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Growth and characterization of $REBa_2Cu_3O_{7-\delta}$ superconductor single crystals obtained from xenotime mineral

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ABSTRACT

Single crystals of $REBa_2Cu_3O_{7-\delta}$ (RE=natural mixture of *Y* and heavy lanthanides in the single crystals) superconductor were successfully grown using rare-earth oxides extracted from xenotime mineral, allowing an alternative and simple route for superconductor single-crystal production. The methodology to extract the rare-earth mixed oxides from the xenotime mineral has three main steps: alkaline fusion, acid lixiviation and oxalic precipitation. Large single crystals with a typical $5\times5\times0.03\,mm^3$ size were obtained by using a CuO–BaO self-flux and were characterized by scanning electron microscopy (SEM), energy-dispersive electron spectroscopy, X-ray diffraction, magnetic measurements and nanoindentation. The composition of the rare-earth elements of the crystal was different from the starting mixture, possibly due to the different solubilities of the elements in the melt. The final crystal stoichiometry was RE:Ba:Cu=1:2:3. X-ray diffraction analysis showed highly oriented *c*-axis (c=11.716$\pm$0.002 Å). The critical temperature was determined to be around $T_C\cong88$–89 K after the crystals have been submitted to oxygen annealing. Hardness and elastic modulus for *ab*- and *b*(*a*)*c*-planes were 8.5$\pm$0.5 and 160$\pm$20 GPa, respectively.

1. Introduction

High-temperature superconductors have been the subject of intensive and extensive studies with the aim of a better comprehension of its theoretical mechanisms and improvement of its physical and chemical properties for better technological applications. In particular, $XBa_2Cu_3O_{7-\delta}$ (X=Y or any lanthanides elements except Ce, Pr, Pm and Tb) has turned out to be one of the most important high-T_C oxide superconductors. Large and good single crystals from these compounds allow the study of the great anisotropies of some fundamental superconductivity parameters such as critical fields, current density, coherent length and gap, among others [1–5].

All the lanthanides elements and yttrium came mainly from minerals such as monazite, bastnäsite and xenotime [6]. The first two ores are rich in light lanthanides, which include the deleterious cerium and praseodymium. On the other hand, xenotime is a phosphate of yttrium and the heavy lanthanides (from gadolinium to lutetium), but with minor traces, at most, of terbium. From the xenotime mineral one can easily extract a natural mixture of trivalent oxides, such as Re_2O_3 (Re=natural mixture of *Y* and lanthanides in the precursor powder), which can be used if one is aiming an alternative high-T_C superconductor isostructural to $YBa_2Cu_3O_{7-\delta}$ that does not demand high-purity yttrium or other pure lanthanide element on Y site [7]. Besides the practical value of this kind of superconductor, it is also a way of introducing disorder that could affect some important issues such as fluctuation effects near the critical point [1,8]. Also, a melt-processed polycrystalline sample of this material prepared by the top seeding technique was also studied for applications needing high critical current densities [9].

In the present work, we describe the successful preparation of $REBa_2Cu_3O_{7-\delta}$ single crystals that are isostructural to $YBa_2Cu_3O_{7-\delta}$. The methodology employed to extract the mixed-oxide Re_2O_3 from the xenotime is shown. The as-grown crystals are not superconductors. However, after oxygen annealing at

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420 °C for 5 days, superconductivity is observed at $T_C \approx 88$–89 K. The characterization was performed by scanning electronic microscopy (SEM), electron-dispersive energy spectroscopy, X-ray diffraction and *dc* magnetization. Hardness and elastic modulus were also determined by nanoindentation.

2. Experimental

2.1. Crystal growth

The chemical procedure to obtain the natural mixture of trivalent rare-earth oxides Re_2O_3 from xenotime mineral is briefly described as follows. At first, the xenotime ore powder was mixed with $NaOH_{(s)}$ in a 1:1.3 weight ratio and heated at 700 °C for 4 h. After cooling to room temperature, the mixture was ground and washed in water until a pH of 7.0 was reached. After that, the liquid–solid mixture was stirred with HNO_3 at a ratio of 1:1 at 90 °C for 10 min. Afterwards, the mixture was filtered using a sintered glass funnel and the pH of the liquid was adjusted to 1.5. The addition of oxalic acid solution caused the precipitation of the rare-earth oxides. After a resting period of 24 h at approximately 5 °C, the mixture was filtered again. The resulting powder was calcinated at 850 °C for 2 h to obtain the final rare-earth oxides mixture. Fig. 1 shows a flowchart that resumes the employed methodology to extract the mixed Re_2O_3 oxides by starting from the xenotime ore. In this chart, the three main steps are shown: alkaline fusion, acid lixiviation and oxalic precipitation. The process details of each step are described in Table 1.

Table 2 shows the composition of our particular mixture of rare-earth oxides, characteristic of the Pitinga mine [10] in the Brazilian Amazonia. All world-spread xenotime shows a similar composition [6], with a predominance of yttrium and the heavy lanthanides with the exception of terbium, which is deleterious to this kind of superconductor.

