

Thermopower measurements on BiSrCaCuO system

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Abstract. We report thermoelectric power measurements on BiSrCaCuO (2212) superconducting oxide and compare the observed behaviour with that of the YBaCuO (123) system. The relative importance of phonon drag and diffusion thermopower contributions is evaluated for the two systems by analysing the data using a generalized expression of the type $S = \alpha T + \beta/T$. The thermopower enhancement effect just above T_c gives parameter values comparable to those of YBa₂Cu₃O_{7-x} system.

Keywords. Phonon drag; diffusion thermopower; electron-phonon mass enhancement.

1. Introduction

There has been a great deal of interest in the study of thermopower behaviour of high- T_c oxide superconductors in the past three years. For the YBaCuO system, a majority of workers have reported a small and positive thermopower (Mawdsley *et al* 1987; Uher and Kaiser 1987; Henkie *et al* 1987; Srinivasan *et al* 1987), although the actual magnitude and temperature dependence are a sensitive function of the oxygen stoichiometry (Hlopkin *et al* 1988; Jha *et al* 1989). There has been only one report on the BiSrCaCuO system for the composition BiSrCaCu₂O_x by Mandal *et al* (1988), who observed a positive sign with a temperature dependence similar to that of LaSrCuO system. In this work we report the thermopower measurement on the Bi₂Sr₂CaCu₂O_{8+x} composition in the temperature range 80–273 K and compare the observed behaviour with that of YBa₂Cu₃O_{7-x} system to understand the differences in diffusion, phonon drag, and electron-phonon mass enhancement effects in these canonical systems of high T_c oxide superconductors.

2. Experimental

In the preparation of bismuth oxide superconductors by the solid-state reaction method, care has to be taken in the final heat treatment since the melting point of Bi₂O₃ is low (≈ 1100 K) compared to the other component oxides. This leads to a loss of Bi and to intergrowth of different phases in an inhomogenous fashion. Hazen *et al* (1988) reported that one generally gets a mixture of phases comprising (2212), a minor component of (2223) and some other insulating phases like (CaSr)₂CuO₃, (CaSr)Cu₂O₃ and (CaSr)BiO_{3-x}. We prepared the samples with two starting compositions of the constituent oxides: Bi₂O₃ + 2SrCO₃ + CaCO₃ + 2CuO and Bi₂O₃ + 2SrCO₃ + CaCO₃ + 3CuO. The X-ray diffraction pattern for a sample in which the final heat treatment was an anneal at 820°C is shown in figure 1a. The lines in the region of $2\theta = 25^\circ$ to 35° are not fully resolved and the reaction is not fully complete at this temperature. Hence the temperature of final anneal was chosen to be 850°C after several trial runs and the following preparation method was adopted:

