Thermoelectric power of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$

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(Received 6 November 1991)

The effects of oxygen nonstoichiometry and substitution of composition elements on the thermoelectric power of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ were investigated. Experiments studying the Seebeck coefficient S for the $Bi_2Sr_2CaCu_2O_{8+y}$ sample sintered in air yielded negative values for S in the temperature range from 310 K down to T_c. However, the Seebeck coefficient for $Bi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_{8+y}$ was negative around room temperature, then became positive around 270 K, and remained positive down to T_c. Also, the Seebeck coefficients for the $Bi_2Sr_2CaCu_2O_{8+y}$ sample reduced in Ar and for the $Bi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_{8+y}$ sample sintered in air exhibited a similar temperature dependence. From these results, it was considered that the characteristic behavior of the Seebeck coefficient was controlled by the Cu valence. To explain these results, it was considered that the Fermi-surface geometry for the midgap states was two dimensional. When the Fermi level is located near the van Hove singularity point, the states both above and below the van Hove singularity point may contribute to S. This model agreed with Seebeck coefficient measurements. From the results on S for antiferromagnetic insulating $Bi_2Sr_2Ca_{0.2}Y_{0.8}Cu_2O_{8+y}$ and $Bi_2Sr_2YCu_2O_{8+y}$ sintered in air, it was considered that the electrical conduction of these compounds was by a variable-range-hopping mechanism.

I. INTRODUCTION

The thermoelectric power TEP has been measured for the Bi cuprate superconductors.[1–4] The data for sintered samples of $Bi_2Sr_2CaCu_2O_{8+y}$ were similar to those for single crystals, and indicated that the decrease in the TEP (or Seebeck) coefficient, S, extended up to around 500 K. The sign of S was negative at high temperatures, but a positive peak was observed at low temperatures. On the contrary, according to Rao et al.'s data,[4] S was always negative as the temperature increased above T_c, although it had a negative slope with respect to temperature as other measurements exhibited. Also, the substitution of Ca by Y shifted the S-vs-T curve upwards to give positive values above T_c because the oxygen content was increased by the substitution.[4] Thus, a fairly consistent pattern of an approximately linear decrease above T_c emerged for the thermoelectric power of $Bi_2Sr_2CaCu_2O_{8+y}$. Therefore, it is important to investigate the effects of oxygen nonstoichiometry (or oxygen content) on the thermoelectric power of the Bi cuprate superconductors. In this paper, we investigate the effects of oxygen nonstoichiometry on the thermopower of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ and discuss the substituting effects of composition elements and the relationship between oxygen nonstoichiometry and S.

II. EXPERIMENT

The samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x = 0.0, 0.2,$ 0.4, 0.5, 0.8, and 1.0) were synthesized by a conventional solid-state reaction method. High-purity powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, Y_2O_3, La_2O_3, Nd_2O_3, Pr_6O_{11}, and CuO were mixed and then calcined. After calcined at a

temperature with range of 1073–1173 K for 10 h in air, the mixed powders were ground and pressed into parallelepiped bars of $3 \times 3 \times 20$ mm^3. The bars were sintered at the temperature range from 1113 to 1190 K at $P_{O_2} = 0.21$ atm. The phases contained in the samples and the structure of the phases have been analyzed by x-ray powder diffraction (XRD). All the samples were found to be of single phase. The crystallographic structure was found to be of the 232 type.

The Seeback coefficients were measured by a dc differential method at temperatures between 25 and 310 K. The temperature and temperature gradient across the sample were measured using, respectively, a calibrated Si diode sensor and two pairs of copper-Constantan thermocouples.

The average valence of the Cu and Bi ions was determined by a Coulometric titration technique.[5] 1N HCI was used for the solvent. This technique involves two steps of titration. The oxygen contents of the 2:2:1:2 samples were determined by the sum of the amounts of Bi^{5+} and Cu^{3+} ions and by charge valance.

