Superconductivity of REBa$_2$Cu$_3$O$_{7-\delta}$ (RE= Y, Dy, Er) Ceramic Synthesized Via Coprecipitation Method

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Abstract. The REBa$_2$Cu$_3$O$_{7-\delta}$ (RE= Y, Dy, Er) superconducting ceramics have been prepared via coprecipitation(COP) method from nearly saturated solutions of metal acetates and 2-propanol solution of oxalic acid. The metal oxalates powders were subjected to thermal treatment of 12 hours calcination at 900°C. The pelletized powder was sintered for 15 hr at 920°C. All samples showed a single step transition in the R-T curves. The $T_C(0)$ for samples Dy123, Y123 and Er123 were 93 K, 91 K and 90 K, respectively. XRD data showed single phase of an orthorhombic structure for all samples. SEM micrographs showed large grain sizes that are randomly distributed. These results showed that COP method using metal oxalates starting powders is very effective to synthesize high quality superconductors and shorten the sintering time required due to the formation of sub micron oxalate powders.

1. Introduction

YBa$_2$Cu$_3$O$_{7-\delta}$ (Y123), DyBa$_2$Cu$_3$O$_{7-\delta}$ (Dy123) and ErBa$_2$Cu$_3$O$_{7-\delta}$ (Er123) are members in RE123 family. They have been prepared using conventional solid state technique which normally requires high temperature (940-1000°C), long calcination and sintering durations (48-72 hours) accompanied with intermittent grinding to improve the solid state reaction [1-3].

Wet chemical methods such as sol–gel [4,5], freeze-dry [6] and co-precipitation techniques [7-13] have been employed to overcome these problems. The powders obtained by the co-precipitation technique have a smaller grain size and are of higher purity and homogeneity than the powders produced by the solid state reaction method. This is due to the initial mixture of cations on an atomic scale in solution so as to enhance the reaction during the heat treatment and the resulting powder which is more homogenous with shorter thermal and time processing.

In this paper, we report the preparation conditions of nano starting powders of RE123 (RE= Y, Er, Dy) superconductors by the solid-state synthesis method using coprecipitation technique. The oxalate coprecipitation method was conducted using a stoichiometric ratio for the superconducting compound having the nominal compositions of REBa$_2$Cu$_3$O$_{7-\delta}$. Systematic investigations on the superconducting properties were performed using DC electrical resistance-temperature measurements; XRD and SEM are reported.
2. Experimental

2.1. Preparation of \( \text{REBa}_2\text{Cu}_3\text{O}_{7-\delta} \) superconductor

\( \text{REBa}_2\text{Cu}_3\text{O}_{7-\delta} \) superconducting ceramics \((\text{RE}=\text{Y, Dy and Er})\) were synthesized by mixing metal acetates of \( \text{RE} \) (III) acetate \([\text{RE(OOCCH}_3)_3\cdot\text{xH}_2\text{O}]\), barium acetate \([\text{Ba(OOCCH}_3)_2]\) and copper (II) acetate \([\text{Cu(OOCCH}_3)_2\cdot\text{H}_2\text{O}]\) \((\text{purity}>99\%)\) to form solution \((\text{A})\). The oxalic acid was dissolved in water: isopropanol \((1:1.5)\) to have a concentration of 0.5M \((\text{solution (B)})\). Solution \((\text{B})\) was added to the stirred solution \((\text{A})\) in an ice bath and a uniform, stable, blue suspension was obtained. The slurry was filtered after 5 minutes of reaction followed by the drying stage in the temperature range of 80-85°C for 8 hours. The blue precipitated powders were heated up to 900°C in air for 12 hours to remove the remaining volatile materials. The calcined powders were reground in a marble mortar for 10 minutes and pressed into pellets of ~12.5-mm diameter. The pellets were sintered at 920°C for 24 hours and slowly cooled to room temperature at 1 °C/minute.

2.2. Characterization:

The heat treatment profile and weight loss were detected by Thermo Gravimetric Analysis (TGA). The solid samples were examined by X-ray powder diffraction with Cu \( \text{K}_\alpha \) radiation using PANalytical's X'Pert PRO X-ray diffraction system at 40 kV and 30 mA with a step of 0.02° over the range 4–60°. Electrical resistance study of the samples in the range 50–300 K 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.