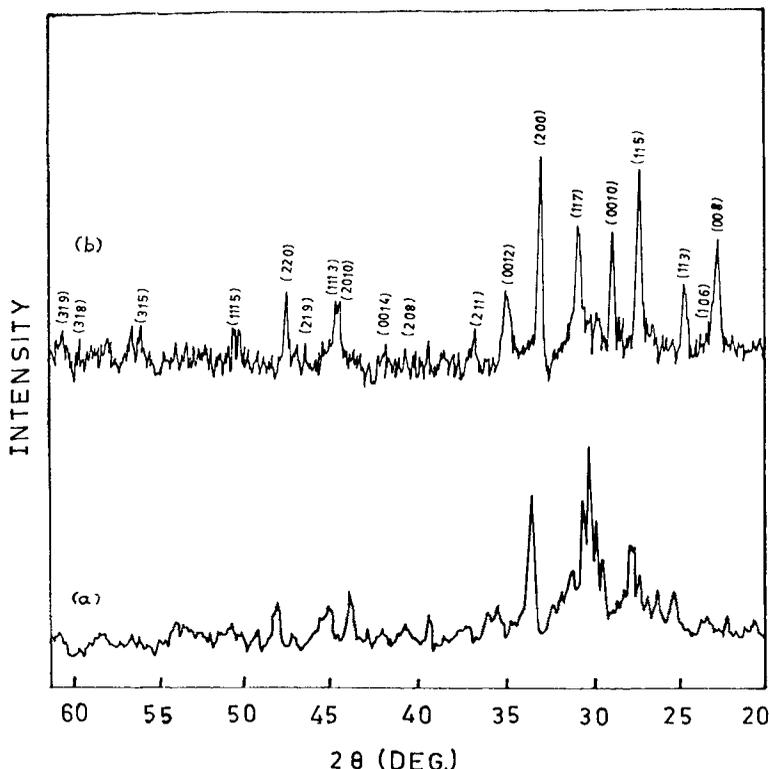


Figure 1. X-ray diffraction patterns for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_3\text{O}_{8+x}$ sample for a final anneal at (a) 820°C and (b) 850°C . The lines do not appear fully resolved at 820°C .

(i) The components were thoroughly mixed and ground in a mortar and pestle for about 30 min to 1 h; (ii) The charge was heated in porcelain crucibles at 800°C for 12 h and furnace-cooled; (iii) The sample was reground and again heated to 820°C and kept for 14 h; (iv) After grinding, the powder was formed into pellets (10 mm dia.) in a hydraulic press at a pressure of 9 to 10 tonnes; (v) The pellets were heated to 840°C for 14 h and the temperature raised to 850°C and cooled after 5 to 10 min. Thermopower was measured using an experimental setup described in detail elsewhere (Anil Kumar 1989).

3. Results

The X-ray diffraction pattern as shown in figure 1b was indexed using the analytical method of Xuequan and Chang (1984). All the 20 lines could be indexed on the basis of a tetragonal unit cell of dimensions $a = b = 5.394 \text{ \AA}$, $c = 30.63 \text{ \AA}$. For the starting composition which has excess of CuO the X-ray diffraction pattern shows two additional lines at $2\theta = 30^\circ$ and 43.375° which could not be indexed on the tetragonal unit cell. These could be due to the insulating phases as observed by Hazen (1988).

The normalized resistivity, $\rho(T)/\rho(273 \text{ K})$ given in figure 2, shows a linear decrease between 273 K and 120 K, a slight deviation from linearity at 120 K and a sharp decrease towards zero resistance starting from 91 K. The temperature for zero

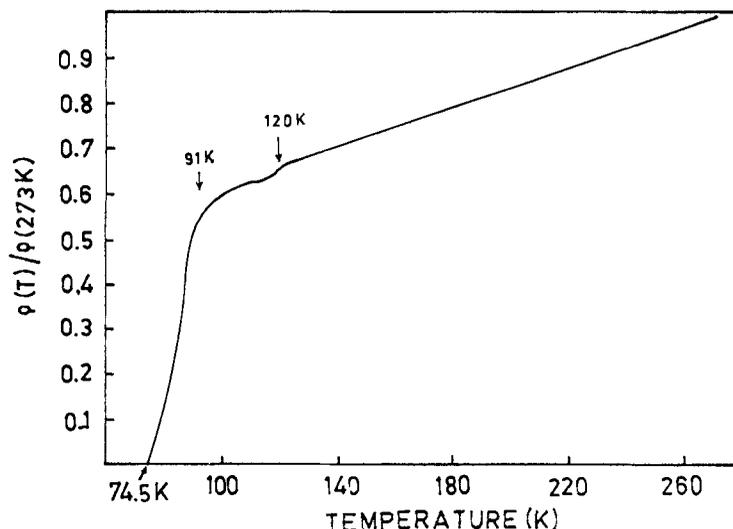


Figure 2. Temperature dependence of normalized resistivity for (2212) oxide superconductor, showing onset and zero resistance temperatures.

resistance is 74.5 K. These values agree with the temperature range of onset and zero resistance temperature observed by other groups. The reported values of zero resistance temperature for 2212 composition lie in the temperature range 75 K to 91 K and depend on strontium to calcium ratio, sintering and quenching heat treatments and oxygen stoichiometry. Torrance *et al* (1988) reported a T_c of 75 K for samples which were prepared by firing in air at 850°C for 16 h followed by slow cooling to room temperature. Tallon *et al* (1988) were able to produce this phase with a T_c of 91 K by a final heat treatment consisting of a rapid quench from 860–870°C. This is the highest value reported for this phase. Others give differing values: Roberts *et al* (1988) ($T_c = 75$ K), Yeh *et al* (1989) ($T_c = 80$ K), Ramakrishna *et al* (1988) ($T_c = 87$ K), Sunshine *et al* (1988) ($T_c = 84$ K), Laborde *et al* (1988) ($T_c = 90$ K).

