

Microstructure and superconducting properties of Bi-2223 conductors quenched from various temperatures on different quenching media

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The Bi-2223 (110K) phase high T_c superconductors were synthesized by conventional melt quenching technique. The nominal composition of the (110K) phase was (Bi_{1.6}Pb_{0.4})Sr₂Ca₂Cu₃O_{10+δ} which was prepared from powders of Bi₂O₃, PbO, SrCO₃, CaCO₃ and CuO having 99.99% purity. The synthesized precursors were quenched from 1200°C, 1250°C and 1300°C to room temperature and sandwiched between brass, stainless steel, copper and bronze blocks. These samples were analyzed by X-ray diffraction (XRD), DC electrical resistivity, scanning electron microscopy (SEM), EDS and density measurements. Lattice constants of the material were determined by indexing the diffraction peaks. Major phase is high-T_c 2223 phase with small percentage of 2212 phase. The highest volume fraction of 2223 phase is obtained for sample quenched on brass from 1250°C. The SEM results indicate that 2223 phase may have been formed and the long grains of this phase might be obtained by quenching at this temperature. The atomic distribution ratio of each component element on the surface of the sample was investigated by EDS. The change in structural and electrical parameters could be ascribed to the oxygen diffusion behavior, resulting in hole carrier concentration.

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1. Introduction

The development of materials processing and characterization in the field of HTSCs for magnet and energy technology has been fairly fast in recent years [1]. Since the discovery of high temperature superconductivity in the Bi-Sr-Ca-Cu-O system by Maeda et.al. [2], a number of studies have been carried out on this system. In the Bi-based system, three phases are observed with the general formula Bi₂Sr₂Ca_{n-1}Cu_nO_y where n=1 (2201), n=2(2212), n=3(2223) with corresponding superconducting temperatures of 10 K, 85 K, 110 K, respectively [3]. The 2223 phase is regarded as one of the most technologically significant high T_c phases in the Bi-Sr-Ca-Cu-O system though difficult to prepare in the pure form as it undergoes a change to 2212 (85K) phase. It was observed that the partial substitution of Bi by Pb enhanced the formation of nearly single phase 2223 material and increase in T_c [4–6]. The lead (Pb) addition results in the creation of a superconductivity solid solution Bi_{2-x}Pb_xSr₂Ca₂Cu₃O₈ by partial substitution of Bismuth (Bi) and the optimum lead content 'x' lies between 0.3 and 0.4 [7–9]. It was reported that the substitution of lead for bismuth was effective in stabilizing and the formation process of a high T_c phase [10]. It was also found that the Ca₂PbO₄ phase, which is formed during heat treatment, plays an important role in the formation of the high T_c phase [11–14]. Various methods of preparation to enhance

2223 phase had been reported [15–25]. The melt processing consists of partially melting a precursor powder, with subsequent slow cooling and further annealing. The 2212 phase is routinely melt processed, being peritectically decomposed into liquid and solid phases and then recrystallized through the inverse peritectic reaction by further slow cooling. Attempts to grow 2223 from the melt have already been done but its narrow stability range and sluggish formation kinetics prevents its crystallization from the melt. Conventional melt quenching technique is one of the melt processes to produce high-T_c single phase materials [26–31]. Although the single phase material is useful due to its enhanced critical temperature, however in terms of application, a wide operating temperature range is important, that can be obtained by multiphase material. Producing single phase material is very important for practical use of high-T_c oxide superconductors because grain boundaries of these materials act as weak links. Furthermore, Quench Melt Growth (QMG) crystals are interesting materials in terms of applications because of excellent J_c properties, QMG crystals can be used as superconducting magnets, superconducting bearings and current leads, etc. Although the understanding of the materials science of Bi-based superconductors is still limited and process optimization is for now rather empirical, they have progressed to the point of being commercially available, with acceptable mechanical properties and practical current densities in the

30–77 K range. Besides there is a lack of knowledge on the concentration region where 2223 is in equilibrium with the liquid, but some works indicated the feasibility of the 2223 crystallization from the melt [32,33]. We report here the effect of quenching the melts from various temperatures on different quenching media on the structural, electrical properties and understanding of the phase relationships involved in the 2223 melting and crystallization regions.

