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Synthesis of $ErBa_2Cu_3O_{7-\delta}$ Superconducting Ceramic Material via Co precipitation and Conventional Solid State Routes

M. F. Nazarudin[1,2*], **Z. Zainal**[2], **I. Hamadneh**[3]
[1] *Institute of Bioscience, Lebuh Silikon, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia.*
[2] *Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia.*
[3] *Department of Chemistry, Faculty of Science, The University of Jordan, 11942 Amman, Jordan*

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Corresponding Author. E-mail: m_farhannaza@upm.edu.my; Tel: (+60389472237)

Abstract

High temperature superconductors (HTSC) of microcrystalline ceramic material $ErBa_2Cu_3O_{7-\delta}$ (ErBCO) have been successfully synthesized via chemical co-precipitation (COP) using metal acetate precursors, and physical mixtures of oxides and carbonates, by conventional solid state route (SSR). The COP sample requires 27 hours for the heat treatment while the SSR sample needs 72 hours. We compare the superconducting properties of ErBCO produced from both methods. Resistivity versus temperature measurements (R-T) showed that all samples exhibit very good metallic behaviour. The transition temperature, $T_{C(R=0)}$ for the COP sample~~s were~~ was found to be at 91.4 K while it occurs at 90.9 K for the SSR sample sintered at 920°C. X-ray diffraction (XRD) data showed a single phase of an orthorhombic structure for all the samples. Scanning electron micrographs (SEM) showed grains of sizes ≤ 40μm were randomly distributed in all the highly compacted samples. However, the sample prepared via COP exhibited smaller pores in comparison to those in the SSR sample. COP method simplifies the preparation, and gives good quality sample with shorter time of preparation as compared to the quality of sample prepared by conventional solid state route.

Keywords: High temperature superconductors (HTSC), $ErBa_2Cu_3O_{7-\delta}$, Co- precipitation, Solid state route

Introduction

The physical properties of superconductors depend on the synthesis methods and processing technologies used. Progressive research efforts have led towards improving the sample preparation with significant cost and time savings for producing good quality samples. Preparation of a complex system such as $REBa_2Cu_30_{7-\delta}$ (in this study RE (rare earth) = Er) superconductor needs a crucial approach in order to obtain a high quality product. There are several methods for the preparation of a ceramic superconductor that includes conventional solid state route (SSR), the most common process which is widely used and most commonly reported in [1-3]. In general, the starting materials, for instance, metal oxides, carbonates or other salts are mixed in appropriate ratio, homogenized, and heated typically at a high temperature. However, this technique has several drawbacks such as long processing times (48-72 hours), higher temperature for heat treatment, and several cycles of grinding processes in order to attain higher purity and homogeneity of samples. Moreover, this technique also exhibits other drawbacks such as odd particle size and size distribution, slow reaction rate and has the tendency to produce contaminations (non-superconducting phase) [4-6].

At present, solution routes such as co-precipitation (COP), [7-10] freeze drying, [11] and spray drying have been developed in order to overcome these problems. COP has been broadly used for fabricating superconducting materials. COP engages the partition of a precipitate containing several of ionic species chemically bound to one another from a solution [12] and the main products are hydroxides, carbonates and oxalates. Usually, metal nitrates, chlorides, carbonates, acetates and a combination of those have been used as starting material while the precipitating agent can act either alone or in combination with pH adjusting agent. The use of oxalates, hydroxides and acetates as starting reagents in various wet chemical methods allows optimization of the synthesis of superconducting materials. Most of the COP methods offer unique advantages and have been used by various workers in order to overcome problems exhibited from the solid state route. The final products have better homogeneity, improved phase purity and fine powder particles. Besides, it requires lower heating temperature for synthesis, shorter thermal and processing time to produce samples with better superconducting properties than those obtained using conventional solid state method.

