Journal of Alloys and Compounds 469 (2009) 66–72

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Thermal and electrothermal characterization of bismuth based high-T_c superconductors

M. Anis-ur-Rehman *

Applied Thermal Physics Laboratory, Department of Physics, COMSATS Institute of Information Technology, Islamabad, Pakistan

Received 19 December 2007; received in revised form 1 February 2008; accepted 7 February 2008
Available online 14 February 2008

Abstract

This paper investigates the relationships among macroscopic physical properties and features at atomic level for the high-T_c superconducting material with nominal composition $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_y$, which was prepared by a solid-state reaction method. The samples were analyzed by dc electrical resistivity, ac susceptibility, thermal transport, electrothermal conductivity and thermoelectric properties all as a function of temperature (from room down to LN_2 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-T_c phase with $T_{c,0} \simeq 110 \pm 1$ K. The lattice constants of the material were determined by indexing the diffraction peaks. Samples are investigated for thermal transport properties, i.e. thermal conductivity, thermal diffusivity and heat capacity per unit volume, by an advantageous transient plane source method. Simultaneous measurement of thermal conductivity and thermal diffusivity makes it possible to estimate specific heat and the Debye temperature Θ_D. Thermoelectric power (Seebeck coefficient) and electrothermal conductivity is also measured with a newly developed and calibrated apparatus. Using electrical resistivity, thermal conductivity and thermoelectric power, the Figure of merit factor was calculated.

Keywords: High-T_c superconductors; Thermoelectric materials; Solid-state reactions; Crystal structure; Electron–phonon interactions; Heat capacity; Heat conduction; Phase transitions; Thermoelectric; Thermal analysis; X-ray diffraction

1. Introduction

Dissipation phenomena in high temperature superconductors are governed by the microstructure that develops during the preparation process. Therefore, detailed investigations of the electrical and thermal transport and ac magnetic susceptibilities in superconductors prepared either in the form of single crystals, thin films or polycrystalline are important for understanding superconductivity as well as for practical applications.

The effect of elements (Pb, Fe, Co, Ni, Zn) doping in Bi-based superconducting materials have been extensively investigated [1–8]. It was reported that the superconducting properties of these materials decrease with increase of the amount of doping, regardless of the nature of the dopants. The suppression of superconductivity was concluded to be due to local disorder induced by the amount of doping. However, the details of the current limiting mechanisms in the Bi-2223 system are not well established. Consequently, it is of interest to try these doping elements in the Bi-2223 system with a different nominal composition, of which we intend to investigate $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_y$ in order to provide additional observations to contribute further understanding of their role on the superconductivity of the system.

It is well established that ceramic high-T_c superconductors comprise a collection of tiny, randomly oriented anisotropic grains which are connected to each other by a system of so called 'weak links' or 'matrix'. The linear temperature dependence of the electrical resistivity is one of the most important properties of the normal phase kinetics of high-T_c layered cuprates [9].

In superconductors where the dc electrical resistivity diverges to zero below T_c, the thermal conduction is almost a unique measurement to study the transport properties below T_c. The magnitude and temperature dependence of the thermal conductivity are parameters which have an impact on a broad spectrum of devices. In high-T_c superconductors, such information is even more valuable to know how the free carriers and lattice vibrations contribute to the transport of heat. Transient Plane Source (TPS) technique is a well developed and a well known method [10–12] to study the thermal transport properties. For TPS method single

* Tel.: +92 321 5163059.
E-mail addresses: marehman@comsats.edu.pk, rehmananis@hotmail.com.

0925-8388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2008.02.023

transition phase will be of great help to study such properties. Multiple phases, in the material, will make the situation more complicated and increase in measurement errors also. The TPS technique is modified and improved for the measurements of thermal transport properties of high-T_c superconductors. The modified arrangement is referred to as the advantageous transient plane source (ATPS) technique [13].

The circuit components are reduced with this new arrangement as compared to the bridge used earlier [14]. The modified bridge arrangement is already calibrated with fused quartz, carbon steel and AgCl crystals [13,15].

Peltier refrigerators use the thermoelectric materials for refrigeration. Peltier thermoelectrics are more reliable than compressor based refrigerators, and are used in situations where reliability is critical like deep space probes. Thermoelectric material applications include refrigeration or electrical power generation. Thermoelectric materials used in the present refrigeration or power generation devices are heavily doped semiconductors. The metals are poor thermoelectric materials with low Seebeck coefficient and large electronic contribution to the thermal conductivity. Insulators have a large Seebeck coefficient and a small contribution to the thermal conductivity, but have too few carriers, which result in a large electrical resistivity. The Figure of merit is the deciding factor for the quality of thermoelectric materials. In order to increase the whole Figure of merit, it is of interest to replace the p-type leg of the Peltier junction by a thermoelectrically passive material with a Figure of merit close to zero [16]. This is why it is interesting to study the Figure of merit of the ceramic superconductors.