Figures 3 and 4 show the measured thermoelectric power for BiSrCaCuO and YBaCuO. A comparison of the two data shows that (i) the thermopower has small positive values ($1 \mu\text{V/K}$ for 123 and $0.55 \mu\text{V/K}$ for 2212) at 273 K; (ii) there is an increase in thermopower with decreasing temperature from 273 K to 150 K and (iii) there is an enhancement in thermopower below 150 K before falling to zero at T_c for both systems. It is convenient to understand the behaviour separately in the temperature range 150 K to 275 K and below 150 K.

(a) 150–273 K: The two predominant contributions to thermopower are

(i) diffusion thermopower which varies linearly with temperature as

$$S_D = \alpha T \quad (1)$$

(ii) the phonon drag contribution whose magnitude depends on the number of charge carriers and at sufficiently low temperatures this contribution is given by

$$S_g = C_g/3ne \quad (2)$$

where C_g is the lattice specific heat per unit volume and n the number of carriers of charge e . If the number of carriers is large as in metals this contribution becomes

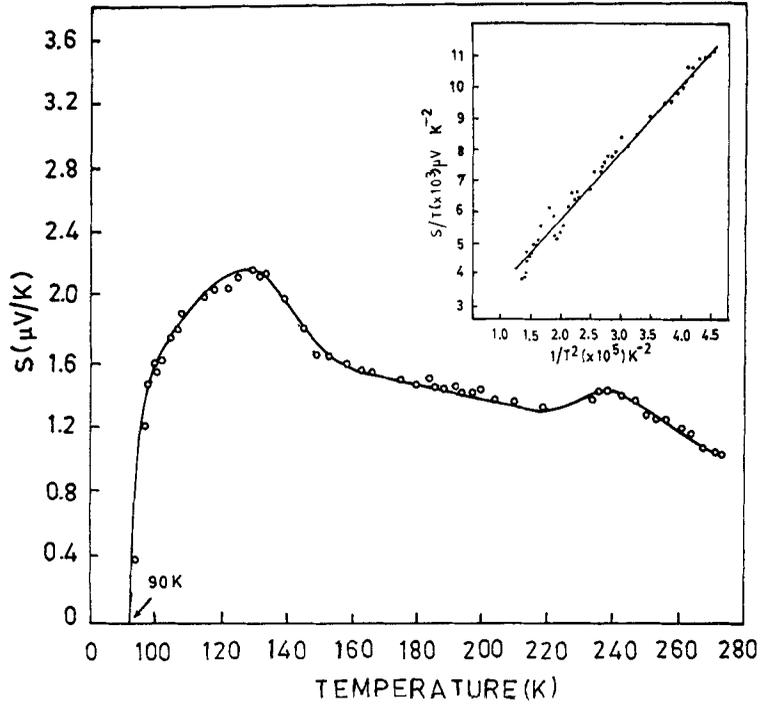


Figure 3. Thermopower behaviour of (123) sample. Inset shows a plot of S/T against $1/T^2$ to separate the phonon-drag and diffusion thermopower contributions.