However, using metal nitrates, metal hydroxide or metal oxides as starting salt in the oxalates co-precipitation, it requires sodium hydroxide to adjust the pH of the solutions and several washings in order to remove residual sodium from the co precipitation. These processes lead to the material loss during precipitation and washing process [13]. In addition, it is necessary to optimize the experimental conditions such as pH, solubility product, dilution and precipitating medium because of the different solubilities of individual oxalates in order to obtain desired composition [14]. It is useful to point out that using metal carbonates as starting salts requires at least 18 hours to precipitate, limited by the slow decomposition of some material like $RE_2(CO_3)_3$ in REBCO leading to the growth of large oxalate grains that produce non uniform co-precipitates.

By using metal acetate as raw materials with 2-propanol and deionized water as solvents in the oxalate co-precipitation, the fabrication process does not require pH adjustment and several washings to the precipitate [15] and thus avoids the material loss during precipitation and washing process.

In this paper we focus on the preparation of High Temperature Superconductor (HTSC) $ErBa_2Cu_3O_{7-\delta}$ (ErBCO) material through oxalate co-precipitation method and compare its properties with those of samples obtained by solid state technique. Besides, this work also discusses how the samples were prepared using metal acetate as raw material. Systematic investigations of superconducting properties were performed using DC electrical resistance-temperature measurements. We also report X-ray Diffraction XRD and Scanning Electron Microscopy SEM investigations on the same samples.

2. Materials and methods

2.1. Instrumentation and Apparatus.

X-ray powder diffraction with Cu Kα radiation was examined using PANalytical'sX'Pert PRO X-ray diffraction system at 40 kV and 30 mA with a step of 0.02^o over the range of 2θ angle from 4 to 60^o. Electrical resistance study of the samples in the range 50–300K was measured by means of a standard four-probe technique using constant current of 30 mA (DC). The cryogenic system used was a Closed Cycle Helium Cryostat. Scanning electron microscope (SEM) micrographs of fractured surface of the samples were recorded using JEOL 6400 and FEI QUANTA 200.

2.2 Preparation of $ErBa_2Cu_3O_{7-\delta}$ Superconductor.

2.2.1 Coprecipitation method (COP)

$ErBa_2Cu_3O_{7-\delta}$ sample was prepared via oxalate co-precipitation method as described by Hamadneh et al [16]. The metal acetate powder was calcined at 900°C for 12 hours in order to remove the remaining volatile materials and yield a very consistent product. The calcined powders were ground into fine powder using an agate mortar and pestle for 30 minutes and pressed into pellets under a pressure of 7000 to 8000 kg/cm^2. The pellets was subjected for heat treatment at 920°C for 15 hours under oxygen atmosphere and slowly cooled to room temperature at 40°C/hour. The chemical equations for the co-precipitation reaction are:-

$$2Er(CH_3COO)_3.4H_2O_{(aq)} + 3C_2O_4H_{2(aq)} + 6HOCH(CH_3)_{2(aq)} \rightarrow Er_2(C_2O_4)_{3(s)} + 6CH_3COOCH(CH_3)_{2(aq)} + 10H_2O_{(l)} \quad (1)$$

$$4Ba(CH_3COO)_{2(aq)} + 4C_2O_4H_{2(aq)} + 8HOCH(CH_3)_{2(aq)} \rightarrow 4Ba(C2O_4)_{(s)} + 8CH_3COOCH(CH_3)_{2(aq)} + 8H_2O_{(l)} \quad (2)$$

$$6Cu(CH_3COO)_2.H_2O_{(aq)} + 6C_2O4H_{2(aq)} + 12HOCH(CH_3)_{2(aq)} \rightarrow 6Cu(C_2O_4)_{(s)} + 5CH_3COOCH(CH_3)_{2(aq)} + 13H_2O_{(l)} \quad (3)$$

2.2.2 Conventional solid-state route (SSR)

For conventional method, the $ErBa_2Cu_3O_{7-\partial}$ samples were prepared by mixing appropriate amounts of Er_2O_3, $BaCO_3$ and CuO powders with purity >99:99%. The materials were ground in an agate mortar and pestle and then calcined in air at around 900°C for 48 hours with several intermittent grindings, followed by oven cooling.

