Pak. J. Agri. Sci., Vol. 46(4), 2009
ISSN (Print) 0552-9034, ISSN (Online) 2076-0906
http://www.pakjas.com.pk

EFFECT OF HEAT TREATMENT ON THE PROPERTIES OF HIGH-T_C BI-BASED SUPERCONDUCTORS

Muhammad Azam[1]*, Adnan Haider[1], Yasir Jamil[1] and Nasir Amin[1]
[1]Department of Physics, University of Agriculture, Faisalabad
*Corresponding author's e-mail: mazamcheema@yahoo.com

Increase in critical temperature of superconductors is a major area of research. We have used ceramic technique in order to synthesize high Tc conductors. We have also studied the temperature dependence of the electrical resistivity of high-Tc Bismuth based superconductors. These superconductors have been prepared from the materials Bismuth Oxide (Bi_2O_3), Lead Oxide (PbO), Strontium Carbonate ($SrCO_3$), Calcium Carbonate ($CaCO_3$), Barium Oxide (BaO) and Copper Oxide (CuO) with conventional solid state reaction using general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$. The structural properties of the samples were investigated through X-ray diffraction analysis performed at room temperature. Electrical resistivity has been measured using four probe method. The critical temperature of the Bi-based superconductors has been found to be 100 K.
Keywords: Bi-based superconductor, X-ray diffraction, electrical resistivity

INTRODUCTION

Some materials show zero resistance to the flow of electric current when cooled to certain low temperature called critical temperature. Such materials are called Superconductors. The phenomenon of superconductivity was first discovered in 1911 by Heike Kammerlingh Onnes when mercury was cooled to a very low temperature (4.15K). He discovered that mercury had suddenly lost all of its resistance to electric current. He named this as superconducting state. Superconductors are of following two types:

Type 1 superconductors are characterized as the soft superconductors which were discovered first and require the coldest temperatures to become superconductive. They exhibit a very sharp transition to a superconducting state and perfect diamagnetism. They have ability have to repel a completely an applied magnetic field.

Type 2 superconductors are also known as the hard superconductors. They differ from Type 1 in that their transition from a normal to a superconducting state is gradual across a region of "mixed state" behavior. This type of superconductors will allow some penetration by an external magnetic field into its surface; this creates some rather novel mesoscopic phenomena like superconducting "stripes" and "flux-lattice vortices".

The magnetic field applied on the superconducting sample with an orientation parallel to electric or temperature gradient generates magneto-transport phenomena. We can deduce that an excess electrical resistivity or an excess thermoelectric power or an excess thermal conductivity (Ausloos, 2001).

The location of the various mixed state phases in the so-called technological phase diagram of high Tc superconductors (HT_c's) as well as the behavior of vortices are of major interest for inventing low temperature devices (Ausloos, 2001).

The measurement of the specific heat played a central role in the development of conventional superconductors. The study of the specific heat of the high temperature superconductors provides valuable insight into behavior of superconductivity of these new and those usual systems. Application of various magnetic field environments realized by high-T bulk superconductors is one of the main research areas (Murakami, 1994).

The normal-state transport properties of high-Tc superconductors (HT_c's) exhibit differences with that what is usually found in most metallic systems.

Many methods have been used for the preparation of superconductors.

In the present research work we have used solid state reaction tcchnique to synthesize type- II superconductors. The effect of thermal treatment on the structure and properties of the materials has also been studied.

Ceramic technique is the most common method for the preparation of superconductors. the resultant products are not necessarily always stoichiometric and homogeneous on microscopic scale and their properties are many times non-reproducible. The non-stoichiometry is due to extensive grinding and high heating temperatures involved in the conventional preparation process and due to the possibility of the presence of un reacted phases in the finished product. The stringent demands on the quality of high-performance superconductors, especially for applications requiring low losses at high frequencies, have created the need for a more appropriate method

for preparing composition and structure wise perfect superconductors.

This method is simple and inexpensive, not requiring costly chemicals or elaborate experimental set-up, and less time consuming compared to some other methods.

