Effect of Rubidium Substitution on the Physical and Superconducting Properties of Textured High- T_c BSCCO Samples

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Abstract

In this research, the effects of rubidium (Rb) substitution on the microstructural, physical, and superconducting properties of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Rb}_x\text{Cu}_2\text{O}_{8+y}$ with $x = 0.0, 0.025, 0.05, 0.075, 0.10,$ and 0.125 superconductor have, in detail, been studied. For this purpose, samples were prepared through the classical solid state reaction route, followed by directional grown using the laser floating zone technique and annealing. XRD measurements showed that all samples are composed of Bi-2212 phase as the dominant one, together with less amount of secondary phases. The crystal symmetries of samples were determined as pseudo tetragonal. SEM-EDX confirmed that Bi-2212 phase is the major one, with minor amounts of $\text{Bi}_{2+x}(\text{Sr,Ca})_2\text{O}_{6+d}$, $(\text{Sr,Ca})\text{CuO}_2$, CuO_2 and CaO secondary phases. In magnetization versus temperature measurements, very sharp diamagnetic transition is observed. The critical onset temperatures, T_c , for all samples are obtained around 90 K. From M-H measurement, it has been found that all samples have very large loop areas. By using the data from M-H measurements in the Beanmodel, the intragranular critical field, J_c , has been determined. It has been found that the $x = 0.05\text{Rb}$ sample shows the highest superconducting properties and the largest J_c values ($2.2 \cdot 10^5 \text{ A/cm}^2$ at 10 K). Moreover, the maximum pinning force, $F_{P\max}$, at this temperature has also been obtained in $x = 0.05\text{Rb}$ sample ($8.5 \cdot 10^8 \text{ Oe A/cm}^2$).

Keywords: Bi-2212; Rubidium substitution; Magnetic properties; Laser floating zone technique

1 Introduction

The Bi-Sr-Ca-Cu-O, abbreviated as BSCCO, superconductors are promising materials for technical and industrial applications due to their excellent advantages, such as low oxygen sensitivity, absence of rare earths, high magnetic field-carrying capacity (H_c), high critical current density (J_c), and high critical temperature (T_c). This family has also some disadvantages which can limit their technological applications, such as weak links, high anisotropy, and small coherence length. The BSCCO family having the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ general formula, in which $n = 1, 2$, and 3 indicate the number of CuO_2 layers in the crystal matrix, describing the (2201), (2212), and (2223) superconducting phases, having temperatures of 20 K, 85 K, and 110 K, respectively [1–3]. Among them, the (2212) phase is known more stable high- T_c one in a wide range of processing temperatures. In addition, the critical temperature of this phase is not fixed and is affected by the elementary substitutions. For example, if bismuth and calcium contents are diminished revealing constant the oxygen content, T_c value significantly increases [4]. In order to better understand the microstructural, physical, and superconducting properties of BSCCO family, many experiments have been performed with the goals of improving its T_c and J_c , for technological applications [5–12].

As it is well known, BSCCO system is very anisotropic and, consequently, grain orientation plays a very important role on the J_c values. In order to obtain materials with highly oriented grains, leading to increased transport properties at 77 K, many strategies have been proposed. One of them is the laser floating zone (LFZ) method. By using this effective technique, grains in Bi-2212 system can be oriented [13–15]. This technique is characterized by the enormous thermal gradients obtained in the front of solidification, promoting the orientation of grains with their c-axis perpendicular to the growth direction [16]. As a result, the conducting ab-planes are parallel to the growth axis, maximizing the transport properties along the growth axis.

In addition, it has been reported that the superconducting properties of the BSCCO system are improved by alkaline metal substitutions, as Na and K [17,18], increasing the magnetic J_c in more than 25% when adequately processed. This effect is due to their + 1 valence state, which produces a variation in the charge carrier concentration when substituting Ca or Sr, as it is

well known that Sr and Ca can interchange their positions in the crystal structure in a limited amount. Moreover, their ionic radii, ranging between 73 and 181 pm, superpose with the Bi, Sr, Ca, and Cu ones [19–21]. Consequently, even if a limited solubility of Rb is expected when Ca or Sr is substituted, the fact that Rb can enter in the crystal structure can produce an internal pressure which can enhance superconducting properties, as demonstrated in other systems by applying external pressure [22]. In this work, the optimum amount of Rb substitution for Ca into LFZ-textured BSCCO system will be determined through the variation of structural, electrical, and magnetic properties of the doped systems as a function of Rb concentration.