The powders were then pressed into pellets of ~12:5 mm diameter and 3 mm thickness under a pressure of 7000 to 8000 kg/cm^2. The pellets were reground before sintered at 920 °C for 24 hours and cooled to room temperature at 40°C per hour. Figure 1 (a and b) shows a flow chart of the synthesis of $ErBa_2Cu_3O_{7-\partial}$ samples by co-precipitation and solid state technique. The quantity of each chemical was determined according to the stoichiometry in the chemical reaction below:

$$0.5Er_2O_{3(s)} + 2BaCO_{3(s)} + 3CuO_{(s)} \rightarrow ErBa_2Cu_3O_{7-\delta(s)} + 2CO_2 \qquad (4)$$

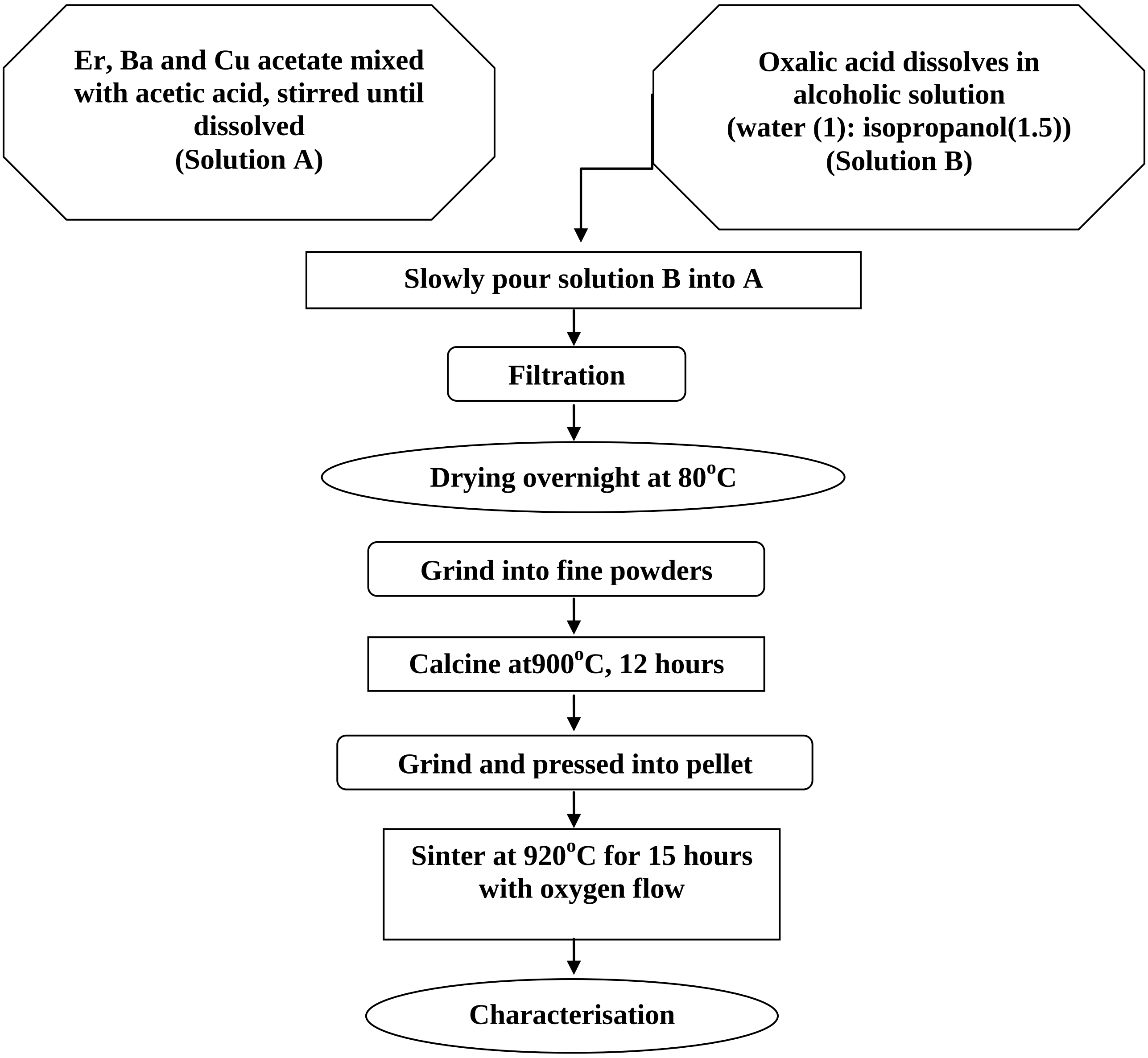


Figure 1a: Flow chart of the synthesis of $ErBa_2Cu_3O_{7-\partial}$ by (a) co-precipitation and (b) solid state method.

3. Results and discussion

3.1. Phase identification

Figure 2 (a and b) shows Powder X-Ray Diffraction (PXRD) pattern for ErBCO samples prepared via co-precipitation and solid state route, respectively. All samples consist of essentially single 123 phase of orthorhombic structures and well match the JCPDS standards (01-086-0478). The space group, Pmmm, No.47, Z = 1, α = β = γ = 90o with lattice parameters, a= 3.820 ± 0.001, b = 3.882 ± 0.001, c = 11.67 ± 0.01 Å, respectively. The average crystallite size for the resulted materials can be estimated using Sheerer equation below (Padam et al 1991):

$$D_{hkl} = k\,\lambda/\beta \cos\theta \qquad (5)$$

Where k is Shape factor (~ 0.9), λ-wavelength of the radiation λ_{Cu} = 1.5418 Å and β is full width at half maximum (FWHM) in radians. The crystalline size for SSR sample is 12.4 nm where the COP sample is 33.0 nm (Table 1), this implies that co-precipitation method allows the orthorhombic structure of 123 phase to grow and reducing the gaps between the grains which resulted in increase the connectivity with just a single step sintering [17 and 18].