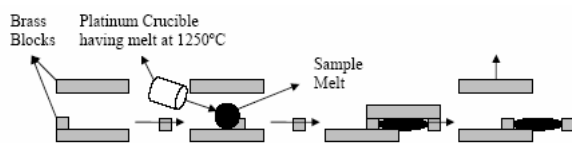
2. Experimental techniques and characterization methods

The high- T_c superconducting samples of composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ were prepared by conventional melt quenching method. The samples were characterized by XRD, dc electrical resistivity, scanning electron microscopy, EDS and density measurements.

2.1. Sample preparation

Pure powders (99.99%) of Bi_2O_3 , PbO , SrCO_3 , CaCO_3 , CuO were used as starting materials. The materials were carefully weighed with in 1 mg accuracy and then well blended in an agate mortar to give a nominal composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$. Several calcinations with intermediate grindings were done at temperature $\sim 850^\circ\text{C}$. Finally, the resultant precursor was reground and melted in alumina crucibles at temperatures 1200°C , 1250°C and 1300°C in an electric furnace (Carbolite 1300). The melts were then quenched by pressing the cast liquid between two blocks of brass, stainless steel, copper and bronze. Thickness of the samples is $\sim 1\text{cm}$. As the cavity in which the samples were quenched is of the same size for all the blocks, therefore the thickness of all the samples is the same. The glass thus obtained was annealed at 850°C for 240 hours [15,29,34].

Block diagram of the method adopted is shown below.



2.2. XRD measurements

XRD patterns of the bulk samples (after 240 hours of sintering) were recorded at room temperature using (Philips 3710) diffractometer with $\text{Cu-K}\alpha$ radiation in 2θ range ($20^\circ - 80^\circ$) with a scan step size of 0.02. Measurements were done at room temperature since there is no change in the superconducting materials before and after transition. XRD data was used to identify different phases present in the samples and lattice parameters.

2.3. DC electrical resistivity

Standard four probe technique was used for electrical characterization of superconducting samples. Silver conducting paste was used to make the contacts on the sample, the contact resistance being in the order of $0.1\ \Omega$ or lower. Resistivity measurements were carried out from 77 K to 140 K by four probe configuration with $1\ \mu\text{V}/\text{cm}$ used as criterion for J_c measurement. Janis Cryostat (VFP-700) equipped with Turbo Molecular pump (Edwards) and Temperature controller (Lake Shore-331) was used for measuring resistance down to liquid nitrogen temperature. A constant current of 10 mA was passed through the samples, with the help of constant current source (Keithley Model-224) and voltage drop measured by nano-voltmeter (Keithley Model-196). K-type thermocouple was used for temperature measurement.

2.4. SEM and EDS analysis

In order to study the microstructure of the samples the SEM was employed. EDS analysis was carried out to investigate the distribution and composition ratio of atoms on the surface of the samples [35].

2.5. Density and porosity measurements

Bulk density of the superconducting samples was measured by liquid immersion method [36,37]. Toluene was used as a liquid for weighing the sample. The bulk density is calculated by the relation.

$$\text{Density of sample} = \frac{\text{Weight of sample in air}}{\text{Loss in weight}} \times \text{Density of Toluene}$$

Calculated density of the sample quenched on brass from 1250°C is 97% of the theoretical density of BSCCO i.e. $5.947\ \text{g}/\text{cm}^3$ [38].

X-ray density of the samples is calculated by lattice parameters (a b c) obtained by XRD data.

Porosity of the samples quenched on brass, steel, copper and bronze was measured by using the relation.

$$\text{Porosity} = 1 - \frac{\rho_{\text{Bulk}}}{\rho_{\text{XRD}}} \quad (1)$$

3. Results and discussion

3.1. XRD analysis

Fig. 1 a, b and c illustrate the XRD patterns of the samples quenched from 1200°C , 1250°C and 1300°C on stainless steel, respectively.