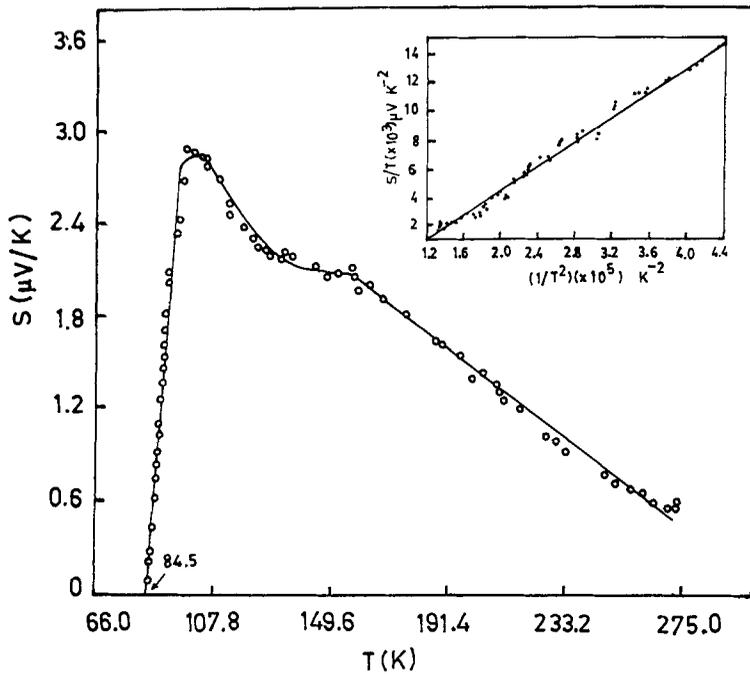


Figure 4. Temperature dependence of thermopower for (2212) oxide superconductor. Inset shows S/T plotted against $1/T^2$.

small compared to the diffusion thermopower. However the normal state resistivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor is large ($\sim 1000 \mu\text{ohm-cm}$) and the number of charge carriers deduced from Hall effect measurements (Henkie *et al* 1987) is $\sim 2.4 \times 10^{21} \text{ cm}^{-3}$. This low carrier concentration favours a large phonon-drag thermopower and cannot be ignored.

The phonon-drag contribution to thermopower at higher temperatures has been shown (MacDonald 1962) to vary as T^{-1} and this dependence has in fact been observed to fit the data of Henkie *et al* (1987) in the temperature range 112–180 K. We have therefore attempted to fit our data in the entire temperature range (150 K–273 K) by a generalized expression of the type

$$S = \alpha T + \beta/T \quad (3)$$

which considers both the diffusion and phonon-drag thermopower in a general way. The insets of figures 3 and 4 show S/T plotted against $1/T^2$. From the slope (β) and intercept (α) one can estimate the relative importance of the phonon-drag (S_g) and diffusion contributions (S_D). The following values are obtained for α and β .

$$\begin{aligned} \text{for 123: } & \alpha = 2.7 \times 10^{-3} \mu\text{V/K}^2, \quad \beta = 2.12 \times 10^2 \mu\text{V}, \\ \text{for 2212: } & \alpha = 1.0 \times 10^{-3} \mu\text{V/K}^2, \quad \beta = 4.2 \times 10^2 \mu\text{V}. \end{aligned}$$

These values imply that at a temperature of 200 K the relative importance of diffusion and phonon-drag contribution is as follows:

$$\begin{aligned} \text{for 123: } & S_D = 0.54 \mu\text{V/K}; S_g = 1.06 \mu\text{V/K}, \\ \text{for 2212: } & S_D = 0.2 \mu\text{V/K}; S_g = 2.13 \mu\text{V/K}. \end{aligned}$$

(b) *TEP enhancement below 150 K*: The unusual thermopower behaviour in the temperature range 100–150 K has been a subject of intensive discussion. For the 123 compound, Trodahl and Mawdsley (1987) and Uher and Kaiser (1987) attribute it to an enhancement in phonon-drag contribution due to an increase in phonon-flux as T_c is approached. The diffusion thermopower is not enhanced. The net thermopower as T_c is approached is considered to be a weighted average of normal and superconducting thermopowers. Although the diffusion thermopower will decrease due to decrease in contribution of superconducting electrons as we approach T_c but the phonon-drag contribution will decrease more slowly giving rise to an enhancement effect as observed.

On the other hand, careful experiments and analysis of thermopower data of YBaCu_3O_7 and Er-doped YBaCu_3O_7 samples by Srinivasan *et al* (1987) show that phonon drag is not likely to be the cause of the enhancement observed just above T_c . It was expected that for the $\text{Y}_{0.8}\text{Er}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$ system the enhancement effect would be suppressed due to the presence of Er substitution if it is due to phonon-drag effects. However the thermopower behaviour was similar to $\text{YBa}_2\text{Cu}_3\text{O}_7$ although with a slight less enhancement. The more recent experiments of Vijayshree Radhakrishnan *et al* (1989) from the same group on $\text{YBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ ($0.025 \leq x \leq 0.4$) also provide unambiguous evidence that phonon-drag is not responsible for the enhancement effect near T_c . Their results clearly show that the peak in thermopower for Zn-doped samples does not occur at the same temperature although the Debye temperature is almost independent of zinc concentration. The peak is also not suppressed with increasing Zn concentration. Both these effects are contradictory to a phonon-drag effect being the cause for the peak. Their thermopower data for YBaCu_3O_7 and for

Table 1. Comparison of parameters in equation (4) for the 2212 and 123 superconductors.