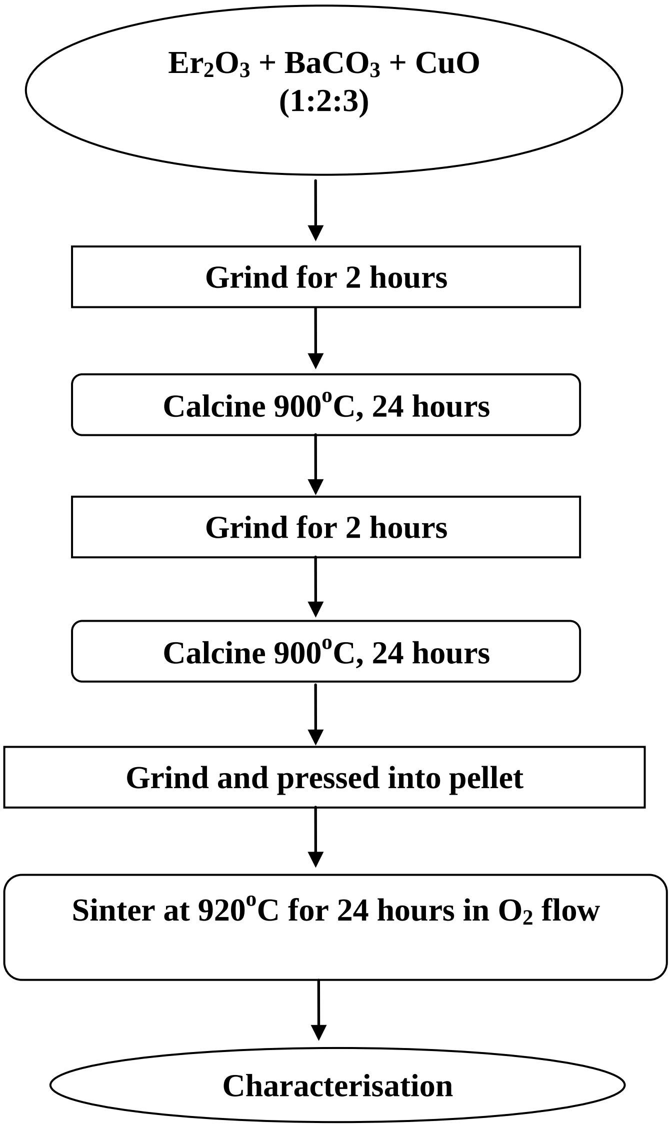


Figure 1b: Flow chart of the synthesis of $ErBa_2Cu_3O_{7-\partial}$ by (a) co-precipitation and (b) solid state method.

In comparison, conventional method (solid state route) require multiple regrinding and long heat treatment process as to acquire good superconducting phase. It can be seen that the peaks intensity are slightly higher than samples prepared via COP. This is probably due to fine powder produced after