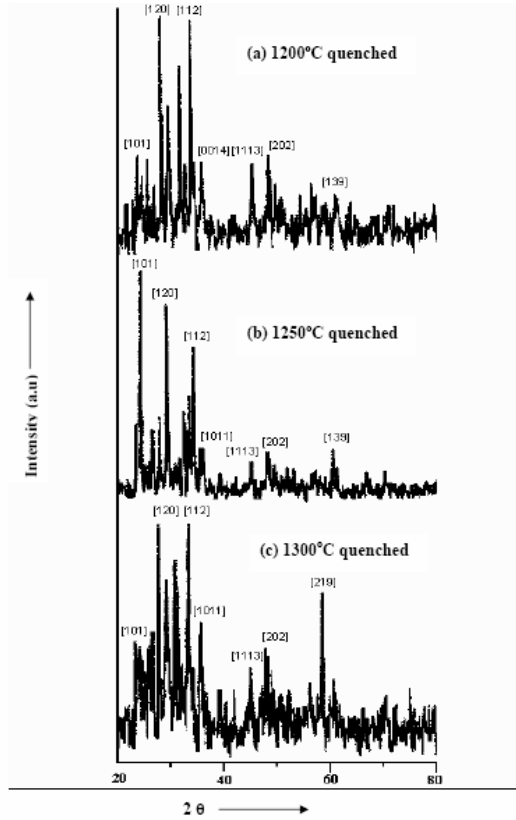


Fig. 1. XRD patterns at room temperature for the samples quenched on stainless steel from (a) 1200 °C (b) 1250 °C (c) 1300 °C.

All the three samples are multiphase, 2223 phase co-exist with 2212 phase. Fig. 2.a,b,c,d depicts the XRD patterns of sample quenched from 1250 °C on brass, steel, copper and bronze.

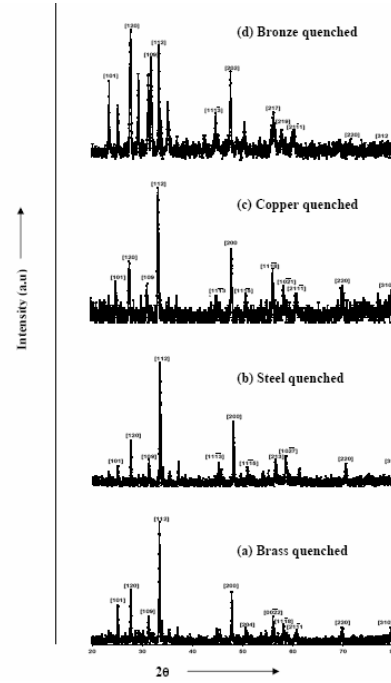


Fig. 2. XRD patterns at room temperature for the samples quenched from 1250 °C on (a) Brass (b) Steel (c) Copper (d) Bronze.

It can be seen from Figs 1 & 2 that the number and intensities (I) of the high- T_c 2223 phase reflections are predominant compared to those of the low- T_c 2212 phase. The intensity and peak positions of the observed reflections for the high- T_c 2223 phase are in good agreement with the values reported in the literature [15,39,40]. The 'c' value of high- T_c phase is 37 Å and that of low- T_c phase is 31 Å, this confirms that the high- T_c phase and low- T_c phase differ mainly in the length of c-axis. From the XRD results it was revealed that samples have an anisotropic tetragonal structure. The lattice parameters of the samples are given in Table 1.

Table 1. Lattice parameters of BSCCO samples.

Composition ($\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\sigma}$)	2223 Phase (Å) ($\pm 0.01\text{Å}$)			2212 Phase (Å) ($\pm 0.01\text{Å}$)		
	a	b	c	a	b	c
Quenched on brass	5.80	5.86	37.00	5.45	5.39	30.05
Quenched on steel	5.82	5.81	36.93	5.41	5.41	30.68
Quenched on copper	5.81	5.78	36.72	5.38	5.39	30.90
Quenched on bronze	5.81	5.85	36.97	5.44	5.39	30.84

Table 2 shows the volume fraction of Bi-2223 and Bi-2212 phases in the samples determined by using the following expressions [22],

$$f_{2223} \% = \frac{\sum I_{2223}}{\sum I_{2223} + \sum I_{2212}} \times 100 \quad (2)$$

$$f_{2212} \% = \frac{\sum I_{2212}}{\sum I_{2212} + \sum I_{2223}} \times 100$$

Table 2. Superconducting transition temperature, volume fraction of 2223 & 2212 phases of BSCCO samples.

Composition ($\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\sigma}$)	T_c (0)K (± 1 K)	T_c (onset)K (± 1 K)	f_{2223} (%)	f_{2212} (%)
Quenched from 1200°C	97	101	30.56	69.44
Quenched from 1250°C	99	104	63.41	36.58
Quenched from 1300°C	92	99	55.56	44.44
Quenched on brass	100	104	87.56	12.43
Quenched on steel	94	102	66.05	33.95
Quenched on copper	90	101	68.63	31.36
Quenched on bronze	93	99	50	50

From X-ray diffraction patterns we noticed that the volume fraction of the high- T_c phase increased for the melt quenched at 1250 °C on brass blocks. These results indicate that $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223) starts appearing in this sample by reaction between the phases formed at the other temperatures and thus the volume fraction of high- T_c phase increases, this is in agreement with the reported data [33].