3. Results and discussion

Figure 1 shows the result of Thermo Gravimetric Analysis (TGA) of RE-123 samples right after coprecipitation. It can be observed that there are five major drops of weight lost in the samples. These five drops are named Drop 1, Drop 2, Drop 3, Drop 4 and Drop 5.

![TGA curve of the oxalate coprecipitated RE-123 powders](image1.png)

**Figure 1.** TGA curve of the oxalate coprecipitated RE-123 powders

![DC electrical resistance as a function of temperature for sintered RE123 samples.](image2.png)

**Figure 2.** DC electrical resistance as a function of temperature for sintered RE123 samples.
The first drop in weight is due to moisture loss from the powders as the drop ends at about 150°C. The second drop is associated with the loss of water molecule from Cu(C_2O_4)_2.H_2O, Ba(C_2O_4).0.5H_2O and RE_2(C_2O_4)_3.xH_2O. While the third drop in weight shows the decomposition of CuC_2O_4.H_2O, BaC_2O_4.0.5H_2O and RE_2(C_2O_4)_3.xH_2O to CuO, RE_2O_3 and Ba_2CO_3, respectively. The fourth drop is associated with the decomposition of Ba_2CO_3 to Ba_2O_3. The final drop shows a complete decomposition and the formation of REBa_2Cu_3O_7-δ that begins at about 900°C. This temperature suggests a good calcination and sintering temperature to be at the range 900-920°C.

Figure 2 shows the DC electrical resistance (R) as a function of temperature (K) for the sintered samples. The R-T curve indicates a metallic behavior in the pellets with single step feature which is an indication for good grain connectivity. However, the onset temperature (T_{C-onset}) and the zero resistance temperature (T_{C(R=0)}) are (97K, 93K), (98K, 91K) and (95K, 90K) for samples Dy123, Er123 and Y123, respectively. In comparison with conventional method; these results can only be achieved with long calcination and sintering durations [1-3].

Figures 3a and 2b show the XRD pattern for the calcined and sintered samples of Y123, Dy123 and Er123 systems. It is clearly shows that the orthorhombic structure of 123 phase was dominant for all samples with existence of peaks belong to 211 phase.

| Table 1. Summarized data of the lattice parameters and lattice density for samples RE123 (RE=Y, Dy, Er). |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| RE123  | T_{C(R=0)} (K) | a (Å)           | b(Å)            | c(Å)            | Density (g/cm^3) |
| Y123   | 90             | 3.896 ±0.001    | 3.824 ±0.001    | 11.691 ± 0.004  | 6.335±0.001      |
| Dy123  | 93             | 3.885 ±0.001    | 3.830 ±0.001    | 11.691 ± 0.001  | 7.066±0.001      |
| Er123  | 91             | 3.877 ±0.001    | 3.811 ± 0.001   | 11.665 ± 0.001  | 7.151±0.001      |
Coprecipitation method does not require multiple calcinations and regrinding to obtain a good superconducting phase. This also suggests that the co-precipitated REBCO powder can be converted to superconducting phase with just a single step sintering and controlled cooling rate in order to enrich the RE123 lattice with enough oxygen and thus enhance the growth of the orthorhombic phase.

SEM micrograph Figure 4 displayed the formation of nano particles for metal oxalate powders with average grain size >40 nm for all samples. However, large grains (20-50µm), highly compacted and randomly distributed were observed for all sintered samples. Pores are also observed at the grains with a size of about 2µm. It can be concluded that the formation of nano-sized precursor powders simplified the preparation technique and enhanced the formation of 123 superconducting phase with just a single step sintering and controlled cooling rate in order to enrich the RE123 lattice with enough oxygen and thus enhance the growth of the orthorhombic phase.

Figure 4. SEM micrographs of coprecipitated powders of the (a) Y123, (b) Dy123, (c) Er123, while (a'), (b') and (c') are for the sintered samples, respectively.
4. Conclusions
REBa$_2$Cu$_3$O$_{7-\delta}$ (RE=Y, Dy and Er) superconducting ceramics have been prepared via coprecipitation method extracted from the metal acetate precursors. The nano-sized precipitated powders simplified the preparation technique and enhanced the formation of 123 superconducting phase with just a single step sintering and controlled cooling rate in order to enrich the RE123 lattice with enough oxygen and thus enhance the growth of the orthorhombic phase. The materials produced showed very good metallic behavior. Highly compacted large grain size of 20-50µm and randomly distributed leading to good grain connectivity are also observed.

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