Properties of Bi-Sr-Ca-Cu-O high T_c superconductor

B SRINIVASULU NAIDU, B JAGANNADHA REDDY,
Y PRABHAKARA REDDY and P JAYARAMA REDDY

Department of Physics, Sri Venkateswara University, Tirupati 517 502, India.

Abstract. The effect of sintering in air and annealing in oxygen flow at various temperatures and times on the superconducting transition of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ ceramic was studied. Samples sintered at 1138 K for 24 h in air and slowly-cooled to room temperature are single-phase with the highest zero resistivity temperature of 88 K. XRD pattern showed that the single-phase was characteristic of tetragonal structure with $a = 0.5398$ nm and $c = 3.0620$ nm. Both a.c. susceptibility and resistivity measurements give similar values for the onset (100 K) of superconducting transition.

Keywords. High T_c superconductor; annealing conditions; solid-state reaction; structure; resistivity; a.c. susceptibility.

1. Introduction

Superconductivity in Bi-Sr-Ca-Cu-O system was first reported by Maeda *et al* (1988), and depending on the composition of the system, the T_c values go up to 110 K (Syono *et al* 1988; Takayama-Muromachi *et al* 1988). It is reported to have two superconducting phases; the low- T_c phase (85 K) was identified as $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ (2212) by Hazen *et al* (1988a), while the high- T_c phase is believed to have the composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223) (Torrance *et al* 1988; Tallon *et al* 1988). The low- and high- T_c phase samples have similar XRD and electron diffraction patterns but exhibit different temperature dependence of resistance. The high- T_c phase is believed to have three closely-spaced Cu-O planes instead of two as in the low- T_c phase and the number of Cu-O layers per unit length relates to the superconducting transition temperature (Hazen *et al* 1988b). Most of the studies reported suggest that it is easy to obtain a ceramic sample containing both low- T_c (2212) and high- T_c (2223) phases. The annealing temperature and time have been found to be crucial for the formation of high- T_c samples (Liu Zhi Yi and Persson 1988) and to obtain sharp transitions (Perrin *et al* 1988). It is generally agreed that the oxide which forms most readily has the chemical composition $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ (2212) and a tetragonal structure with $a = 0.54$ nm and $c = 3.08$ nm and a T_c of about 80 K (Almond *et al* 1988). The other phase with $T_c = 110$ K, appears to be formed by a subsequent modification of the lower- T_c phase by the inclusion of an additional copper oxide layer (Zandbergen *et al* 1988). However this conversion proved to be difficult and to date no single-phase sample with a T_c of 110 K has been reported. Tallon *et al* (1988) reported an increase in the T_c of 2212 from 80 to 91 K produced simply by quenching. In the present investigation an attempt has been made to study the effect of sintering in air and the effect of subsequent annealing in the oxygen flow at various temperatures and times on the superconducting behaviour of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ single-phase ceramic.

2. Experimental

$\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ samples were prepared by the standard solid-state reaction technique. It has been reported (Tarascon *et al* 1988; Gadkari *et al* 1988) that the single-phase 2212 compound is not formed easily when the constituent oxides/carbonates are reacted in the stoichiometric ratio. The method employed to obtain a single-phase compound in the present study is as follows: SrCO_3 and CaCO_3 powders were mixed in the molar ratio 2:1, ball-milled to promote thorough mixing and calcined at 1273 K for 10 h and at 1673 K for 5 h. Separate high temperature calcination of SrCO_3 and CaCO_3 mixtures at 1673 K resulted in complete decomposition. The reacted powder was cooled and ground well. To this material Bi_2O_3 and CuO powders were added in stoichiometric proportion, mixed, milled and heated at 1198 K in air for about 5 min till the mixture turned black. The reacted powder was slowly cooled and ground well. The mixture was calcined for 24 h in air at 1100 K and allowed to cool to room temperature in the furnace. The resulting material was subjected to second calcination for 12 h in air at 1135 K and allowed to cool to room temperature. The double-calcined powder was ground to a particle size of $100\text{ }\mu\text{m}$ and pressed (4.5 kbar) to form pellets. The pellets were sintered in air at various temperatures ranging from 1073–1173 K for various periods (10–30 h), and slowly furnace-cooled to room temperature. The sintered samples were annealed in flowing oxygen atmosphere at various pressures (0.01–100 bars), temperatures (873–1073 K) and times (4–24 h). The sample resistance was measured using the four-probe technique in the temperature range 303–70 K. The temperature dependence (303–70 K) of a.c. susceptibility was studied at 317 Hz and 0.05 Oe. The temperature of the sample was determined with a calibrated copper-constantan thermocouple. The crystal structure was determined by a Philips X-ray diffractometer at room temperature using nickel-filtered CuK_α radiation.

