Thermoelectric power of $Bi_{2-x}Pb_xCa_2Sr_2Cu_3O_{10}$ based on the two-band model

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A two-band model has been applied to explain the observed behavior of the thermoelectric power of Bi-2:2:2:3. The model invokes the Cu-O planes, which contribute to the metallic conduction of holes, while Bi-O planes contribute to the semiconductorlike behavior of electrons. The results indicate a good fit to the observed data and are consistent with the recently reported scanning-tunneling-spectroscopy studies of Bi-O layers in Bi cuprates.

INTRODUCTION

The measurement of thermoelectric power is among the frequently pursued transport investigations in solids primarily performed to gain insight into the nature of the charge carriers responsible for the conduction process. It also provides information about the bandwidths and the band gaps which govern the transport properties of the materials.[1,2] With the advent of high-T_c superconductors much of the experimental and theoretical efforts have been directed to understand the thermopower of these cuprates exhibiting high-T_c phenomena.[3,4] Some of these studies have considered the two-band model[5,6] to explain the observed behavior of most of the high-T_c cuprates. In the case of Bi-based high-T_c systems, e.g., Bi 2:1:2:2/2:2:2:3 the band-structure calculations[7,8] seem to suggest that in addition to Cu-O planes taking part in the metallic conduction, the Bi_{6p}-O_{2p} band of Bi-O also dip down in E_f and contribute to the Fermi surface of the material. Further as suggested by some recent investigations, an electron-type conduction is dominant in Bi-O layers,[9-11] while Cu-O planes are known to have a hole-type conduction. Reduction in the valence state of Bi^{3+} to $Bi^{3-\delta}$ gives rise to an electronic conduction in Bi-O planes, while the oxidation of Cu^{2+} to $Cu^{2+\delta}$ gives rise to the hole conduction in Cu-O planes. The mechanism of the oxidation and reduction processes can be given as[11]

$$Bi^{3+}+Cu^{2+}=Bi^{3-\delta}+Cu^{2+\delta}\ . \quad (1)$$

In the above background we find it reasonable to apply a two-band model explanation to the thermopower behavior of Bi-based systems. Recently, such a model has been successfully applied to understand the observed thermoelectric power (TEP) data on the T1 2:2:2:3 system.[6] The Bi 2:2:2:3 system is essentially analogous to T1 2:2:2:3. We have, in this paper, followed Xin *et al.*,[6] to understand TEP behavior of the Bi 2:2:2:3 system.

EXPERIMENT

The sample of nominal stoichiometry $Bi_{1.6}Pb_{0.4}Ca_2Sr_2Cu_3O_{10}$ was prepared by the usual solid-state reaction method using ingredients of better than 4*N* purity. The calcinations were carried out at 800, 810, and 820 °C, respectively, for 15 h each with intermediate grindings. The sintering was carried out at 870 °C for 120 h and finally the sample was furnace-cooled down to room temperature. The sample was then characterized through resistivity, susceptibility, and x-ray diffraction (XRD). Thermoelectric power measurements were carried out on a closed-cycle refrigerator.