MATERIALS AND METHODS

In the Bi-based high-Tc superconductors the B_{i-2223} phase is stable within a narrow temperature range and exhibits phase equilibria with only a few compounds existing in the system. Precise control over the processing parameters is required to obtain the phase-pure material. All specimens were prepared from 99.9% pure powders of $B_{i2}O_3$, PbO, $SrCO_3$, $BaCO_3$, $CaCO_3$ and CuO. The powders were mixed to give nominal composition of Bi_1. 6Pb0.4Sr_1. 6Ba0. 4Ca_2Cu_3Oy and were thoroughly ground for 2 hours in an agate mortar to give very fine powder. The grinded powder was calcined for 24 hours at 800°C. Pellets were produced in equal sizes with the help of hydraulic press at the pressure of 100 bar, from the well mixed material and controlled heating and cooling carried out, in 6 hr, using a open box furnace. Poly vinyl alcohol (PVA) was used as binder in the samples. PVA is one of the few high molecular weight commercial polymers, which is water soluble and is dry solid, commercially available in granular or powder 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 hydrolysed form with medium viscosity grade PVA was used in our case. Samples were in the rectangular shape. These samples were sintered at 850°C for the intervals of (100, 120 and 140) hours in each sintering step. These procedures do affect the properties. The superconducting properties were characterized electrically by using standard four-probe method. Contacts were made by high quality silver paste, the temperature was measured by using a calibrated Pt-100 thermometer. The measurements were taken from room temperature down to 100 K. X-ray diffractograph (XRD) of sample was taken after the final sintering. The radiation used for XRD was Cu Kα and the measurements were made at room temperature. Measurements were done at room temperature since there is no change in the structure of the superconducting materials before and after transition.

Different methods and techniques are being used for the measurement of different parameters of superconductors of which resistivity are of supreme importance. It is important because it is used not only for finding the critical temperature but also for characterizing the superconductors. In fact, it was the resistivity measurement experiment, which gave rise to the concept of superconductivity in 1911.

According to Ohm's law potential difference is directly proportional to the resistance provided that physical condition remains same.

Mathematically, Ohm's law can be written as

$V = IR$ $\quad R = V/I$ (i)

$R \alpha L$ (ii) and $R\alpha 1/A$

$R \alpha L/A$

$R = \rho L/A$ (iii)

Let R be a function of temperature, then

$R(t) = \rho L/A$

P (t) = AR/L putting value of R from equation (i) in equation (iii)

P (t) =A V/L I

Where v is a function of (t) and P (t) = V (t) A/L I

The length L current I and area of cross-section A of the sample remains constant during the experiment. The V (t) [voltage drop] varies with temperature and so p (Tj varies with temperature. In the present work we have used four probe methods to determine the resistivity at different temperatures. The critical temperatures have been found from the graph drawn between the resistivity and temperature. The superconducting state was determined by checking the Meissner effect.

The relationships among macroscopic physical properties and features at atomic level for the high-Tc superconducting material with nominal composition $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_y$, was prepared by a solid-state reaction method. The samples were analyzed by dc electrical resistivity, ac susceptibility, thermal transport, electro thermal conductivity and thermoelectric properties all as a function of temperature. Room temperature X-ray diffraction studies were also done. All the above measurements showed that in the samples, there exists almost a single high-Tc phase with $T_{c,0}$ ~110±1K. The lattice constants of the material were determined by indexing the diffraction peaks. Samples were investigated for thermal transport properties, i.e. thermal conductivity, thermal diffusivity and heat capacity per unit volume, by an advantageous transient plane source method. (Rehman, 2008).

RESULTS AND DISCUSSIONS

Before taking the resistivity measurements, the Meissner effect was checked. The sample was dipped into the liquid nitrogen for some time till it attained the liquid nitrogen temperature. It was then brought near a permanent magnet. The sample showed strong

