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Preparation of Pb Doped 110 K Phase BiSrCaCuO Thick Films by Screen Printing*

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Abstract

Thick Films of $Bi_2Sr_2Ca_2Cu_3O_x$ were obtained on cleaved MgO (100) substrates from a component gel of stoichiometric composition with partial Pb substitution of Bi. Formation employeed screen printing method. Films were subjected two step annealing at temperatures above 850°C and 880°C for the formation of the crystal structure and to attain superconducting properties. X-ray diffraction patterns and R-T measurements showed coexistence of the (2212) and (2223) phases for most of the films. Metallic behaviour in resistance and 110 K onset temperature were observed for good quality films with a completed superconducting transition between 78-103 K. Critical current densities were found in the range 3-5 A/cm^2 at 80 K from current-voltage measurements.

1. Introduction

The $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ (BSCCO) family of superconducting compounds has three different stoichiometric compositions, namely $Bi_2Sr_2CuO_x$, $Bi_2Sr_2Ca_1Cu_2O_x$ and $Bi_2Sr_2Ca_2Cu_3O_x$. These are known as the (2201), (2212) and (2223) phases of the compound for value of n=1,2,3 and their critical temperatures (Tc) occur in the ranges 10-20 K, 65-85 K, 100-110 K, respectively. Because of the highest critical temperature, the (2223) phase of the compound has attracted greater interest and many workers have spent much effort to obtain the pure 110 K phase of the compound in the bulk, thin and thick film form. In early studies it is seen that (2223) phase has unstable structure and during single crystal growth, in-situ thin film preparation and solid state synthesis of the polycrystal material, (2212) phase of the compound forms in addition to the required chemical composition. The low Tc phase has more stable structure then the other phases

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and the during the (2223) phase formation some fraction of the material may be in the low Tc phase [1]. Many research groups succeeded in pure 110 K phase preparation by using stoichiometric composition of the precursors and long duration annealing the composed material just below the melting point in the oxygen-rich atmosphere. For successful results different receipts can be found in the literature [2]. However these formulations differ from one system to another as well as the preparation techniques like thin film, thick film and bulk material. Almost all of these reports has a common approach for the stabilization of crystal structure of the (2223) phase. One approach that has been found useful is the substitution of Pb (∼15-30%) for Bi [3-5]. Most research groups used PbO compound for lead doping, and other lead oxides such as PbO_2 and Pb_2O_3 were also used to observe the effects of lead doping into the BSCCO system [6].

In this work we aimed to prepare the 110 K phase BSCCO thick films by using a very simple thick film preparation technique: the screen printing method, as is used in the electronic industry for preparing hybrid electronic devices.

2. Experimental

For the preparation of the high Tc phase of the compound, stoichiometric composition of the starting materials were measured via electronic scale within ± 0.1 mg precision. The starting materials were the powders of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO with 99.99% purity and the doping powder PbO with 99.9% purity. The powders were mixed and ground for several hours in an agate mortar. To obtain an homogenous gel, some amount of pure thriethanolamine ($C_6H_{15}NO_3$) also added into the mixture during grinding process. The obtained gel of the mixture is transferred onto cleaved MgO(100) substrates through a steel screen. The film were then put into a furnace to evaporate the organic compound. 300°C was found to be a suitable temperature. After the solvent was removed the films were annealed, being long term heated to obtain the desired phase of the compound. Temperature ranges and annealing durations were explored. Thicknesses of the films were found in the range 40-100 μm. Successful results are summarized in the Table. In the early stage of our work we observed semiconductor-like behaviour for the resistance temperature variation for samples annealed in the 750-830°C range. After observing superconducting behaviour of the resistance for films obtained at higher annealing temperatures, most of the films were treated under a two stage annealing methodology in the 830-890°C range, similar to annealing cycles in Ref. [7]. Furnace temperature is set to the highest temperature for a short duration, typically 1 to 3 hours, for chemical formation, the temperature is lowered to 830-850°C and long-term annealed. Films were cooled down to room temperature slowly. The purpose of the low temperature annealing and slow cooling is to insert oxygen into the structure and to attain the superconducting properties. Throughout our work the intention was to use ambient atmosphere to supply the oxygen into the film composition, except for one case. For the ratter case we provided oxygen to the samples by allowing pure O_2 gas flow through the furnace at 600°C for 9 hours.

Table. Annealing temperatures, annealing durations, Tc(zero), Tc(onset), R(250K) and ΔT(K) values for films having superconducting properties.