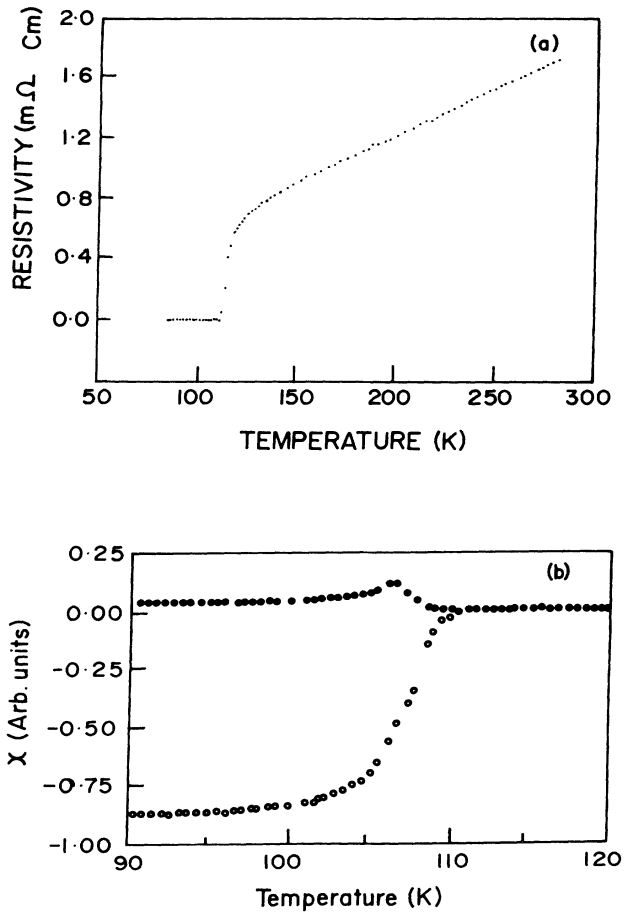

FIG. 1. (a) Resistance versus temperature behavior of Bi 2:2:2:3 system. (b) Ac susceptibility versus temperature behavior of Bi 2:2:2:3 system.

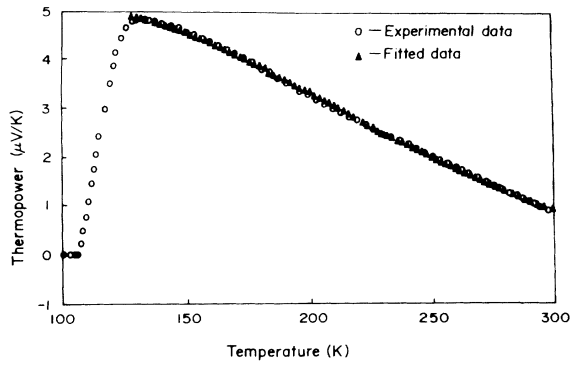

FIG. 2. TEP versus temperature behavior of Bi 2:2:2:3 system.

RESULTS

The sample, when gradually cooled from room temperature, showed a resistive transition to superconducting state at 109 K [Fig. 1(a)]. From XRD patterns a near single-phase nature of Bi 2:2:2:3 was confirmed with $a=b=5.39$ Å and $c=36.79$ Å. Ac susceptibility measurement showed a diamagnetic transition at 109 K [Fig. 1(b)], in close accord with resistive transition. The results of the thermoelectric power measurements of the sample are depicted in the form of the S-T curve in Fig. 2. The Seebeck coefficient was found to be zero at 108 K, consistent with the critical temperature as determined through resistivity and magnetic susceptibility.

DISCUSSION

Thermoelectric power of a metal which satisfies the Fermi-liquid model, is given by[1]

$$S=-\frac{\pi}{2}\frac{k}{e}\frac{kT}{E_{f0}}\left[\frac{d\ln(E)}{d\ln E}+\frac{d\ln v^2(E)}{d\ln E}+\frac{d\ln\tau(E)}{d\ln E}\right], \tag{2}$$

where $\tau(E)$ is the relaxation (scattering) time of electronic charge carriers of energy E, e is the magnitude of electronic charge and E_{f0} is the zero-temperature Fermi energy. Equation (2), with a single kind of charge carriers cannot describe the S-T dependency shown in Fig. 2. As suggested in introduction part, a two-band model is to be applied for this material, where one band is formed by Cu-O planes and the other by Bi-O. For a semiclassical and nearly half-filled single-band model with p-type conduction (i.e., Cu-O planes), Eq. (2) results as

$$S^+=-\frac{\pi}{3}\frac{k}{e}\frac{kT}{E_{f0}}\left[\frac{d\ln\sigma^+(E)}{d\ln E}\right], \tag{3}$$

where $\sigma^+(E)$ is the electrical conductivity of the material. A p-type conduction is believed to be responsible for superconductivity in these high-temperature superconducting (HTSC) materials. Contribution from the e^--type Bi-O planes would be given by the nondegenerate semiconductor expression, as below:[1,12]

$$S^-=\frac{k}{e}\left[\frac{E_c}{kT}+\frac{d\ln\tau(E)}{d\ln E}\right]. \tag{4}$$