3.2. DC electrical resistivity

Fig. 3 and Fig. 4 shows the plots of normalized resistance (R_T / R_{max}) as a function of temperature for all the samples down to liquid nitrogen temperature.

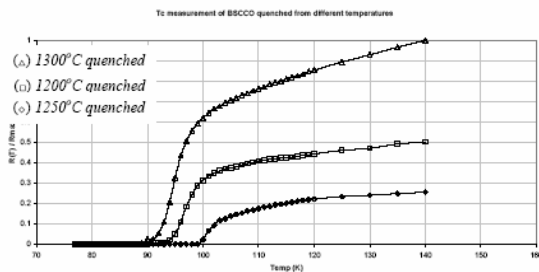


Fig. 3. Plot of normalized resistance (R_T/R_{max}) as a function of temperature down to liquid nitrogen temperature for samples quenched from 1200 °C, 1250 °C and 1300 °C on stainless steel.

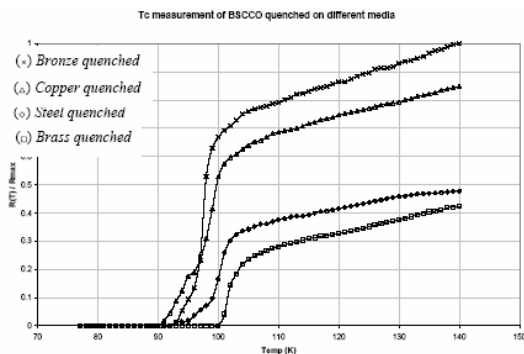


Fig. 4. Plot of normalized resistance (R_T/R_{max}) as a function of temperature down to liquid nitrogen temperature quenched from 1250 °C on brass, steel, copper and bronze.

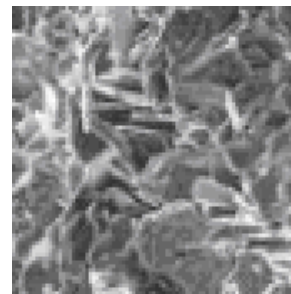
All the plots depict a positive slope indicating metallic behavior. The linear temperature dependence of electrical resistivity is one of the most important properties of the normal phase kinetics of high- T_c layered cuprates. It is commonly observed that for these ceramics, the higher the slope in the normal state of the sample, the better the superconducting behavior [41]. $T_{c, \text{onset}}$ of the sample quenched from 1250 °C on brass is higher than other samples as shown in Table 2. The results indicate that at these temperatures the superconducting 2223 phase get degrades, leading to a decrease of T_c and other superconducting properties. It is clear from the graph that residual resistance at the onset temperature is larger in case of the sample quenched from 1300 °C. The increase in T_c at 1250 °C confirms the hole carrier concentration at optimum value in the as grown pure phase. This observation is in agreement with earlier reports [42–44].

3.3. Microstructure analysis by SEM

Fig. 5. a, b, c show the SEM scans of the samples quenched from the 1200 °C, 1250 °C and 1300 °C at a magnification of $\times 1000$ for microstructure of the samples.



a



b



Fig. 5. SEM micrographs at 1000 x (a) Sample quenched from 1200 °C, (b) Sample quenched from 1250 °C, (c) Sample quenched from 1300 °C. (d) Sample quenched on brass, (e) Sample quenched on steel, (f) Sample quenched on copper.

From micrographs a strong dependence of morphology of crystallites on quenching temperatures is observed. Sample quenched from 1200 °C shows nearly spherical crystallites with rounded edges, also some voids / porosity is observed. Quenching from higher temperatures (1250 °C) tends to change this morphology to a plate like structure. This feature becomes more prominent in sample quenched from 1300 °C, where the structure is clearly and completely plate like. The plate like morphology of 2212 and 2223 grains had earlier been observed [32]. This shows that the morphology is strongly dependent on quenching temperatures.