III. RESULTS

The Seebeck coefficients, S, for the superconducting samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x = 0.0, 0.2, 0.4,$ and 0.5) are plotted against temperature in Fig. 1. $Bi_2Sr_2CaCu_2O_{8+y}$ ($x = 0.0$) had negative values for S in the temperature range from 310 K down to T_c, and S decreased linearly as temperature increased. This suggests that the transport property in the normal state of the sample with $x = 0.0$ was metallic. However, the Seebeck coefficient of $Bi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_{8+y}$ ($x = 0.2$) was negative around room temperature, then become
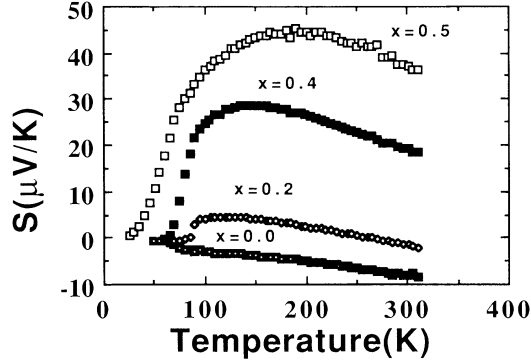
FIG. 1. Temperature dependence of the Seebeck coefficient S of Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ (x =0.0, 0.2, 0.4, and 0.5) sintered in air.

TABLE I. p, q, $8+y$, T_c^{dc}, and $T_c^{R=0}$ for Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ sintered in air.

Composition	p	q	$8+y$	T_c^{dc} (K)	$T_c^{R=0}$ (K)
(a) x =0.0	2.16	3.12	8.28	76	61
(b) x =0.2	2.15	3.09	8.34	86	71
(c) x =0.4	2.10	3.06	8.36	76	50
(d) x =0.5	2.10	3.04	8.39	66	20
(e) x =0.8	2.06	2.99	8.45		
(f) x =1.0	2.04	2.99	8.53		

positive around 270 K, and remained positive down to T_c. It also decreased linearly as temperature increased. The data for Bi$_2$Sr$_2$Ca$_{0.6}$Y$_{0.4}$Cu$_2$O$_{8+y}$ (x =0.4) and Bi$_2$Sr$_2$Ca$_{0.5}$Y$_{0.5}$Cu$_2$O$_{8+y}$ (x =0.5) were positive in the temperature range from 310 K to T_c. The Seebeck coefficient curves above T_c for all the samples (except one with x =0.0) showed broad peaks and started to decrease linearly as the temperature increased further. Figure 2 shows the temperature dependence of S for antiferromagnetic insulating Bi$_2$Sr$_2$Ca$_{0.2}$Y$_{0.8}$Cu$_2$O$_{8+y}$ (x =0.8) and Bi$_2$Sr$_2$YCu$_2$O$_{8+y}$ (x =1.0). The Seebeck coefficients for the two compounds increased with increasing temperature. It was reported that a large anomaly in S around the Néel point was observed in La$_{2-x}$Sr$_x$CuO$_{4-y}$.[6] However, the existence of such an anomaly around the Néel point was not seen in these compounds. The Cu oxidation levels in the samples of Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ were determined by employing a Coulometric titration technique. In Table I, the experimental results for the Cu valence, p, the Bi valence, q, and the oxygen content, $8+y$, are given for the Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ samples with (a) x =0.0, (b) x =0.2, (c) x =0.4, (d) x =0.5, (e) x =0.8, and (f) x =1.0. Note that a valence of -2 was assumed for the oxygen ions. The superconducting transition temperatures obtained from the dc magnetization
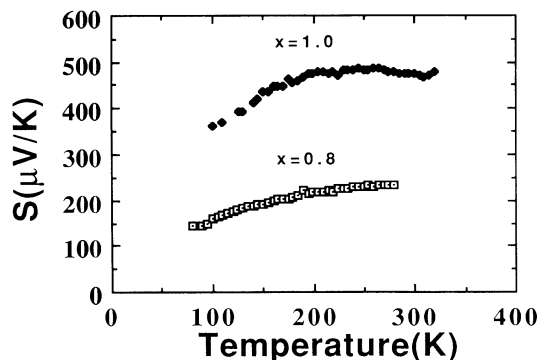
(T_c^{dc}) and the dc resistivity ($T_c^{R=0}$) are also given in Table I. It is obvious that the superconducting properties of these compounds were dependent on the substitution of Y for Ca.

