Hall effect and thermoelectric studies on Pb and Ag-doped $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ superconductors

B V REDDI*, N E KOSTSOVA[†] and E G SALMAN[†]

*National Physical Laboratory, New Delhi 110012, India

[†]Institute of Inorganic Chemistry, Novosibirsk- 630090, USSR

Abstract. Hall effect and thermoelectric power measurements at room temperature in the magnetic field of 18 kOe on Ag- and Pb-doped $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples indicate that the density of charge carriers decreases with increase in Ag concentration whereas the reverse is observed with Pb. From the reduced scattering factor, it is assumed that the scattering of the charge carriers occurs due to acoustic phonons in the normal state at room temperature.

Keywords. Hall effect; thermoelectric power; dopants; electronic conductivity; Bi–Sr–Ca–Cu–O system.

1. Introduction

An intensive research work is being done all over the world to understand the mechanism of high temperature superconductivity in the recently discovered oxide superconductors. In this direction, the Hall effect in various oxide superconductors has been studied experimentally (Ong *et al* 1987; Tozer *et al* 1987; Karpe and Rao 1988; Clayhold *et al* 1988; Lu *et al* 1989; Briceno and Zettl 1989). Though the influence of various dopants on superconducting transition, T_c in Bi–Sr–Ca–Cu–oxide system has been studied (Kanai *et al* 1989; Jin *et al* 1988; Reddi *et al* 1989 a and b) there seems to be no report on the Hall effect of this system with dopants. Therefore, we have made a systematic study of the influence of Pb and Ag dopants on Hall effect of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$. The preliminary results of Hall effect measurements in the low magnetic field of 8 kOe have appeared elsewhere (Reddi and Uskov 1989). In this paper, we report the dependence of Hall coefficient (R_H), resistivity (ρ), coefficient of thermoelectric power (α), density of charge carriers (n) and mobility of charge carriers (μ) as a function of Pb and Ag concentration in Bi–Sr–Ca–Cu–O system and an attempt is made to find a scattering mechanism of charge carriers in the normal state at room temperature.

2. Experimental

Samples were synthesized from the powders of Bi_2O_3 , SrCO_3 , CaCO_3 , CuO , Ag_2O and PbO , by the powder metallurgy technique as mentioned elsewhere and the samples used in this investigation were the same as reported earlier (Reddi and Uskov 1989). Briefly, the samples investigated have nominal composition of $\text{Bi}_{2-z}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ with z (Pb) varying from 0 to 0.5 and $\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_{3-y}\text{O}_x$ with y (Ag) varying from 0 to 0.2. Two series of samples with different heat treatments were used in this investigation. Series I were sintered at 870°C for 30 min followed by long treatment at 855°C for 68 h. Series II

were sintered at 855°C for 73 h. Sintering was done in air. The dimensions of samples used in this work were 12 mm dia and 0.7 to 2 mm thickness. The Hall effect was measured by van der Pauw method using direct current in the magnetic field of 18 kOe at room temperature. The coefficient of TEP was determined by the method of low-frequency response modulation of the sample $T = 3-4$ K (Antsygin *et al* 1988).

3. Results and discussion

The sign of the Hall coefficient, R_H and the coefficient of thermoelectric power, α indicate that these samples under investigation have electronic conductivity irrespective of Pb and Ag dopants. The increase in Ag concentration leads to decrease in the density of charge carriers (figure 1). Interestingly, the reverse dependence of charge carriers on the Pb concentration was observed (figure 2). Such behaviour may be due to the fact that Ag substitutes Cu and plays the role of acceptor by capturing the electrons. However, Pb substitutes Bi and donates electrons, thereby increasing their concentration. The trend of dependence on n , α and μ on Ag/Pb-doped samples is the same regardless of the heat treatment received by the samples (figures 1 and 2).

Figure 1. Influence of silver concentration on density of charge carriers (n), resistivity (ρ), mobility of charge carriers (μ) and coefficient of thermoelectric power (α).

Figure 2. Influence of lead concentration on n , ρ , μ and α .

In the case of $Bi_2Sr_2CaCu_2O_x$ single crystals, decrease in oxygen content decreases the hole concentration (Briceno and Zettl 1989). We know that the change in carrier concentration affects mobility. Therefore, doping also affects mobility (figure 3). This is observed generally in degenerate semiconductors (Ravich *et al* 1968). High concentration of free charge carriers and the value of the effective mass, 1 to $9m_0$ determined in high temperature superconductors (Konstantinov *et al* 1988) indicate a similar condition, as also observed in degenerate semiconductors in the Bi-Sr-Ca-Cu-O system. For such system, we can write the following (Anselm 1962):

$$Z_0/kT = \hbar^2(3\pi^2n)^{2/3}/2m^*kT \gg 1, \quad (1)$$

where $Z_0 = E_F - E_C$ where E_C is the energy of the conduction band and E_F the Fermi energy. The coefficient of thermoelectric power, α , may be found from the following formula (Ravich *et al* 1968):

$$\alpha = \frac{2\pi^{3/2}k^2 \cdot T \cdot m^*(r + 3/2)}{3^{5/3} \hbar^2 e n^{2/3}} \quad (2)$$

where r is scattering factor and e the charge of electron. The parameter, $S = m^*(r + 3/2)/m_0$ has been determined and its dependence as a function of con-

Figure 3. Effect of change in carrier concentration, over mobility of charge carriers, μ in Ag-doped samples of both series.

Figure 4. Dependence of S on concentration of Ag and Pb.

centration has been shown in figure 4, using the correlation for R_H and α . From the formula (2), the scattering factor (r) has been found to be less than zero and its value range from -1.15 to -1.47 . Therefore, it may be assumed that the scattering of the charge carriers occurs due to acoustic phonons in the normal state at room temperature.

It may be pointed out that we have observed a negative Hall coefficient in the high magnetic field (18 kOe) whereas positive Hall coefficient has been observed in the low magnetic field of 8 kOe (Reddi and Uskov 1989). It may be that the strong magnetic field caused such a change in its sign. This needs further investigation.

4. Conclusion

Our work on Ag and Pb-doped polycrystalline $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ in the normal state at room temperature reveals the following: (i) Density of charge carriers decreases with increase in Ag concentration, whereas reverse dependence is observed with Pb irrespective of their thermal processing history. (ii) All Ag- and Pb-doped samples indicate electronic conductivity. (iii) Scattering mechanism of the charge carriers is believed to be due to acoustic phonons.

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