Fig. 5.d,e, f show the SEM scans of the samples quenched from 1250 °C at brass, stainless steel, copper and bronze at a magnification of 1000 × for microstructure of the samples. Figures clearly show the grain orientation of the specimens. Each specimen was polycrystalline and grain orientation was anisotropic. Sample quenched on brass substrate is uniform and homogenous, relating to better superconducting properties. The structure is needle / plate like (lathe type). Although copper quenched structure is finer and more needle like than brass quenched, yet clear structure inhomogenities can be seen from the micrographs. This structural inhomogeneity may be the factor responsible for lower T_c as compared to the brass quenched sample. Sample quenched on stainless steel has clearly a very coarse microstructure, partially plate like and partially needle like. Thermal conductivity of stainless steel is lower than brass and copper resulting coarse structural growth. There is a marked structural inhomogeneity with voids and porosity as compared to brass and copper responsible for its degraded superconducting properties.

3.4. Composition of the sample by EDS analysis

Fig. 6 presents the EDS spectrum of the surface of the sample quenched on brass from 1250 °C. All the peaks are related to Bi, Pb, Sr, Ca, Cu, C and O, neglecting the possibility of any impurity in the sample.

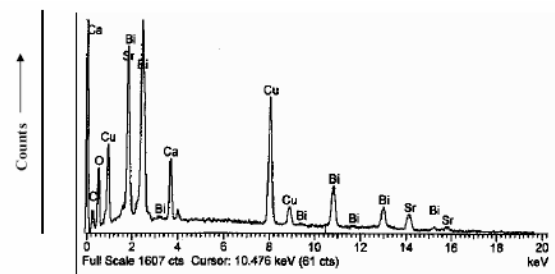


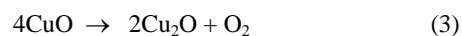
Fig. 6. EDS analysis of sample quenched on brass from 1250 °C

3.5. Density measurements

Densities of the samples were measured by the liquid immersion method. All the samples densify to great extent.

The measured values of density for the samples quenched from 1250 °C on brass, steel, copper and bronze are given in Table 3. Highest value of density is obtained for sample quenched on brass from 1250 °C i.e. 5.774 g/cm³ which is about 97% of the theoretical density of BSCCO i.e. 5.947 gm/cm³ [38,45]. This shows that more oxygen is incorporated in the sample in the formation stage. It was found that copper ions in glasses mainly exists in Cu(I) ionic states. All of the glasses that contain large amount of Cu(I) ions, heat treated at ~850 °C produce the Bi₂Sr₂CaCu₂O₈ phase which has the mean valence of copper ion of about 2. The weight gain of these phases is

due to the need for oxygen to oxidize Cu(I) ions into Cu(II) ions. The weight gain is actually due to the transition of Cu(I) ions into Cu(II) ions [46].



Since the crystallization takes place when the Cu(I) ions convert to Cu(II) ions, the crystallization process of BSCCO glasses is an oxidizing process.

Table 3. Density and porosity of BSCCO samples quenched on brass, steel, copper and bronze.

Composition (Bi _{1.6} Pb _{0.4})Sr ₂ Ca ₂ Cu ₃ O _{10+σ}	Bulk density (gm/cm ³) (±0.001)	% density	XRD density (gm/cm ³) (±0.001)	Porosity (±0.0001)	% porosity
Quenched on brass	5.774	97.09	5.970	0.0328	3.28
Quenched on steel	5.569	93.64	5.899	0.0559	5.59
Quenched on copper	5.531	93.00	6.076	0.0897	8.97
Quenched on bronze	4.425	74.40	4.995	0.1141	11.41

3.6. Porosity measurement

Porosity of the samples is measured by using eq.1. Bulk density is measured by liquid immersion method whereas X-ray density is calculated by using lattice parameters taken from XRD data. The results reveal that the sample quenched on brass from 1250 °C has smallest amount of porosity i.e. 3% as compared to other samples, the results are given in Table 3. Porosity affects the superconducting properties i.e. critical temperature and volume fraction of 2223 phase.

4. Conclusions

It could be concluded from the XRD data, resistivity measurements, scanning electron microscopy and density measurements that samples quenched from 1250 °C on brass show good results than those quenched from 1200°C and 1300 °C. XRD results reveal that the volume fraction of high-T_c phase is enhanced for sample quenched from 1250°C. Dc electrical resistivity data confirms the increase in transition temperature for this sample. Also the density measurement results show that the sample quenched on brass has maximum value (97% of theoretical density) along with the smallest amount of porosity i.e. 3%. It was found that the change in the superconducting properties could be due to the difference in the diffusion of the oxygen, calcium and copper ions. Crystallization behavior of glasses is strongly affected by the oxygen diffusion behavior. Thus oxygen at this temperature changed the valence of copper in Cu₂O plane resulting enhancement in the superconducting properties.

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