3. Results and discussion

The influence of sintering temperature and time on the superconducting characteristics of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ is shown in figure 1. It is seen from figure 1(a) that to achieve the highest T_c , the samples must be sintered in air at 1138 K for 24 h and slowly cooled to room temperature. T_c increases almost linearly with increasing sintering temperature up to 1138 K and then decreases. This decrease may be due to the fact that thermal treatment near or above the melting point degrades the superconducting properties as well as the structure. During slow furnace-cooling, the high- T_c phase, even if present, decomposes while the low- T_c phase is retained. Figure 1(b) reveals that a sintering time of at least 22 h is necessary to have the highest T_c in the samples. There is no systematic change in T_c beyond 22 h. Long-term sintering followed by slow cooling to room temperature appears to improve the bulk superconducting properties.

$\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ samples sintered at 1138 K in air for 24 h and slowly cooled to room temperature showed a resistivity of the order of milliohm-cm. They are black in colour and are stable towards exposure to atmospheric conditions. To measure the resistance, voltage and current leads (platinum wires) were connected to the pellets with silver epoxy. Temperature dependence of resistivity of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ is shown

Figure 1. Superconducting characteristics of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ as a function of (a) sintering temperature and (b) sintering time.

Figure 2. Temperature dependence of electrical resistivity of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ sintered at 1138 K for 24 h .

in figure 2. The behaviour is metallic between 303 and 100 K and the resistivity drops at about 100 K becoming zero at 88 K . The transition width and temperature dependence of resistivity above T_c strongly depend on the sintering temperature and time. The sharp transition observed implies that the samples are homogeneous and single-phase and that the major phase must be superconducting.

The temperature dependence of a.c. susceptibility was determined by monitoring the mutual inductance of two coils close to the sample. The a.c. susceptibility measured on a sample is shown in figure 3. At room temperature the specimen is paramagnetic and on cooling, changes to diamagnetic state at 100 K . A large change in inductance signal suggests the bulk nature of the superconductivity and this paramagnetic to

Figure 3. Temperature dependence of a.c. susceptibility of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ sintered at 1138 K for 24 h.

Figure 4. X-ray diffraction pattern at room temperature for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ sintered at 1138 K for 24 h.

diamagnetic transition may be related to the fact that the sample is single-phase and homogeneous.

The X-ray diffraction pattern of the sample is given in figure 4. The observed reflections were characteristic of a tetragonal structure with lattice parameters, $a = 0.5398$ nm and $c = 3.0620$ nm, which are consistent with those previously reported (Almond *et al* 1988). No other phase is present.

Table 1. Effect of annealing conditions on the superconductivity of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$

Annealing conditions			T_c	
Temperature (K)	Time (h)	O ₂ pressure (bar)	Onset (K)	Offset (K)
873	24	0.01	100	85
873	24	0.1	98	83
873	24	1.0	95	80
873	24	10.0	90	75
873	24	100.0	85	70
873	12	0.01	100	85
873	4	0.01	100	85
973	24	0.01	100	85
1073	24	0.01	100	85

