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Synthesis and Thermopower of Vanadium-Doped Bismuth-Based (Bi-2223) High-T_c Superconductors

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Abstract. A superconducting sample with nominal composition of $Bi_{1.3}Pb_{0.4}V_{0.3}Sr_2Ca_2Cu_3O_\delta$ prepared by using solid-state reaction method. DC electrical resistivity of the sample determined by using a standard four-probe technique within a temperature range of 77-300 K. Zero electrical resistivity of the sample was found at a critical temperature ($T_{c,zero}$) of 108 ± 1 K. Whereas, the onset temperature ($T_{c,onset}$) was observed at 122 ± 1 K. Temperature dependent thermoelectric power (Seebeck coefficient) of the superconducting sample was measured with a newly developed and calibrated apparatus.

Keywords: $Bi_{1.3}Pb_{0.4}V_{0.3}Sr_2Ca_2Cu_3O_\delta$ superconductors, vanadium doping, thermoelectric power, electrical resistivity

Introduction

The Bismuth Strontium Calcium Copper Oxide (BSCCO) ceramic system is known to have large number of existing or co-existing crystal structures or phases. Among the cuprate high-T_c materials, the Bi(Pb)-Sr-Cu-O are considered to be the most promising candidates for various reasons, in particular for their rather high critical temperature T_c, high critical current density J_c and power transmission in electric cables at liquid nitrogen temperatures. A large amount of work has been done on this system in order to make technical applications possible (Kaiser, 1997; Awana *et al.,* 1992). It is known that the Bi-(2223) phase is stable within a narrow temperature range and exhibits phase-equilibrium with only a few of the compounds existing in this system (Larbalestier *et al.,* 2001). Two major issues seemed to make the development of the Bi-(2223) phase complicated are its stabilization in a very narrow temperature range and that the kinetics of its formation are so slow that it is almost impossible to obtain the pure Bi-(2223) phase material (Zhang *et al.,* 1990). The doping materials like Al, La, Sb, Pb have been attempted by different authors in Bi-based superconductors (Sugai and Soto, 1989). Substitution may play an important role on the properties of high temperature superconducting materials. The existence of doping element in substitution lattice sites lead to the formation of a superconductor with altered properties. The presence of high valence cations V^{5+}, Nb^{5+} and Ta^{5+} in the stoichiometry can sufficiently enhance the formation of high-T_c Bi-(2223) phase (Kazin *et al.,* 1990). In this work, the effect of Vanadium doping on thermoelectric power and resistivity of $Bi_{1.3}\ Pb_{0.4}\ V_{0.3}\ Sr_2Ca_2Cu_3O_\delta$ superconducting sample are presented as a function of temperature in a range of 77 to 300 K.

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Materials and Methods

Sample preparation. The specimen was prepared from 99.9 % pure powders of Bi_2O_3, V_2O_5, PbO, $SrCO_3$, $CaCO_3$ and CuO. The powders were mixed and thoroughly grinded in an agate mortar to give a homogeneous composition of $Bi_{1.3}Pb_{0.4}V_{0.3}Sr_2Ca_2Cu_3O_\delta$. The grind powder was calcined for 24 h in open air at 800 °C (by using a tube furnace, open at its both ends to the atmosphere for better oxidation process of the sample powder). The prepared pellet was given a controlled heating and cooling in air by using a horizontal tube furnace. Poly vinyl alcohol (PVA) was used as binder in the sample. PVA is one of the few high molecular weight commercial polymers, which is water-soluble and is dry solid, commercially available in granular and powdered form. The properties of poly vinyl alcohol vary according to the molecular weight of the parent poly vinyl acetate and the degree of hydrolysis. Fully hydrolyzed form with medium viscosity grade PVA was used in our case. Sample was in the shape of cylindrical disks having diameter of 25 mm and height 10 mm. For deoxygenization, the sample was sintered at 840 °C for 196 h.

Calibration of the apparatus. In the present work, thermoelectric power (TEP)used as a medium to investigate the physical properties, in particular the properties that can be correlated with the transport mechanism that occur in such type of superconductors. TEP is a sensitive property in high temperature superconductors, particularly to determine the sign of the charge carriers. The thermoelectric power apparatus was calibrated with a copper sample having a diameter of 34.50 mm and thickness of 1.06 mm. The temperature range during the calibration was kept between 90 to 300 K. The main aim of this calibration was to prepare the apparatus for TEP measurement of superconducting samples. A sketch diagram of the setup is shown in Fig. 1.

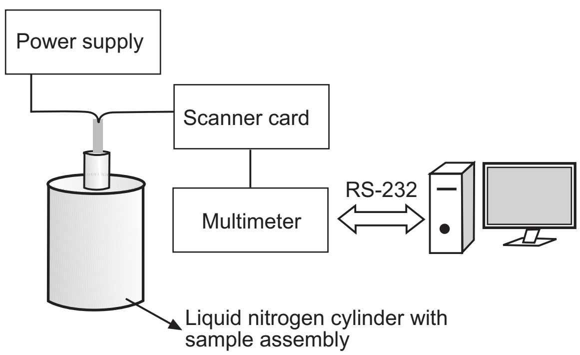

Fig. 1. Block diagram of the apparatus used for thermoelectric power measurement.

