconductors have a strong influence on the magnitude and even the sign of the thermoelectric power S. Although it might still be possible that the observed sign change in S could be due to the mixed phase or grain boundary effect, one cannot neglect the strong correlation between the thermoelectric power sign and the ionic radius size observed in the rare-earth-compound superconductors.

In summary, we have shown that the thermoelectric power in $Y_1Ba_2Cu_3O_{7-\delta}$, which has the Y ionic radius of 0.92 Å, can either be positive or negative depending on the fabrication processes in addition to the strong correlation between the ionic radius and the thermoelectric power in

TABLE II. Properties of $R_1Ba_2Cu_3O_{7-\delta}$.

					T_c				
R	r (Å)	c	c/b	a/b	Onset	Mid	Zero	ΔT_c[a]	S (μV/K)[b]
Nd	1.04	11.780	3.005	0.987	96.7	93.5	86.0	5.5	8.8
Sm	0.98	11.727	3.012	0.994	85.0	73.0	61.0	12.0	21.9
Eu	0.98	11.753	3.003	0.986	86.5	82.2	70.0	7.0	1.6
Gd	0.97	11.743	3.000	0.981	96.6	95.7	94.4	1.2	3.4
Dy	0.92	11.726	3.003	0.982	96.1	95.1	93.4	1.3	−1.2
Ho	0.91	11.700	3.002	0.983	93.5	91.3	88.8	2.5	−2.7
Er	0.89	11.705	3.005	0.981	93.2	91.1	88.8	2.8	−3.0
Tm	0.87	11.783	3.010	0.982	94.6	92.1	89.4	2.5	−2.2
Yb	0.86	11.746	3.007	0.980	97.8	96.1	91.7	2.5	−4.9
Lu	0.85	11.663	3.007	0.979	95.8	92.4	89.8	4.0	−4.7

[a] $\Delta T_c = T_c(90\%) - T_c(10\%)$.
[b] Thermoelectric power at room temperature.

rare-earth-element superconductors. These observations seem to indicate that the high-T_c oxide superconductors have a multiband nature with a partially filled electron band and a hole band as proposed by Lee and Ihm.[13] With a slight shift in the Fermi energy possibly caused by internal strain from the excessive oxygen deficiency, structural deformation, or ionic size difference, the sign of the thermoelectric power could have changed due to the change in occupation of the electron band and the hole band.

Elucidation of observed behavior of thermoelectric power in high-T_c superconductors can lead to a better understanding of the nature of superconducting mechanisms in these materials.

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