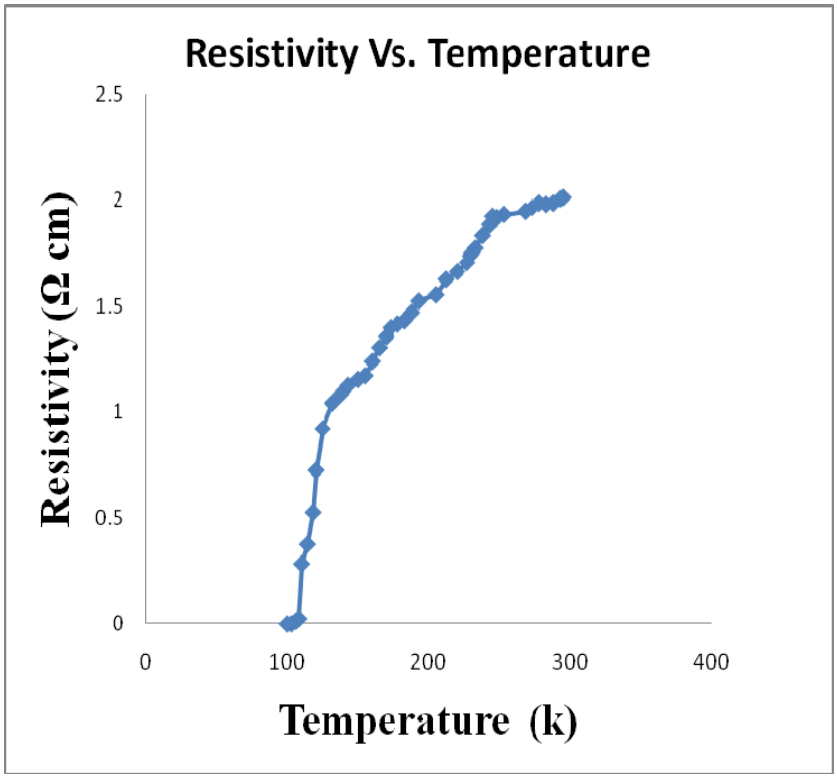

Fig. 1. Resistivity as a function of temperature for the sample 1 after each sintering step

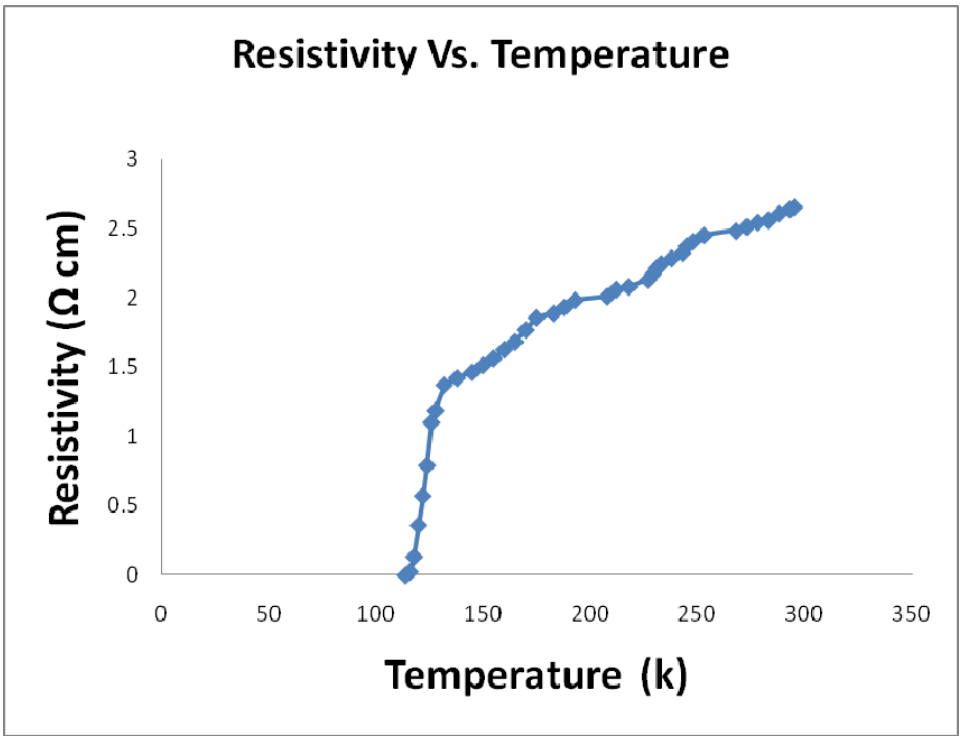

Fig. 2. Resistivity as a function of temperature for the sample 2 after each sintering step