If σ^+ is the conductivity the Cu-O planes and σ^- is the conductivity of Bi-O planes, then the total thermopower is given by[1]

$$S=\frac{(\sigma^+S^++\sigma^-S^-)}{\sigma}. \tag{5}$$

σ is the net conductivity of this system. Now Cu-O is metallic hence, $\sigma^+\alpha 1/T$, and the Bi-O planes are semiconductorlike[9,10] hence, $\sigma^-\alpha\exp(Ec/KT)$. On the basis of Xin *et al.*, the total TEP can be given by

$$S=-g\pi^2\left[\frac{d\ln\sigma^+(E)}{d\ln E}\right]T+\left[\frac{E_c}{e}+\frac{k}{e}\frac{d\ln\tau(E)}{d\ln E}T\right]e^{-E_a/kT}, \tag{6}$$

which in general can be represented by the equation[6]

$$S=AT+(B\lambda+CT)\exp(-\lambda/T). \tag{7}$$

A, B, C, and λ are the constants for a particular material. The filled triangles in Fig. 2 are the fit of Eq. (6) to the experimental data. The fitting parameters A, B, C, and λ are found to be $A=0.066\,87$, $B=-0.137\,95$, $c=-0.042\,57$, and $\lambda=342.16$. As temperature decreases the absolute value of TEP increases with p-type conduction dominating, while at high temperatures the e-type TEP of Bi-O layers seems to dominate.

We used the above value of λ to calculate the energy gap in semiconductorlike band structure of Bi-O layers. The semiconductor energy gap E_g in the intrinsic semiconductors is usually given by $E_g=2E_c$. According to the relation $\lambda=E_c/K$ with $\lambda=342.16$, E_g comes out to be 0.031 eV.

This is consistent with the scanning-tunneling-spectroscopy studies of Bi 2:1:2:2 system which show the room-temperature gap in a wide range of 0.0–0.3 eV.[9,10] The gap depends upon the extent of intercalation of excess oxygen in the Bi-O layers: For the near absence of excess oxygen, the gap approaches zero.

The value of A gives the contribution for the mobile holes in the Cu-O planes, which can change with doping or with a change in the oxygen content of the samples. Samples processed with various heat treatments lead to a change in the valence state of Bi,[7,8,11] which may result in different values of the energy gap in the Bi-O spectrum.

Since the above model seems to have worked so well with the present Bi series of compounds as well as with the previously reported Tl-based ones,[6] it is natural to question the applicability of the model to other HTSC systems, for instance 1:2:3. The situation, however, does not seem to be so straightforward with 1:2:3, where the existence of an additional band for the semiconductive component is questionable. Surprisingly, however, the

TEP behavior of an untwinned 1:2:3 single crystal along a axes is found to be analogous to that of Bi 2:2:2:3.[13] The reason for this is not understood presently. When the crystal is untwinned and there is no mutual swapping of a and b axes, the Cu(1)-O(1) complex has uninterrupted excess holes along the b axes, while the Cu(1)-O(5) complex is devoid of holes along the a axes.[14–16] For measurements in the a direction the two components involved would be holes from CuO_2 planes plus the absence of holes along the Cu(1)-O(5) complex, the latter may be taken as an n-type semiconductive component. Such a conjecture is, however, purely hypothetical calling for experimental confirmation. In the absence of this, the model presumably works only for Bi- and Tl- based compounds, where the presence of two types of bands is less doubtful.

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