To investigate the oxygen nonstoichiometry effects on S for Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$, the samples sintered in air were ground and pressed, and then reduced at either 1073 or 1093 K for 72 h in Ar or N$_2$. Figure 3 shows the temperature dependence of S for Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ (x =0.0, 0.5, and 0.8). In Table II, the experimental results for the Cu valence, p, the Bi valence, q, and oxygen content, $8+y$, are given for Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ (x =0.0, 0.5, and 0.8) samples. For the samples with

FIG. 2. Temperature dependence of the Seebeck coefficient S of Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ (x =0.8 and 1.0) sintered in air.
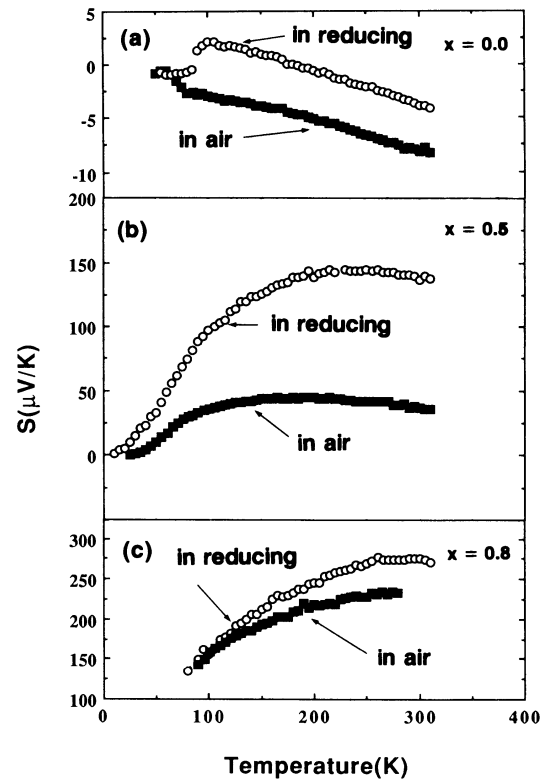
FIG. 3. Temperature dependence of the Seebeck coefficient S of Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ (x =0.2, 0.5, and 0.8) sintered in the reducing conditions.

TABLE II. p, q, $8+y$, T_c^{dc}, and $T_c^{R=0}$ for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x = 0.0, 0.5$, and 1.0) sintered in the reducing condition.

Composition	p	q	$8+y$	T_c^{dc} (K)	$T_c^{R=0}$ (K)
(a) $x = 0.0$	2.10	3.05	8.15	87	40
(b) $x = 0.5$	2.09	3.02	8.36	18	< 4
(c) $x = 0.8$	1.98	3.00	8.38		

$x = 0.8$, we assumed that the Bi valence was equal to $3+$ since this titration does not work when the Cu valence is below $2+$. Also, the superconducting transition temperature obtained from the dc magnetization (T_c^{dc}) and the dc resistivity ($T_c^{R=0}$) are given in Table II. The Seebeck coefficients for the three compounds increased as the oxygen content decreased, the Cu oxidation level was lowered as the degree of reduction increased. Particularly, T_c^{dc} for the $Bi_2Sr_2CaCu_2O_{8+y}$ sample rose from 76 to 87 K by reduction. Furthermore, the Seebeck coefficient, S, for the $Bi_2Sr_2CaCu_2O_{8+y}$ sample reduced in Ar and for the $Bi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_{8+y}$ sample sintered in air exhibited similar temperature dependences. This suggests that the Seebeck coefficient for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ is controlled mainly by the Cu valence.

IV. DISCUSSION

First of all, it should be pointed out that the Seebeck coefficients for both $Bi_2Sr_2CaCu_2O_{8+y}$ and $Bi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_{8+y}$ were negative in a certain region of temperature. The sample with $x = 0.0$ was negative throughout the temperature range. However, Temegai et al.[7] reported that the sign of the Hall coefficient was positive for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x = 0.0$, 0.2, 0.4, 0.5, 0.8, and 1.0) samples. A similar behavior was observed by Uher et al.[8] for $La_{2-x}Sr_xCuO_4$. As the temperature increased, the Seebeck coefficient for $La_{1.75}Sr_{0.25}CuO_4$ changes its sign from positive to negative. When the temperature was fixed, the Seebeck coefficient increased with increasing Sr content. Uher et al. also pointed out that a positive Hall coefficient and a negative thermoelectric power might imply the presence of more than one type of carrier. Also, they proposed that the carriers in the highest Sr-doped $La_{2-x}Sr_xCuO_4$ superconducting compounds should consist of relatively mobile holes which are responsible for superconductivity and of somewhat heavy electrons. In general, the standard expressions for the Seebeck coefficient and Hall constant in the two-band model are[9,10]