A flux method, similar to the one as described by Schneemeyer et al. [11] and Wang et al. [12], was performed in order to grow $REBa_2Cu_3O_{7-\delta}$ single crystals. The main advantage of this method is that it allows the growth of lengthwise single crystals that are easily extracted from the solidified flux matrix. The procedure involves using a shallow crucible (41 × 32 × 7 mm zirconia boat) positioned on a 15° slope inclined leverage, where the raw material is placed and kept at high temperature for a short time period. During this time the liquid phase, pulled out by gravity, starts to flow to the lower side of the crucible. There, single crystals can grow from the flux because the temperature is now slowly decreased.

The starting materials were the powder mixture of Re_2O_3 (extracted from xenotime mineral), $BaCO_3$ (>99.9% of purity) and CuO (>99.99%) at a molar ratio of Re:Ba:Cu=1:4:10 [11]. This means that the starting mixture had a relative excess of Ba and Cu in comparison to the final desired composition of $REBa_2Cu_3O_{7-\delta}$. About 32 g of this mixture was ground for 4 h in a ball mill and then placed in the ZrO_2 crucible that was heated up to 980 °C at a 100 °C/h rate in air. After 1 h at this temperature, a slow cooling process (3 °C/h) began until 880 °C was reached. At the end of this process, grown-up single crystals were extracted and oxygenated at 420 °C for 5 days in flowing atmospheric O_2 in order to achieve the superconductive orthorhombic structure. The temperatures were optimized for $YBa_2Cu_3O_{7-\delta}$ formation, as yttrium represents almost 60% molar of the natural mixture.

2.2. Characterization methods

The surface morphology of as-grown crystals was observed by SEM. Composition and impurities of an as-grown $REBa_2Cu_3O_{7-\delta}$

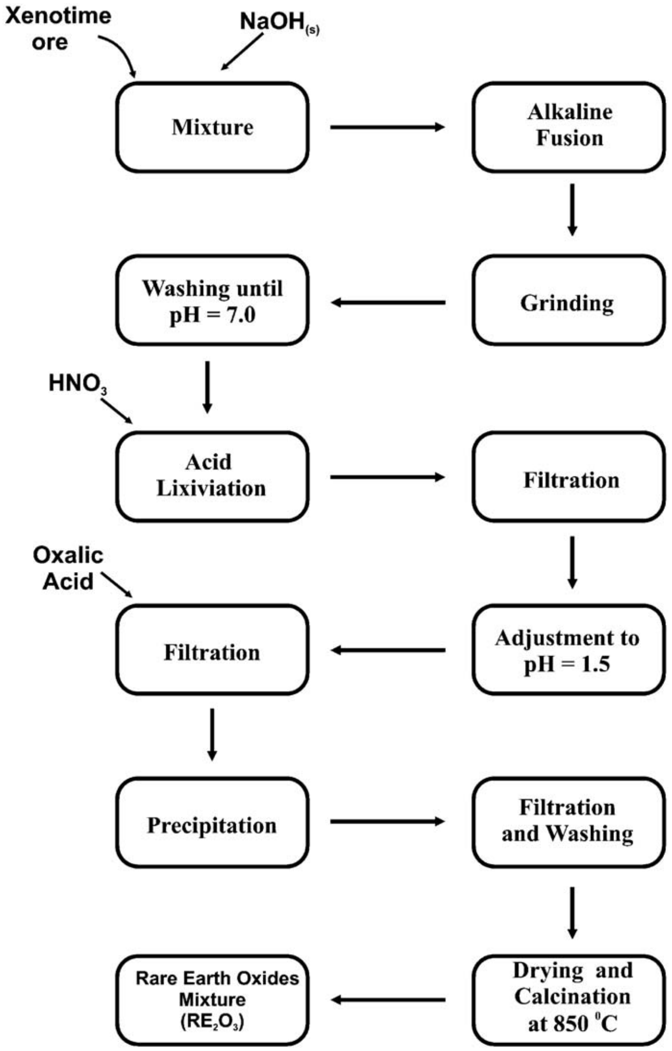

Fig. 1. Employed methodology to extract the rare-earth oxides Re_2O_3 starting from the xenotime ore.

Table 1
Three process steps to extract the mixed oxide Re_2O_3 starting from the xenotime ore.

Alkaline fusion step	
Temperature (°C)	700
$NaOH_{(s)}$/xenotime ratio (g/g)	1.3/1
Fusion time (h)	4
Acid lixiviation step	
Liquid/solid ratio (mL/g)	5/1
HNO_3 1:1 excess (%)	10
Temperature (°C)	90
Lixiviation time (min)	10
Stirring (rpm)	100
Oxalic precipitation step	
Concentration of Y^{3+}+RE Solution (g/L)	5
Concentration of oxalic acid (g/L)	80
pH of Y^{3+}+RE solution	1
Precipitation temperature (°C)	25
Agitation rate (rpm)	200
Stirring time after precipitation finishing (min)	1
Resting temperature (°C)	5
Resting time (h)	24