One of the important thermomagnetic transport quantities is the electrothermal conductivity and is shown to be one of the powerful probes of high-temperature superconductors. Cryogenic bolometers are sensitive detectors of infrared and millimeter wave radiation and are widely used in laboratory experiments as well as ground-based, airborne, and space-based astronomical observations [17]. In many applications, bolometer performance is limited by a trade off between speed and sensitivity. Superconducting transition-edge bolometer can give a large increase in speed and a significant increase in sensitivity over technologies now in use. This combination of speed with sensitivity should open new applications for superconducting bolometric detectors [18].

Other potent applications for electrothermal conductivity of superconductors is actuators in MEMS technologies, electrothermal rockets, etc. [19].

The temperature dependence of the dc electrical resistivity, along with low field ac magnetic susceptibility, X-ray diffraction, thermal transport, electrothermal conductivity and thermoelectric power studies and calculations of Figure of merit factor are undertaken in this paper.

2. Experimental

2.1. Preparation and characterization

In the Bi-based high-T_c superconductors the Bi-2223 phase is stable within a narrow temperature range and exhibits phase equilibria with only a few of the compounds existing in the system [20]. Precise control over the processing parameters is required to obtain the phase-pure material [21].

All specimens were prepared from 99.9% pure powders of Bi_2O_3, PbO, $SrCO_3$, $BaCO_3$, $CaCO_3$ and CuO. The powders were mixed to give nominal composition of $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_y$ and were thoroughly ground in an agate mortar to give very fine powder. The grind powder was calcined for 21 h in air at 800 °C. A series of pellets was produced in two sizes, from this well mixed material and controlled heating and cooling carried out, in air, using a horizontal tube 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 shape of cylindrical disks having diameters 13 and 28 mm, and lengths 3 and 11 mm, respectively. These samples were sintered at 830 °C for the intervals of 24 h in each sintering step as sintering procedures do affect the properties [22].

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.

Low field ac susceptibility measurements are very important for the characterization of high-temperature superconductors [23–26]. The sharp decrease in the real part $\chi'(T)$ below the critical temperature T_c is a manifestation of diamagnetic shielding. ac susceptibility of the sample was measured after each sintering step. The low field ac susceptibility properties were studied by the use of mutual inductance bridge method. The measurements were taken from room temperature down to 80 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 [22,27].

2.2. Thermal transport properties

Thermal transport measurements, i.e. thermal conductivity, thermal diffusivity and heat capacity per unit volume were performed using the advantageous transient plane source (ATPS) technique [13,15]. Circuit diagram for the method is shown in Fig. 1. Simultaneous measurement of thermal conductivity and thermal diffusivity is the foremost advantage of this technique. Heat capacity per unit volume is then calculated using the idea that, if all heat is transported via solid specimen then the thermal conductivity (λ), thermal diffusivity (κ) and heat capacity per unit volume (ρC_p) are expressed by

$$\kappa = \frac{\lambda}{\rho C_p} \tag{1}$$

A detailed description of this experimental technique can be found elsewhere [10]. The ideal model presupposes that the double spiral sensor, assumed to consist of a set of equally spaced, concentric, and circular line heat sources, is sandwiched in specimens of infinite dimensions. In practice all real specimens do have finite dimensions. However, by restricting the time of the transient, which relates to the thermal penetration depth of the transient heating, a measurement can still be analyzed as if it was performed in an infinite medium. This means that the ideal theoretical model is still valid within a properly selected time window for the evaluation. The scatter in thermal conductivity measurements is about 0.14% and is 0.66% and 0.52% in thermal diffusivity and volumetric heat capacity respectively [13,15]. Taking into consideration the limitations of the theory of the technique and the experimental sampling errors, the thermal conductivity and thermal diffusivity data contain errors of 4% and 7%, respectively. The errors in volumetric heat capacity are around 10% [13–15].

2.3. Thermoelectric power measurements

An easy to use and simple apparatus was designed and developed for thermoelectric power (S) measurements. Circuit diagram along with the sample holder assembly is shown in Fig. 2.