Effect of Nano Sized oxalate Precursor on the Formation of REBa$_2$Cu$_3$O$_{7-δ}$ (RE= Gd, Sm, Ho) Ceramic Via Coprecipitation Method

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Abstract. The formation REBa$_2$Cu$_3$O$_{7-δ}$ (RE= Gd, Sm and Ho) superconducting ceramics from metal oxalate precursors with average grain size less than 50 nm using the coprecipitation method is reported. The metal oxalate powders were heated at 900°C for 12 hours, pelletized and then sintered at 920°C for 15 hr. The high-T$_C$ phase was observed for all samples as an evidence for the single step transition of (R-T) curves. The T$_C$(R=0) for samples Gd123, Ho123 and Sm123 were 95 K, 93 K, 91 K, respectively. XRD data showed single phase of an orthorhombic structure for Sm123 and Ho123 samples, small amount of impurities (Gd211) phase were detected for Gd123. SEM micrographs showed large grain sizes that are randomly distributed. These results showed that COP method using nano sized metal oxalates starting powders is very effective to synthesize high quality superconductors and shorten the sintering time required. The formation Gd211 phase for the Gd123 sample might act as a pinning centre explaining the enhancement of the transport properties.

1. Introduction

GdBa$_2$Cu$_3$O$_{7-δ}$ (Gd123), SmBa$_2$Cu$_3$O$_{7-δ}$ (Sm123) and HoBa$_2$Cu$_3$O$_{7-δ}$ (Ho123) are widely investigated as members in RE123 family. They have been prepared using conventional solid state technique which normally involves the use of high purity oxides and carbonate powders as starting materials. Multiple grindings and extended heat treatment are necessary to achieve the complete reaction, since the formation of the superconducting phase proceeds via diffusion in the solid state. However, higher annealing temperature (940-1000°C), and longer heating duration (48-100 hours) would bring about the evaporation of the powders, and consequently lower the quality of the samples [1-6].

Co-precipitation techniques [7-14] have been developed to achieve better mixing of the initial products. 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= Gd, Sm, Ho) 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 REBa$_2$Cu$_3$O$_7$-$\delta$ superconductor

The coprecipitated powders with nominal composition of REBa$_2$Cu$_3$O$_7$-$\delta$ were synthesized by mixing metal (III) acetate hydrate [RE (OOCCH$_3$)$_3$.xH$_2$O], barium acetate [Ba(OOCCH$_3$)$_2$], and copper (II) acetate [Cu(OOCCH$_3$)$_2$.H$_2$O] (high purity powders $\geq 99.9\%$ supplied by AlfaAesar) with glacial acetic acid to form an aqueous solution. The solution was then added to a 0.5M oxalic acid dissolved in 2-propanol: water mixture (1.5:1). Blue precipitated slurry was obtained and filtered after 5 minutes of reaction followed by the drying stage at 80 $^\circ$C for 8 hrs. The blue precipitated powders which are slightly aggregated were heated up to 900 $^\circ$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 and 2 mm thickness under a load of 6 tons using a hydraulic press model SPECAC. The pellets were sintered at 920 $^\circ$C under oxygen flow for the durations of 15 hr and slowly cooled to room temperature at 1 $^\circ$C / minute.

2.2. Characterization:

The solid samples were examined by X-ray powder diffraction with Cu 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 resistant study of the samples in the range 50–250 K was measured by means of a standard four-probe technique using 30 mA (DC) in a closed cycle refrigerator system model ARS-EA202A. Field emission microscope (FESEM) and Scanning electron microscope (SEM) micrographs of a starting powder and fractured surface of the samples were recorded using FEI QUANTA 200 and JEOL 6400, respectively.

3. Results and discussion

Figures 1a and 1b show the XRD patterns for the calcined and sintered samples of Gd123, Sm123 and Ho123 polycrystalline systems. They clearly show that the orthorhombic structure of 123 phase was dominant for all samples and well match the JCPDS standards (01-086-0474, 01-081-0366 and 01-086-0476, for Gd123, Sm123 and Ho123, respectively). However, the sintered samples showed lower peak intensities for the impurities in the Ho123 and Gd123 powders as shown in Figure 1b. These impurity peaks are assigned to Gd$_2$BaCuO$_5$ and Ho$_2$BaCuO$_5$ phase (211) (JCPDS # 00-039-1418, 01-081-0800). The measured lattice parameters and lattice density are shown in Table 1.
Table 1. Summarized data of the lattice parameters and densities for samples RE123 (RE= Gd, Sm, Ho).

| RE123  | $T_{C(R=0)}$ (K) | $a$ (Å)   | $b$ (Å)   | $c$ (Å)   | Density (g/cm$^3$) |
|--------|------------------|-----------|-----------|-----------|--------------------|
| Gd123  | 95               | 3.889 ± 0.001 | 3.836 ± 0.001 | 11.704 ± 0.002 | 6.904 ± 0.001     |
| Sm123  | 93               | 3.904 ± 0.001 | 3.861 ± 0.001 | 11.719 ± 0.002 | 6.889 ± 0.001     |
| Ho123  | 91               | 3.876 ± 0.001 | 3.828 ± 0.001 | 11.679 ± 0.004 | 7.115 ± 0.001     |

REBCO powders 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 while 211 phase in Ho and Gd samples was clearly decreased after sintering process. This preparation process does not require multiple calcinations and regrinding to obtain a good superconducting phase.

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 (98K, 95K), (96K, 93K) and (93K, 91K) for samples Gd123, Sm123 and Ho123, respectively. In comparison with conventional method; these results can only be achieved with long calcination and sintering durations [3-6].

According to the ionic size of the respective RE ions used in the experiment; Sm$^{3+}$ (0.964 Å), Gd$^{3+}$ (0.938 Å) and Ho$^{3+}$ (0.901 Å) Sm123 is supposed to have the highest $T_c$ [3]. However, the presence of the 211 phase in Gd123 and Ho123 acts as pinning centers to enhance the transport properties for them [9]. In addition, the small ionic size difference between Sm$^{3+}$ and Ho$^{3+}$ with the presence of 211 phase in Gd123 system might cause higher $T_c$ result for Gd123. On the other hand, a bigger ionic size difference between Sm$^{3+}$ and Ho$^{3+}$ has affected the $T_c$ difference between the two systems even with the presence of 211 phase in Ho123.
FESEM micrographs Figures 3a, 3b and 3c present the agglomerates of nano particles for metal oxalate powders with average grain size ≤40 nm for all samples. However, large grains (20-50μm), that are highly compacted and randomly distributed were observed for all sintered samples as shown in Figures 3 a', 3 b' and 3 c'. 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 2: DC electrical resistance as a function of temperature for sintered RE123 samples.

Figure 3: FESEM micrographs of coprecipitated powders present agglomerates of nanoparticles of the (a) Gd123, (b) Sm123, (c) Ho123, while (a'), (b') and (c') are for the sintered samples, respectively.
4. Conclusions

$\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE=Gd, Sm and Ho) superconducting ceramics have been produced via coprecipitation method extracted from the metal acetate precursors. The agglomerates of 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. Thus, it enhanced the growth of the 123 phase. The resulted materials showed very good metallic behaviour due to the formation of the highly compacted randomly distributed large grain size of 20-50μm. The XRD analysis showed an evident structure of the orthorhombic phase. On the other hand, sintering process can be useful in the fabrication of RE123 conductor with small amount of RE211 phase that act as flux pinning centers, in addition to bigger RE atomic size.

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6. References

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