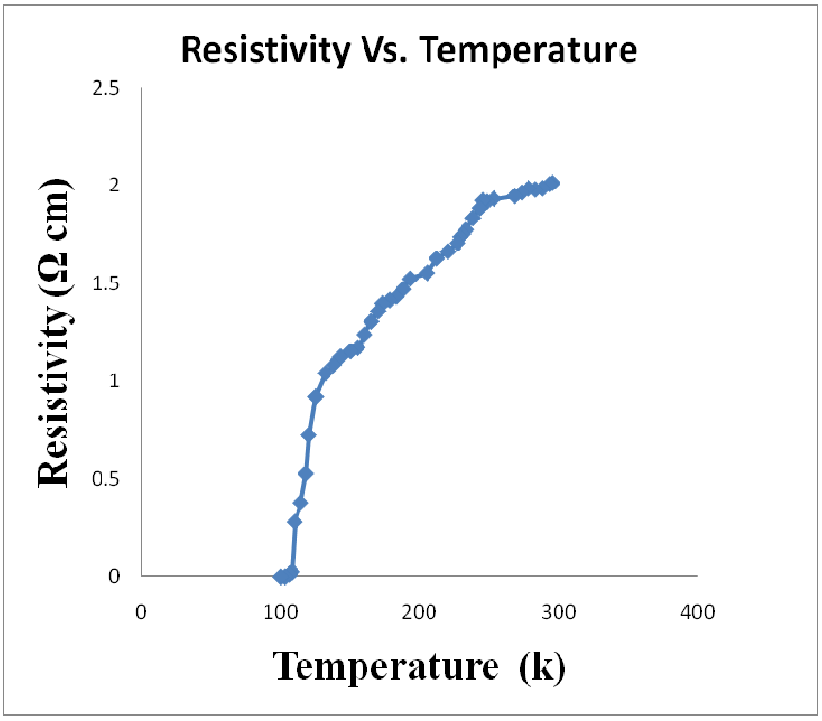

Fig. 3. Resistivity as a function of temperature for the sample 3 after each sintering step

repulsion from the magnet. This confirmed that our pallets were superconductor. The resistivity measurements were taken first in the normal atmosphere and then in the nitrogen atmosphere. Tc (zero) obtained by this composition was 100 ± IK.

Electrical properties of the samples

The samples were sintered at 850 degree centigrade for 140,100 and 80 hours and were air quenched. Before taking the resistivity measurements, the Meissner effect was checked. The samples were dipped into the liquid nitrogen for some time till it attained the liquid nitrogen temperatures. It was then brought near a permanent magnet. The sample showed strong repulsion from the magnet. This confirmed that our pallet was superconductor. The resistivity measurements were taken in normal atmosphere of the nitrogen. T_c (zero) obtained by this composition was 114 ± IK, 100 ± IK and 90 ± IK.

X-ray diffraction studies

Sample 1

Almost all the peaks are indexed in sample 1. The only phase is the orthorhombic high-*T*c B_{i^-2223} phase. Lattice parameters were calculated from the (*h k l*) values of the indexed peaks. The lattice parameters are *a* = 5.01, *b* = 5.77 and *c* = 36.94. Indexed X-ray diffraction pattern is shown in all above figures.

Table 1. Lattice constants of sample 1

Crystal structure	Lattice constants		
	a (Å)	b (Å)	c (Å)
Orthorhombic	5.01	5.77	36.94

The peaks with lattice constant (h k l) having values (111) and (0 115) are of high high-Tc Bi-2223 phase **(**Halim *et al.*, 1999).
In sample 1 the peaks with lattice constant (h k l) having values (1 1 9) and (1 1 17) are of high high-Tc Bi-2223 phase (Halim *et al.*, 1999)
The peaks with lattice constant (h k l) having values (0 0 18) are of high-Tc Bi-2223 phase and the peaks with lattice constant (h k l) having values (0 2 12) are of high-Tc Bi-2223 phase (Rehman, 2008).

Sample 2

Almost all the peaks are indexed in sample 2. The only phase is the orthorhombic high-*T*c Bi-2223 phase. Lattice parameters were calculated from the (*h k l*) values of the indexed peaks. The lattice parameters are *a* = 5, *b* = 5.39 and *c* = 37.24.

Table 2. Lattice constants of sample 2

Crystal structure	Lattice constants		
	a (Å)	b (Å)	c (Å)
Orthorhombic	5	5.39	37.24

The peaks with lattice constant (h k l) having values (0 2 12) are of high-Tc Bi-2223 phase. In sample 2 the peaks with lattice constant (h k l) having values (1 1 9) and (1 1 17) are of high high-Tc Bi-2223 phase (Young and Chaki, 1999; Gul *et al.* 2006).
In sample 2 the peaks with lattice constant (h k l) having values (0 2 0) are of high high-Tc Bi-2223 phase and the peaks with lattice constant (h k l) having values (0 2 12) are of high-Tc Bi-2223 phase. (Rehman, 2008)

Sample 3

Almost all the peaks are indexed in sample 4. The only phase is the orthorhombic high-*T*c Bi-2223 phase. Lattice parameters were calculated from the (*h k l*) values of the indexed peaks. The lattice parameters are *a* = 5, *b* = 5.48 and *c* = 36.74.