Sintered $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ samples were annealed in flowing oxygen at various pressures, temperatures and times. The sample resistivity decreases indicating the disappearance of intermediate phases formed, if any, during calcining and sintering which is also reflected in the XRD spectra taken on these samples. In addition, the zero resistivity temperature was reduced significantly depending on the oxygen partial pressure. The effect of annealing conditions on the superconducting properties of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ is shown in table 1. It is seen that with increasing treatment pressure and oxygen content, T_c shifts progressively to a lower temperature. This may be due to the fact that the added oxygen ions lower the Fermi level thereby reducing the metallic conductivity of the Bi-O layers and hence lowers T_c (Morris *et al* 1989). With increase in oxygen content, the transitions are broadened. With increase in annealing time beyond 4 h, no systematic change in T_c is found, indicating that the treatment time of 4 h is sufficient. Also, increasing the treatment temperature had little effect on zero resistivity temperature. However, increasing the treatment temperature from 873 to 973 K resulted in 25% reduction in a.c. susceptibility at 70 K; and treatment at 1073 K caused about 50% reduction. It is therefore clear that if the samples are annealed in oxygen in a partial pressure of ≤ 0.01 bar at 873 K for at least 4 h and then cooled slowly, it is possible to achieve the highest T_c of 85 K.

4. Conclusions

$\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ ceramics, sintered at 1138 K for 24 h in air and slowly furnace-cooled to room temperature are single-phase, exhibit tetragonal structure with lattice parameters $a = 0.5398$ nm and $c = 3.0620$ nm, and had the highest zero resistivity temperature of 88 K. Resistivity and a.c. susceptibility measurements give similar values for the onset (100 K) of superconducting transition. The T_c gets lowered with increased oxygen concentration.

Acknowledgement

The authors thank the University Grants Commission, New Delhi for financial assistance.

References

- Almond D P, Chapman B and Saunders G A 1988 *Supercond. Sci. Technol.* **1** 123
- Gadkari S C, Muthe K P, Gupta S K, Singh K D, Sabharwal S C and Gupta M K 1988 *Proc. of the Solid State Phys. Symp.* **C31** 198
- Hazen R M, Prewitt C T, Angel R J, Ross N L, Finger L W, Hadidiacos C G, Veblen D R, Heaney P J, Hor P H, Meng R L, Sun Y Y, Wang Y Q, Xue Y Y, Huang Z J, Gao L, Bechtold J and Chu C W 1988a *Phys. Rev. Lett.* **60** 1174
- Hazen R M, Finger L W, Angel R J, Prewitt C T, Ross N L, Hadidiacos C G, Heaney P J, Veblen D R, Shen Z Z, El Ali A and Hermann A 1988b *Phys. Rev. Lett.* **60** 1657
- Liu Zhi Yi and Persson M 1988 *Supercond. Sci. Technol.* **1** 198
- Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 *Jpn J. Appl. Phys.* **27** L209
- Morris D E, Hultgren C T, Markelz A M, Wei J Y T, Asmar N G and Nickel J H 1989 *Phys. Rev.* **B39** 6612
- Perrin A, Li Z Z, Pena O, Pinel J, Padiou J and Sergeant M 1988 *Supercond. Sci. Technol.* **1** 201
- Syono Y, Hiraga K, Kobayashi N, Kikuchi M, Kusaba K, Kajitani T, Shindi D, Hasaya S, Tokiwa A, Terada S and Muto Y 1988 *Jpn J. Appl. Phys.* **27** L569
- Takayama-Muromachi E, Uchida Y, Ono A, Izumi F, Onoda M, Matsui Y, Kosuda K, Takekawa S and Kato K 1988 *Jpn J. Appl. Phys.* **27** L365
- Tallon J L, Buckley R G, Gilberd P W, Presland M R, Brown E W M, Bowden M E, Christian L A and Goguel R 1988 *Nature (London)* **333** 153
- Tarascon J M, Le Page Y, Barboux P, Bagley B G, Greene L H, McKinnon W R, Hull G W, Giroud M and Hwang D M 1988 *Phys. Rev.* **B37** 9382
- Torrance J B, Tokura Y, Laplaca S J, Huang T C, Savoy R J and Nazzari A I 1988 *Solid State Commun.* **66** 703
- Zandbergen H W, Huang Y K, Menken M J V, Li J N, Kadowaki K, Menovsky A A, van Tendeloo G and Amelinckx S 1988 *Nature (London)* **332** 620