Sample No:	Annealing Process		Tc(R=0) (K)	Tcon (K)	R(250K) Ω	ΔT (K)
	Temp(°C)	Duration(hr)				
	890	1	93	110	0.103	17
A1	850	23				
	890	0.5	98	111	0.090	13
D1	850	24				
B2	880	3	103	108	0.085	5
	850	24				
B1	600(O_2)	9	100	106	0.121	6
	880	2	97	106	0.154	9
H1	830	18				
	885	1	84.8	108	0.199	25
L1	840	19				
	885	2	82.5	110	0.463	27.5
K1	840	20				
	875	2	87	110	0.108	23
G1	830	25				
	880	3	89.5	109	0.113	19.5
C1	830	21				
	860	2	78.5	105	0.414	26.5
E1	850	22				
	880	33	83	106	0.845	23
M1	850	20				

Characterization of the obtained films were done mostly by x-ray powder diffraction (XRD) technique and scanning electron microscopy (SEM) photographs. In every case we tried to identify reflections seen in the XRD patterns for matching reflections of (2212) and (2223) phase for the given values in the literature. All films were shown some amount of (2212) reflections in addition to the (2223) reflections despite the $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_x$ starting composition. A typical XRD pattern is given in Figure 1. Intensity of the (2212) reflections vary from one sample to another according to preparation conditions.

Two SEM micrographs obtained under different magnifications were given in Figure 2. The SEM micrograph with 1000 magnification showed quite rough and porous plate-like surface and columnar crystals were observed in different parts of the film. This structure was found very similar to the SEM micrographs given by Chen et al. [8]. A detailed micrograph given in Figure 2 (b) showed the plate-like structure more clearly. The Chen and Tseng explained the columnar crystals as a Bi-poor phase [9]. They also mentioned that the partial-melting process leads to the densification and homogenization of oxide films. A typical grain (see Figure 2(b)) has dimensions with thickness 1mm, 15mm length and 8 mm width.

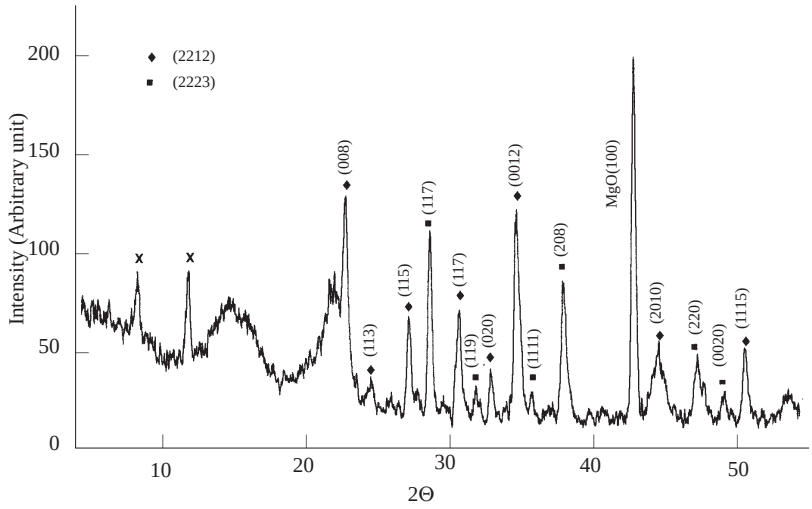
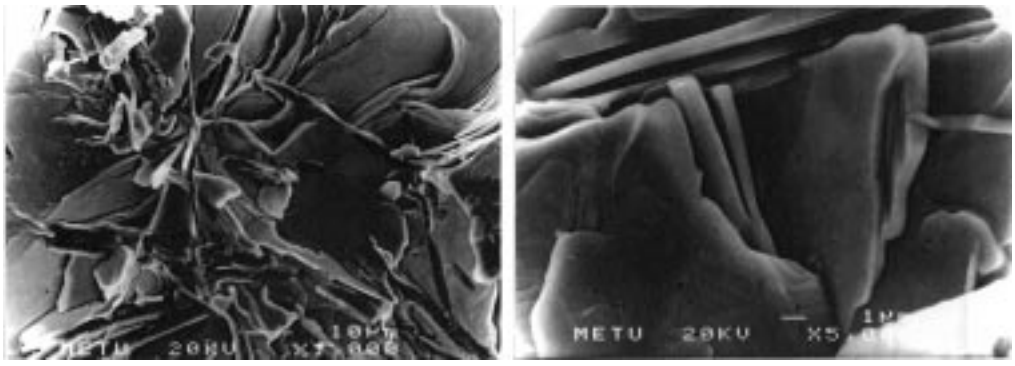


Figure 1. XRD pattern of a BSCCO thick film (sample H1). Identified reflections belong to the (2212), (2223) phases and MgO(100) substrate are shown in the pattern. x indicates unidentified reflections.



a b

Figure 2. Surface morphology, as observed in SEM with (a) 1000 (b) 5000 magnification, for the sample B2

For the purpose of electrical measurements approximately 1000 Å thick Ag contacts were evaporated on to the film surface through a cooper mask at high vacuum. Four Ag contacts were obtained in the shape of a strip 1mm wide and 6 mm long. Distance between the inner contacts was 5 mm.

Electrical properties were observed by measuring dc resistance of the films by four point probe technique from room temperature down to liquid nitrogen temperature. 1

mA dc current is used and voltage drop between the inner contacts is measured with a nanovoltmeter. Direction of the agitating current is reversed and measurements were repeated at every point to eliminate the potential drop due to the thermoelectric power. R-T curves were obtained for each sample automatically with a data aquision system which is explained previously [10]. R-T variations of the four samples showing superconducting behaviour is given in Figure 3. Resistance of all samples have metallic behaviour from room temperature down to transition temperature and also show transition around 110 K.