several grinding during preparation process. However, the disadvantages that can be seen from SSR technique are, it requires long sintering time duration accompanied with intermittent grinding to improve the solid state reaction and to obtain the same quality produced by the co-precipitation technique.

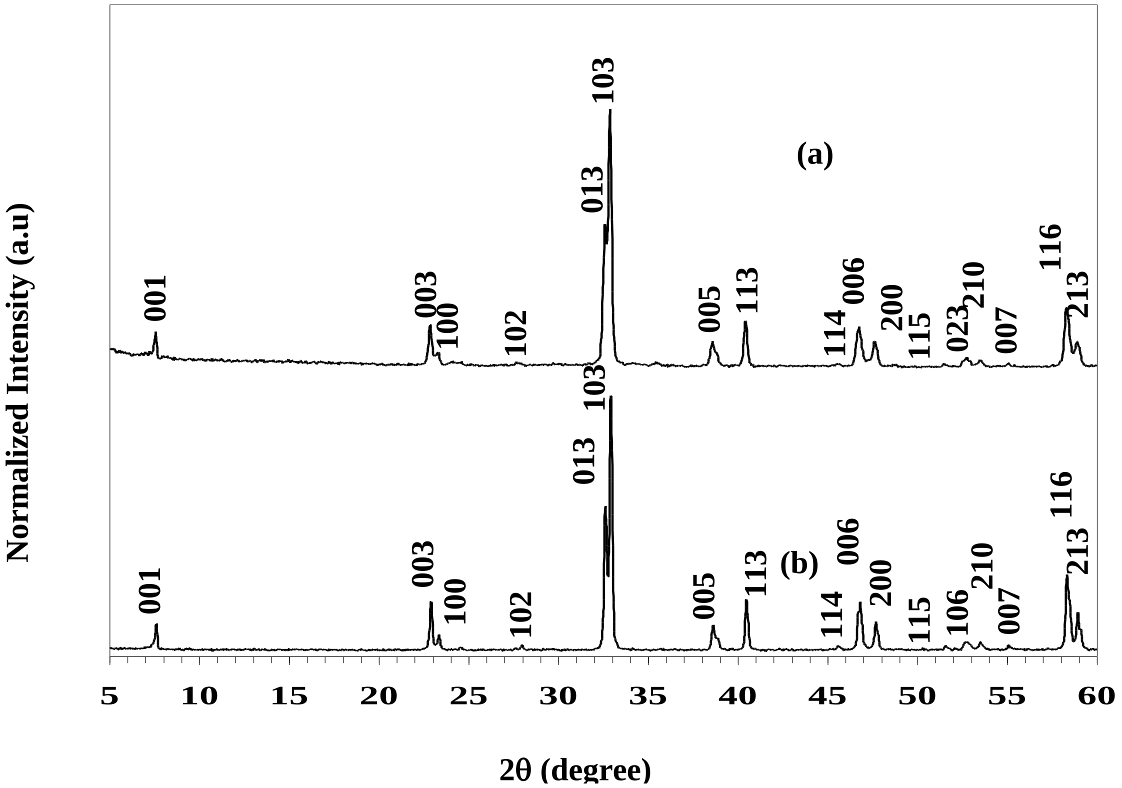


Figure 2: X-ray powder diffractograms for samples prepared via a) co-precipitation and b) conventional method.