$$S = \frac{\sigma_1}{\sigma}S_1 + \frac{\sigma_2}{\sigma}S_2 , \qquad (1)$$

$$R_H = \left[\frac{\sigma_1}{\sigma}\right]^2 R_{H1} + \left[\frac{\sigma_2}{\sigma}\right]^2 R_{H2} , \qquad (2)$$

where σ is the total conductivity, i.e., $\sigma = \sigma_1 + \sigma_2$ in which σ_i is the conductivity in the ith band. It is seen

immediately from the weighting factors that the heavier carriers have a larger contribution to the thermoelectric power than to the Hall constant, and this is accentuated by the fact that the characteristic thermoelectric power S_1 for the heavier carriers is usually large because of the large energy dependence of their mobility. Thus, the heavier electrons can dominate the thermoelectric power while lighter holes dominate the Hall constant. On the basis of this model, Uher et al. explained the electronic transport properties in $La_{2-x}Sr_xCuO_4$ superconducting compounds. In the $Bi_2Sr_2CaCu_2O_{8+y}$ system, the hole concentration in the Cu-O plane is excessively large because of the positive value of y.[11,12] Several authors[13-15] have reported that the T_c of the compound of this system was raised by quenching from 1073 K into liquid nitrogen and a decrease in the hole concentration in the Cu-O plane might occur because of a decrease in oxygen concentration. Also, it has already been reported[7,16] that T_c increases initially with increasing x in the $Bi_2Sr_2Ca_{1-x}L_xCu_2O_{8+y}$ ($L = $the rare-earth elements) system and, also, substitution of Ca^{2+} by an L ion caused a decrease in the hole concentration in the Cu-O plane. Actually, the Cu valence for the $Bi_2Sr_2CaCu_2O_{8+y}$ sample sintered in air ($T_c^{dc} = 76$ K) is larger than those for a reduced $Bi_2Sr_2CaCu_2O_{8+y}$ sample ($T_c^{dc} = 87$ K) and for the $Bi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_{8+y}$ sample sintered in air ($T_c^{dc} = 86$ K). This suggests that $Bi_2Sr_2CaCu_2O_{8+y}$ is a compound in the heavily doped region. Therefore, it is plausible that more than two types of carriers existed in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples as in $La_{2-x}Sr_xCuO_4$.

A systematic photoemission and x-ray-absorption study of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ (Ref. 17) clearly showed that the Fermi-liquid state in the high-T_c superconductors was not a simple one-electron state predicted from the band-structure calculation but was a kind of impurity state. Such "impurity states" have been called midgap states[18] and considered to be yielded through the strong hybridization between doped O $2p$ hole orbitals and empty Cu $3d$ orbitals if a single-band model is employed. This implies that multiple-band models are not most suitable for decreasing the transport properties of high-T_c superconductors. This implication is rather contrary to the two-band model introduced previously for the explanation of our thermoelectric power data. It should be noted that transport phenomena including thermoelectric power may be explained via the behavior of carriers in the midgap states.

Using the single-band model, Newns, Pattnaik, and Tsuei[19] and Kim and Levin[20] independentally calculated the Hall coefficient, R_H. In both calculations, the sign of R_H was found to be positive. It is known that, for a parabolic band structure in a Fermi-liquid scheme, the Hall coefficient, R_H, is given by

$$R_H = 1/ne , \qquad (3)$$

where n is the carrier concentration. However, in general, the sign of the Hall coefficient is determined by the curvature of the Fermi surface rather than the carrier type.[21] When only copper-oxygen overlapping was in-