Table 3. Lattice constants of sample 3

Crystal structure	Lattice constants		
	a (Å)	b (Å)	c (Å)
Orthorhombic	5	5.48	36.74

In sample 3 the peaks with lattice constant (h k l) having values (1 1 1) are of high-Tc Bi-2223 phase (Halim *et al.*, 1999).
The peaks having Miller indices (0 0 18) are of high high-Tc Bi-2223 phase and also the peaks with (h k l) (0 2 12) are of high-Tc Bi-2223 phase.
The peaks having values (0 1 15) are of high high-Tc Bi-2223 phase (Halim *et al.*, 1999).
The preparation of $B_{i\text{-}2223}$ composites so as to obtain some active composites where the superconductive properties of $B_{i\text{-}2223}$ could be modified using a property of the insulating phase. In both cases superconductive percolation was obtained, but only in the case of a Bi-composite was no (or very weak) chemical reaction observed during sintering. Since the superconductive percolation threshold was obtained in that case for a concentration of $B_{i\text{-}2223}$ lotheyr than 20% (Nadifi, 2000).
Thermal measurements were performed to correlate the microstructural and morphological modifications induced by barium doping and the superconducting properties of Bi (Pb)Sr(Ba)$_{\text{-}2223}$. The samples were prepared by a solid state reaction method. The samples were then analyzed by dc electrical resistivity, thermal transport and thermoelectric properties all as a function of temperature (from room down to 77 K). It is concluded that heat treatment, cooling rate, and sintering time period affected the transition temperature of the superconductors. (Rehman and Maqsood, 2005).
We have compared the structural properties of our prepared samples with the reported work of Nadifi (2000), Rehman and Maqsood (2005). It has been observed that our results are in good agreement with their work.

CONCLUSION

In the present research work we prepared superconductor samples by using compound $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_4Ba_{0.2}O_y$ at same temperature but different sintering time. Each sample was sintered at 850^{o}C. The sample 1 was sintered at 850^{o}C for 140 hours. Its T_c was 114 k. Meissner effect was observed for this sample. For the sample 2 sintered time was 78 hours at 850^{o}C same temperature. This sample showed no Meissner effect. As the Meissner effect was failed so resistivity of these samples was not measured. The third sample sintered for 100 hours. Strong Meissner effect observed. Its T_c was 100 k. For the sample 4 sintering time was 120 hours at 850°C temperature. It shows superconductivity at 110 K.
It was observed that transition temperature increased with time. Sample 2 calcinated at 800 degree centigrade for 24 hours and sintering time was 140 hours at 850, which shows superconductivity at 114 K. This results match with pervious work given below.

REFERENCES

Ausloos, M. 2001. Electrical and thermal transport properties in high superconductors. Physica C, 354: 160.

Gul, I.H., M. Anis-ur-Rehman and A. Maqsood. 2006. Temperature dependence of thermal and electrical conductivity of Bi-based high-Tc (2223) superconductor. Physica C. 45: 83.

Halim, A.S., H.A. Khawaldeh and A. Sidek. 1999. physics C, 312: 78.

Murakami, M. 1994. Thermal properties and applications of high-Tc Nd, Eu, Gd/Ba Cu O bulk superconductors. Jpn. J. Appl. Phys. 33: 715.

Nadifi, H. 2000. Superconductive percolation in Bi-based superconductor/Bi-based insulator composites: Case of Bi-2223/Bi-2310 and Bi-2212/$BiFeO_3$. Phys. Rev., 108: 1175.

Rehman, A.M. 2008. Thermal and electrothermal characterization of bismuth based high-Tc superconductors. On line publish in Journal of Alloys and Compounds.

Rehman, A.M. and A. Maqsood. 2005. Study of the thermal behaviour of Bi (Pb)Sr(Ba)-2223 high-Tc granular superconductors. Physica C. Superconductivity, 418: 121.

Young, X. and. T.K. Chaki. 1999. Superconductors. Sci. Techaol., 6: 343.