Table 1: Summarize data of Tc(R=0) (K), Tc-onset (K), ΔT (K), density, porosity, crystalline size and measured lattice parameters of superconducting $ErBa_2Cu_3O_{7-\delta}$ prepared via co-precipitation method and solid state route.

Parameters	**Sample**	
	COP	SSR
$T_{c(R=0)}$ (K)	91.4	90.9
$T_{c\text{-onset}}$ (K)	93.7	93.9
ΔT (K)	2.3	3.0
Density (g/cm^3)	6.2686	5.365
Porosity (%)	18.8	24.8
Crystalline size (nm)	33.0	12.4
Lattice Parameters	a (Å)= 3.814± 0.001	a (Å)=3.812± 0.001
	b (Å)= 3.874±0.001	b (Å)=3.879±0.001
	c (Å)= 11.654±0.002	c (Å)=11.662±0.001

3.2 Electrical resistance measurements

Normalized resistance at room temperature as a function of temperature for the samples which were prepared using co-precipitation (COP), and conventional (SSR) method are shown in Figure. 3. All samples displayed normal metallic behaviour with the R-T curve showed the sharp drop of the curve at Tc-onset which is an indication that the grain connectivity is very good in the ErBCO pellets. The zero resistance temperature $T_{c(R=0)}$ and onset temperature, $T_{c\text{-onset}}$ for COP and SSR sample were at (91.4K, 93.7K) and (90.9K, 93.4K) respectively. The product produced from COP technique were having chemical homogeneity; stoichiometry and fine particles of precursor thus contributed to the $T_{c(R=0)}$ results. From the transition width (ΔT_c = $T_{c\text{-onset}}$ -

$T_{c(R=0)}$), the phase purity of the sample can be known where, the larger the ΔT_c value, more impure the product is [19]. Nevertheless, as the materials prepared are the same materials, similar physical properties are expected as the $T_{c(R=0)}$ of the sample remain relatively unchanged even it was prepared by different preparation technique.