The sample was subjected to a temperature difference ΔT by using a heating resistor and the corresponding voltage difference ΔV across the sample was measured accordingly. Thermoelectric power (*S*) was obtained by taking the ratio of the voltage difference to the temperature difference. The two thermocouples were electrically isolated but thermally connected to the sample. Heat losses through the electrical connections were minimized by using long leads wrapped around the Teflon tube. The voltage leads were then silver pasted to the sample in the vicinity of thermocouples to assure that the voltage and temperature gradients are measured at the same locations on the sample for accurate thermoelectric power measurements. First, the chamber was vacuumed to eliminate any water condensation on the sample that may result in erroneous measurements. Dry nitrogen was then filled in the chamber as a conducting media between chamber walls and the sample. Data were collected by using a computer controlled system. By incorporating multiple measurements in a single run, considerable time can be saved by avoiding remounting and re-cooling of the samples. In this technique, the surface mount resistor (50 Ω) was used to heat one end of the sample to establish a measured temperature gradient of approximately 1 K.

Results of the calibration measurements are shown in Fig. 2 that indicate an excellent agreement with the already published data (Rehman and Maqsood, 2005; Barnard, 1972). The standard deviation in the data is between 0.05 and 0.24 μV/K. The results obtained are within 5% of the earlier measurements by Barnard (1972).

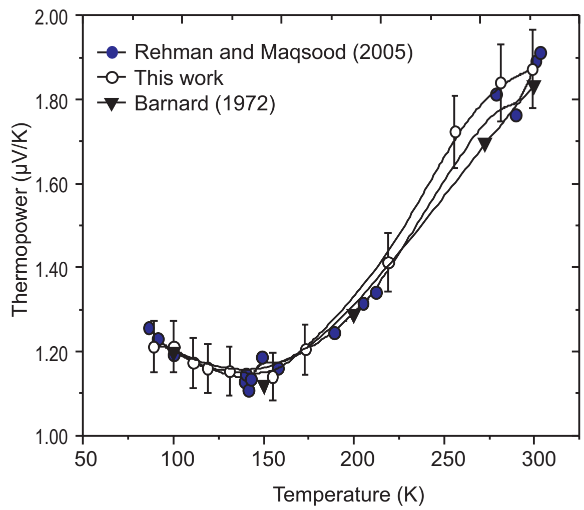

Fig. 2. Absolute thermoelectric power of copper as a function of temperature.

Results and Discussion

DC electrical resistivity of superconducting sample. Electrical resistivity of the specimen was measured in liquid nitrogen atmosphere by using four-probe method (Rehman and Maqsood, 2005). To ensure a better electrical contact, a high quality silver paste was used. The resistivity of the sample was calculated by using equation 1.

$$\rho(T) = \frac{V(T)}{I}\frac{A}{D}$$

Where *I* is the applied current, *D* is the distance between two voltage contacts on the sample and *A* is the cross-sectional area of the sample.

Critical zero temperature $(T_{c,zero}^{RES})$ of this composition was obtained at 108 ± 1 K. Whereas, critical onset temperature $T_{c,onset}^{RES}$ was observed at 122 ± 1 K. Resistivity versus temperature curve of the superconducting sample is shown in Fig. 3.

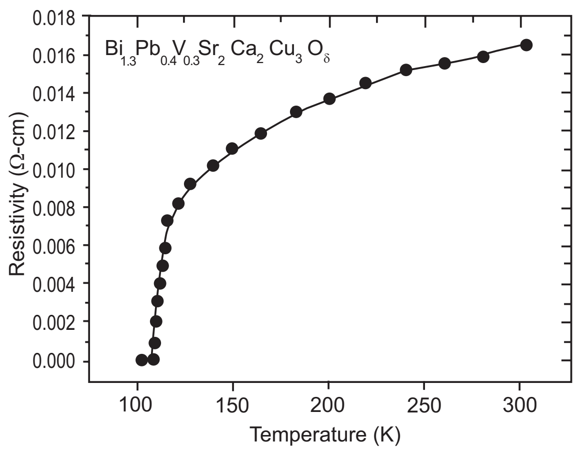

Fig. 3. Temperature dependent DC electrical resistivity of superconducting sample with nominal composition $Bi_{1.3}Pb_{0.4}V_{0.3}Sr_2Ca_2Cu_3O_\delta$ sintered at 840 °C for 196 h.

Thermoelectric power measurement. Thermoelectric power (*S*) of the superconducting sample was measured within the temperature range of 90-300 K. Obtained results show that the thermoelectric power increases with decreasing temperature and after reaching $T_{c,zero}^{RES}$ it decreases abruptly and approaches zero within the experimental uncertainty. The maximum value of thermoelectric power in the sample is very small (i.e. 2.8 μV/K) suggesting a weak Seebeck coefficient that typically shows a metallic behavior.