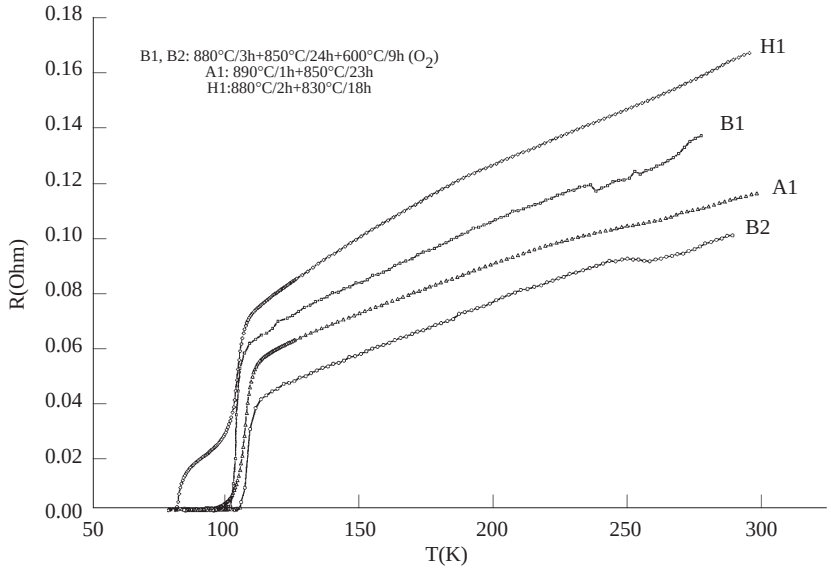


Figure 3. Temperature dependence of resistance for high Tc superconductor BSCCO thick films

Current - voltage characteristics of the superconducting samples below the Tc were also obtained automatically at constant temperatures by scanning the dc current in small steps for the purpose of finding critical current value. Figure 4. shows I-V curves taken at constant temperature below Tc for a high Tc phase sample. Critical current value is found by applying 1 μV/cm criteria.

3. Results and Discussion

Temperature dependence of electrical resistance were shown metallic behaviour from room temperature down to 110 K for the films annealed at two steps above 880°C for short duration and usually at 850°C for long duration. These films were shown resistive transition starting at 110 K but different zero resistance temperatures varying between 78-103 K. For some samples superconductive transition completed in one step, which is a good evidence of having high volume fraction of (2223) phase in the film structure.

For other films we observed two step transition with two onset temperatures, the first one at 110 K and the second at 85 K, which means two phases of the compound being coexist in the film structure. This observation also confirmed in the XRD patterns with the reflections of both (2212) and (2223) phases.

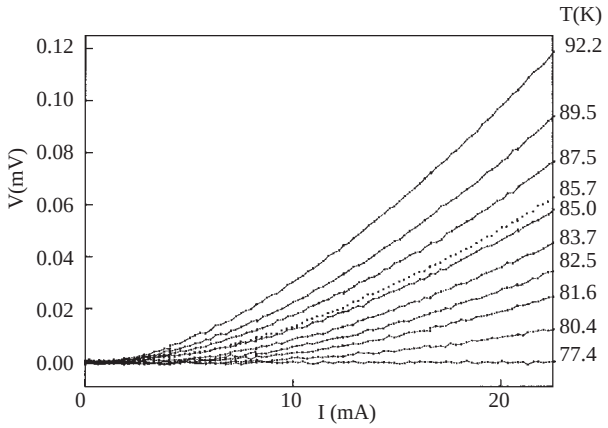


Figure 4. I-V characteristics curves of sample A1 below Tc.

The highest critical temperature and one step resistive transition is obtained for the films annealed around 880°C. Annealing above 870°C can cause melting, and hence melt-textured single phase (2223) structure may be obtained [11]. In addition to the melt grown granular structure, annealing in oxygen atmosphere at 600°C gives sharp superconductive transition and very short resistive tail. This difference is observed clearly for the films B1 and B2. This result shows the importance of oxygen absorption during the annealing process and also shows the inadequacy of the oxygen supply from the ambient atmosphere for short annealing times.

The transport current densities obtained from the current-voltage characteristics were found in the range 3-5 A/cm^2 at 80 K which is comparable with the critical current densities of the bulk materials. Transport critical current densities for bulk materials were given in the range 20-50 A/cm^2 at 77 K in zero field by Miu [12].

4. Conclusion

Single (2223) phase of BSCCO compound can be obtained and stabilized by adding ∼15% Pb for Bi in the stoichiometric proportion. According to the preparation conditions, one can obtain different phases of the same compound being present with different R-T behaviours and critical temperatures. Even the best preparation conditions can give two phases of the compound being present together and granular film structures which cause the presence of low critical current values. However inclusion of oxygen gas flow during annealing steps has an important effect to improve and give high critical temperatures. Annealing around melting point is especially important which causes the

domination of the (2223) phase in the film structure.

Thick films of high Tc superconductors can be obtained by using screen printing method which is a simple and inexpensive preparation technique. Obtaining high quality thick films is important for applications as well as in the study of physical properties of superconductors.

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