cluded in the model Hamiltonian, R_H was found to vanish at half-filling and to be negative when excess holes were added. Recently, Kubo et al.[22] reported the electric states in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ on the basis of the magnetic susceptibility, Hall coefficient, and Seebeck coefficient. They pointed out the possibility that both changes in the sign of the Hall coefficient and Seebeck coefficient were induced by the existence of a van Hove-type singularity. If the Fermi surface geometry for the midgap state is two dimensional (2D), there is more than one van Hove singularity point. When the Fermi surface exists near a van Hove singularity point, the density of states may exist both above and below the van Hove singularity point when the temperature is finite at T (>0 K). In general, the diffusion thermoelectric power in a metallic system is given by the Mott formula[23]

$$S = (\pi^2 k_B^2 T / |e|) \frac{\partial \ln \sigma}{\partial E}\bigg|_{E_F} , \tag{4}$$

where any phonon or magnon drag terms have been ignored. The sign of S gives the sign of the majority carriers, and the magnitude of S is proportional to the density of states at the Fermi level. In the Mott model, S should decrease in magnitude with T for either type of carrier, hole, or electron. It follows from Eq. (4) that S is proportional to the derivative of the Fermi level in respect to the energy at a fixed temperature. When the Fermi level is located near the van Hove singularity point, the states both above and below the van Hove singularity point may contribute to S. Therefore, it is possible that the sign of S changes from negative to positive as the temperature and/or carrier concentration decrease.

For both $Bi_2Sr_2Ca_{0.2}Y_{0.8}Cu_2O_{8+y}$ and $Bi_2Sr_2YCu_2O_{8+y}$, the electrical conduction was semiconductive. The temperature dependence of S for a semiconductor or a material having a mobility gap at the Fermi level is given by[24]

$$S = (k_B / |e|) \left[\frac{\Delta}{T} + A \right] , \tag{5}$$

where Δ is the effective gap energy and A is a constant. In Eq. (5), the magnitude of S decreases with increasing T. Contrary to this, the temperature dependence of the experimentally measured Seebeck coefficients for the two compounds indicated metallic conductions, as shown in Fig. 2. Recently, Jayaram, Lanchester, and Weller[25] reported that the electrical conduction in the insulator regime of $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+y}$ was due to a variable-range-hopping (VRH) mechanism. In the VRH region,

the Seebeck coefficient may be given by[23]

$$S = aT^{1/2} , \tag{6}$$

where a is a constant. Actually, the temperature dependence of S in Fig. 2 obeys Eq. (6). This result agrees with the results of the resistivity measurements.

V. CONCLUSION

The effects of oxygen nonstoichiometry and substituting of composition elements on the thermoelectric power of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ was investigated and the results taken as follows.

(1) From the experiments of S for the $Bi_2Sr_2CaCu_2O_{8+y}$ sample sintered in air, this had negative values for S in the temperature range from 310 K down to T_c, and S decreased linearly as the temperature increased. However, the Seebeck coefficient of $Bi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_{8+y}$ was negative around room temperature, then become positive around 270 K and remained positive down to T_c. It also linearly decreased as the temperature increased. The data for $Bi_2Sr_2Ca_{0.6}Y_{0.4}Cu_2O_{8+y}$ and $Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{8+y}$ were positive in the temperature range from 310 K to T_c.

(2) The temperature dependence of S for the antiferromagnetic insulating $Bi_2Sr_2Ca_{0.2}Y_{0.8}Cu_2O_{8+y}$ and $Bi_2Sr_2YCu_2O_{8+y}$ sintered in air increased with increasing temperature. From these results, it was considered that the electrical conduction of these compounds was the variable-range-hopping mechanism.

(3) From the results of the sample sintered in the reducing condition, it was considered that the characteristic behavior of Seebeck coefficient was controlled by the Cu valence. Particularly, the Seebeck coefficients for the $Bi_2Sr_2CaCu_2O_{8+y}$ sample reduced in Ar and for the $Bi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_{8+y}$ sample sintered in air exhibited a similar temperature dependence.

(4) To explain the results in terms of (1) and (3), we considered that the Fermi surface geometry for the midgap states was 2D. When the Fermi level is located near the van Hove singularity point, the states both above and below the van Hove singularity point may contribute to S. Therefore, it was possible that the sign of S changed from negative to positive as temperature and/or carrier concentration decreased. This model agreed with the results of the Seebeck coefficient measurements.

ACKNOWLEDGMENT

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