At high temperatures, the thermoelectric power is almost linear. Thus, the Mott expression was used in present study to determine the Fermi level (Bougrine *et al.,* 1998; Barnard, 1972). Results of these measurements are shown in Fig. 4.

$$S = S_O - \left(\frac{\pi^2 K_B^2}{3|e|E_F} \right) T \tag{2}$$

Where, S_o is a constant.

Mitra *et al.* (1998) and Lopez *et al.* (1991) have also reported similar profile for the same kind of superconductor. $T_{c,onset}^{TEP}$ in the thermoelectric power versus temperature curve is observed at 124 K ± 1 K. On further decreasing temperature, the thermoelectric power starts decreasing and almost becomes zero at 95 ± 1 K i.e., $T_{c,zero}^{TEP}$ 195 ± 1 K. However, the zero critical

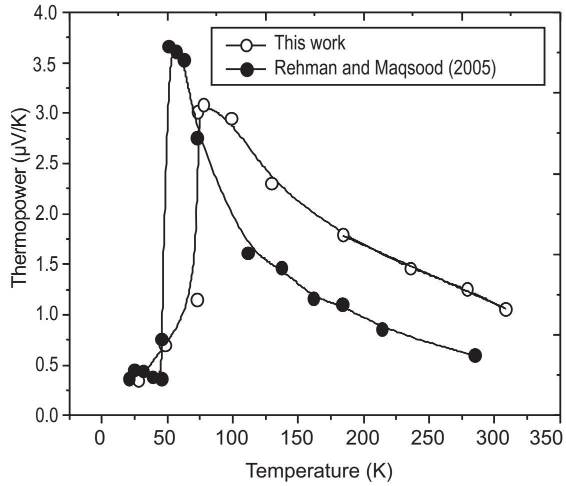

Fig. 4. Temperature dependent thermoelectric power of Bismuth-based high Tc superconductor ($Bi_{1.3}Pb_{0.4}V_{0.3}Sr_2Ca_2Cu_3O_\delta$) sintered at 840 °C for 196 h.

temperature $T_{c,zero}^{TEP}$ as determined from the electrical resistivity experiment was 108 ± 1 K. The difference between the two critical temperatures obtained by two different methods is 16 K.

A possible explanation of this difference can be given as below:

As these materials are granular in nature, therefore one expects a high electrical resistance between two adjacent grains. While on the other hand, during the measurement of thermoelectric power, the temperature drop between the same two grains are expected to be small in comparison the electrical resistivity. Therefore, it is assumed that the granular nature would have less effect on TEP than the electrical resistivity. Similar reasons are also given by Lim *et al.* (1989).

Furthermore, the difference between ($T_{c,zero}^{RES}$) and ($T_{c,zero}^{TEP}$) increases as more and more oxygen is taken out of the compound by deoxygenation. In addition, the width of the peak increases as the sintering temperature is increased and it moves towards higher temperatures. Kang *et al.* (1989) investigated the thermopower of $YBa_2Cu_3O_{7-y}$ as a function of oxygen deficiency. They observed that the position and the shape of the peak strongly depended on the oxygen deficiency. As the oxygen deficiency increases, the positive peak at the superconducting transition temperature moves toward a higher temperature region with its width broadening. They concluded that the magnon-drag effect is the main cause of broadening and shifting of the TEP curve.

Conclusion

A superconducting sample with nominal composition $Bi_{1.3}Pb_{0.4}V_{0.3}Sr_2Ca_2Cu_3O_\delta$ prepared by conventional solid-state reaction method. $T_{c,zero}^{RES}$ of this composition was obtained by DC resistivity four-probe method and obtained value was 108 ± 1 K. Whereas, $T_{c,onset}^{RES}$ was observed at 122 ± 1 K. Thermoelectric power measuring apparatus was calibrated using a copper sample. The values of thermoelectric power of copper were in good agreement with the reported values within the measured temperature range. After successful calibration of the new apparatus, the thermoelectric power of the superconducting sample was measured in temperature range of 90 to 300 K. Thermoelectric power of Bismuth-based high-T_C superconductor was found to be positive. The positive value of thermoelectric power indicates that the dominant charge carriers in the sample are phonons in the measured temperature range. The behavior of the thermoelectric power in superconducting sample was approximately linear with temperature until it reached transition temperature. Similar behaviour has also been observed in other Bismuth-based high-T_c superconductors (Rehman and Maqsood, 2005). Zero transition temperature of the specimen as determined by new thermoelectric power measuring setup $T_{c,zero}^{RES}$ was measured to be 124 ± 1 K whereas, the zero transition temperature of this sample as measured by the four-probe resistivity method $T_{c,zero}^{RES}$ was observed at 108 ± 1 K. The difference between $T_{c,zero}^{RES}$ and $T_{c,zero}^{TEP}$ is about 16 K which might further increase by increasing oxygen deficiency in the sample. There is still need to determine few other parameters like thermal conductivity and critical current density that will help in determining the figure of merit of the superconducting sample and then, the possible application of this work can be tested for low-temperature thermoelectric devices.

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