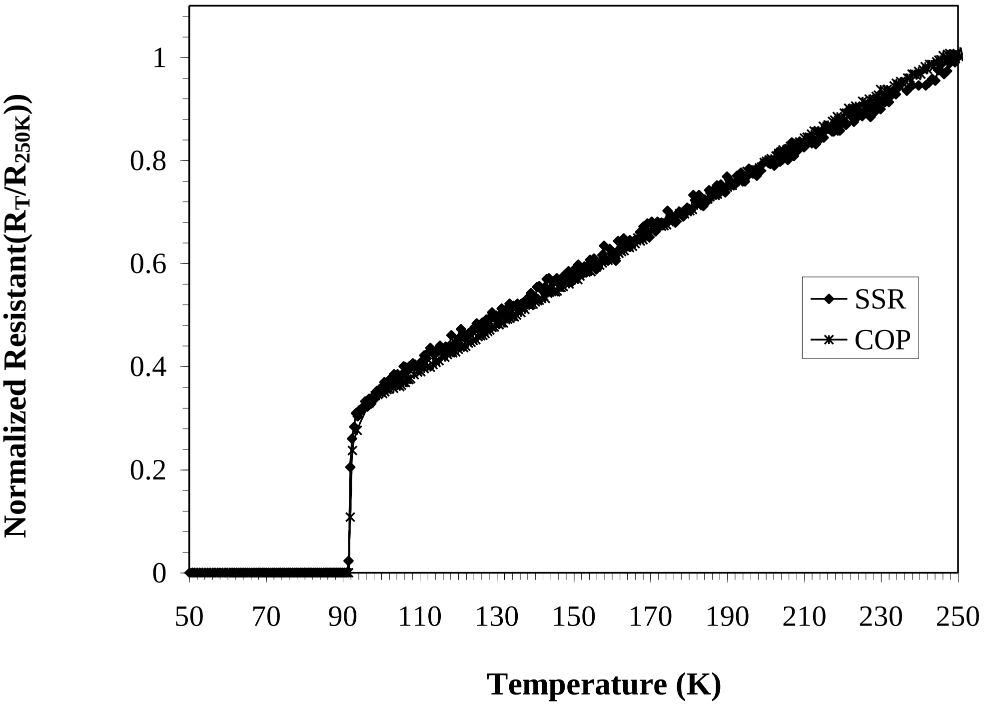
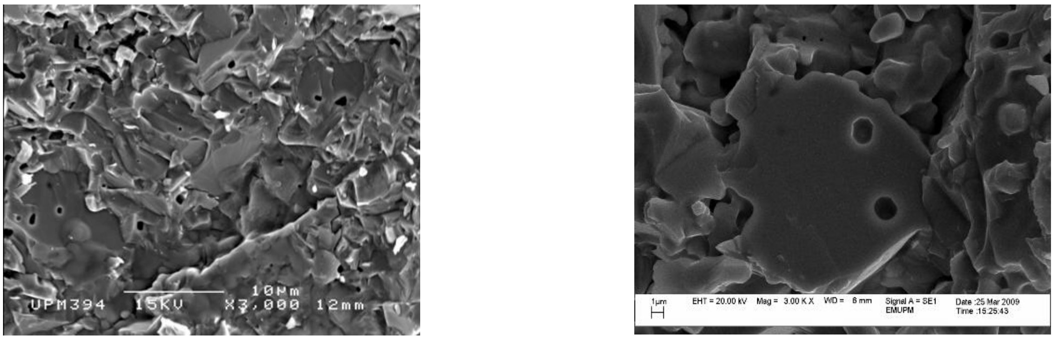


Figure 3: Normalized resistance (R/R (T=250)) as a function of temperature for samples sintered under oxygen atmosphere prepared via co-precipitation and solid state method.

3.3 Microstructure

The internal fractured surface morphology for the superconducting $ErBa_2Cu_3O_{7-\delta}$ samples prepared via COP and SSR are studied with magnification of 3000x and shown in Figures 4(a, b). Microstructure analysis of the samples showed irregular plate-like grain of about 40 μm in size, randomly distributed and highly compacted are also observed for all sintered samples. However, COP samples exhibited a bigger crystalline size as compared to SS samples which could be responsible for the enhancement of the transport properties. This deduction is supported by resistance measurement as already discussed in previous section.



(a) (b)

Figure 4: Scanning electron micrograph of the sintered sample prepared via a) co precipitation b) solid state route.

Conclusion

The high-temperature superconductor (HTSC) $ErBa_2Cu_3O_{7-\delta}$ (ErBCO) ceramic material has been prepared by co-precipitation (COP) and solid state method (SS). All samples were characterized with X-ray Diffraction Analysis (XRD), Four Point Probe Technique and Scanning Electron Microscope (SEM). The results obtained showed that SS method requires longer time (72 hours) for the heat treatment and several rounds of grinding practices during the preparation process as compared to COP method which is requires (27 hours) only. However, both methods exhibited HTSC ceramics with very good metallic behavior and $T_{C(R=0)}$ above 90K. Both samples consisted of essentially single 123 phase of orthorhombic structures. COP samples exhibited a bigger crystalline size less cavities and voids as compared to SS samples. Co-precipitation method offers better quality superconducting ceramics with shorter preparation time required. This make it essential for practical use for current leads, current fault limiter and also for quasi-permanent magnets.

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