System	a (μVK^{-2})	b	T_0
2212	0.014	159.3	20 K
123	0.017	189.5	17.7 K

Zn-doped samples in the concentration range $0.2 \leq x$ were fitted to the following expression:

$$S(T) = aT[1 + b \exp(-T/T_0)] \quad (4)$$

with a , b and T_0 parameters derived from the fits. The enhancement thus observed varied more steeply than what was expected from electron-phonon mass enhancement calculated by Kaiser (1988) and is also different from the behaviour expected on the basis of the model by Tsdilovski and Tsdilovski (1988).

We have also fitted our data on 2212 sample near T_c to this expression of Srinivasan *et al* (1987). Table 1 compares the values of the parameters of this equation obtained by us for 2212 bismuth superconductor with those of 123 compound reported by Srinivasan *et al* (1987).

4. Conclusions

The thermopower behaviour of yttrium oxide and bismuth oxide superconductors can be understood in terms of the same underlying features: (a) a combination of diffusion and phonon-drag contribution in the temperature range 150–273 K and (b) enhancement effects near T_c . The parameters α, β, a, b and T_c have different but comparable values for both the systems.

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References

- Anil Kumar P 1989 M. Phil. Thesis, University of Hyderabad, Hyderabad
 Hazen R M *et al* 1988 *Phys. Rev. Lett.* **60** 1174
 Henkie Z, Horyn R, Bukowski Z, Markowski P J and Klamut J 1987 *Solid State Commun.* **64** 1285
 Hlopkin M N, Toth J, Sikov A A and Zsoldos E 1988 *Solid State Commun.* **68** 1011
 Jha S R, Reddy Y S, Suri D K, Kundra K D, Sharma R G and Deepak Kumar 1989 *Pramana-J. Phys.* **32** 277
 Kaiser A B 1988 *Phys. Rev.* **B37** 5924
 Laborde O *et al* 1988 *Solid State Commun.* **67** 609
 MacDonald D K C 1962 *Thermoelectricity* (New York: John Wiley) 6 92
 Mawdsley A, Trodahl H J, Tallon J, Sarfatinand J and Kaiser A B 1987 *Nature (London)* **328** 233
 Mandal P, Paddar A, Da A N, Chakraborty A and Ghosh B 1988 *Phys. Rev.* **B38** 9205

- Ramakrishna K, Das B, Singh A K, Tiwari R S and Srivastava O N 1988 *Solid State Commun.* **68** 629
- Lorontz R D and Sexton J H 1988 *Appl. Phys. Lett.* **53** 1654
- Srinivasan R, Sankaranarayan V, Raju N D, Natarajan S, Varadaraju U V and Subba Rao G V 1987 *Pramana-J. Phys.* **29** L225–L230
- Sunshine S A *et al* 1988 *Phys. Rev.* **B38** 893
- Tallon J L, Buckley R G, Gilbert P W, Presland M R, Brown I W M, Bowder M E, Christan L A and Gonel R 1988 *Nature (London)* **333** 153
- Torrance J B, Tokura Y, Laplaca S J, Huang T C, Savoy R J and Nazzal A L 1988 *Solid State Commun.* **66** 703
- Traodahl H J and Mawdsley A 1987 *Phys. Rev.* **B36** 8881
- Tsidilkovski L M and Tsidilskovski V I 1988 *Solid State Commun.* **66** 51
- Uher C and Kaiser A B 1987 *Phys. Rev.* **B36** 5680
- Vijayashree Radhakrishnan, Subramanian C K, Sankaranarayan V, Subba Rao G V and Srinivasan R 1989 *Phys. Rev.* **B40** 6850
- Wu Xuequan and Chang-Ping Chang 1984 *J. Appl. Crystallogr.* **17** 395
- Yeh J J, Diczno S B, Hortford E H, Hong M Jr. and Felder R J 1989 *Appl. Phys. Lett.* **54** 377