2 Experimental Details

$\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Rb}_x\text{Cu}_2\text{O}_y$ samples, with $x = 0.0, 0.025, 0.05, 0.075, 0.1$, and 0.125 , have been prepared by using well known solid-state reaction, followed by directional grown using the LFZ technique. Appropriate amounts of Bi_2O_3 (Sigma-Aldrich, 99.9%), SrCO_3 (Sigma-Aldrich, + 98%), CaCO_3 (Sigma-Aldrich, + 99%), Rb_2O (Sigma-Aldrich, + 98%), and CuO (Sigma-Aldrich, 99%) commercial fine powders were well mixed by milling in an agate mortar and calcined twice at 750 and 800 °C for 12 h in order to decompose the alkaline-earth carbonates. It should be emphasized that this two-step calcination process is very important for materials processed using the LFZ technique. If materials contain the carbonates, they decompose inside the molten zone and create some bubbles that, in one side, can be included in the textured materials as porosity and, on the other side, create liquid currents destabilizing the crystallization front. This last effect leads to grain misorientations and parasitic grain growth. After calcination procedure, the powders were isostatically pressed under 200 MPa in a form of cylindrical pellets with diameters between 2 and 3 mm. The as-pressed ceramics were textured through directional solidification in a LFZ installation [23]. Cylindrical as-grown materials produced at a growth rate of 30 mm/h were very homogeneous in dimensions (~ 2 mm diameter and 120 mm length). On the other hand, the Bi-2212 ceramic samples present incongruent melting, producing different secondary phases as Bi-2201, CaCuO_2 , or $(\text{Sr,Ca})\text{CuO}_2$ [24,25]. As a consequence, as-grown samples must be subjected to an annealing treatment process to produce the Bi-2212 phase

[26], consisting of two steps: 60 h at 860 °C, followed by 12 h at 800 °C and, finally, quenched in air to room temperature.

In order to identify the phases, powder X-ray diffraction patterns of annealed materials were recorded at room temperature using Rigaku Miniflex diffractometer system, working with CuK α radiation and a constant scan rate between $2\theta = 10^\circ$ and 40° . From these data, crystal lattice parameters were calculated with an uncertainty of ± 0.001 . SEM micrographs were taken using a LEO Evo-40 VPX scanning electron microscope fitted with an energy dispersive spectrometry (EDS) analysis system. Magnetic measurements were carried out in a 7304 model Vibrating Sample Magnetometer of Lake Shore and the data will be used to determine critical current density (J_C) and pinning force (F_p).

3 Results and Discussion

Powder X-ray diffraction patterns of different Rb-substituted samples are exhibited in Fig. 1. Major peaks correspond to the Bi-2212 phase, indicating that the thermal annealing has been effective to produce this phase. However, still a very small amount of secondary phases remain after the treatment, identified as Bi-2201 (indicated by circle) and CaCuO $_2$ (indicated by asterisk). These patterns show that crystal symmetry is pseudo tetragonal in all cases. Moreover, lattice parameters calculated by using the least squares method are practically the same for all samples (see Table 1), indicating that Rb substitution is very limited. The average crystallite thickness (L_{hkl}) has been determined using the Debye Scherrer equation shown in Eq. 1 [27].

$$L_{hkl} = K \lambda / \beta \cos \theta \quad (1)$$

where the K constant is 0.9, λ is the wavelength, β is the full width at half maximum intensity for the corresponding peak, and θ is the diffraction angle of the peak. As it can be seen in Table 1, the maximum crystallite thickness was found as 514 Å for 0.05Rb-substituted sample, showing that relatively small Rb substitution enhances grain growth. This effect can be associated with the formation of liquid in the LFZ process at lower temperatures when the amount of Rb is increased, as it melts with partial decomposition at around 400 °C [28]. A slight reduction of melting temperature is beneficial, as it decreases the radial gradient during the LFZ process, increasing grain orientation. Consequently, grains are not interfering each other when growing, allowing a larger grain

growth. On the other hand, when the amount of Rb is larger, the melting temperature is too low to maintain the (Ca,Sr)-Cu-O phase in solution, with high melting point, which is known to be the primary solidification phase [16]. Precipitation of these phases, due to the low molten material temperature, produced the formation of many crystallization centers in the liquid, which limit the grain growth.

Figure 2 shows the internal morphology of samples performed in longitudinal polished sections. As it can be seen in the micrographs, a mixture of different contrasts can be observed in all samples. EDS analysis of these contrasts has allowed each of them to associate with different phases: major gray contrast (indicated by no. 1) in all micrographs corresponds to the Bi-2212 superconducting phase, while white (no. 2) and dark gray (no. 3) have been associated with $\text{Bi}_{2+x}(\text{Sr,Ca})_2\text{O}_{6+\delta}$ (Cu-free phase) and $(\text{Sr,Ca})\text{CuO}_2$ (Bi-free phase) secondary phases, respectively. Additionally, a small amount of secondary phases indicated by nos. 4 and 5 appearing in the SEM micrographs of 0.05Rb- and 0.075Rbdoped samples correspond to CuO_2 and CaO , respectively. These last phases are in a very small amount and probably are present in higher Rb-substituted samples even if they have not been found in these micrographs.

Magnetization, M , versus temperature is exhibited in Fig. 3 for all samples. It should be emphasized here that all data were collected by cooling the sample in zero field (ZFC) down to 10 K, applying 50-Oe magnetic field, and then warming up to 100 K. As it can be seen in the M - T graph, the diamagnetic transition for all samples is very sharp and the critical onset temperatures, T_C , corresponding to the diamagnetic transition are around 92 K in all cases (see Table 1), not drastically affected by Rb substitution. The diamagnetic behavior can be associated with the granular nature of these samples, and it can be deduced that the grain boundaries present strong connectivity and, therefore, the magnetic fields cannot easily penetrate into the samples.

The M - H loops measured at 10 K, between ± 1 T applied external fields, and determined under ZFC mode, are presented in Fig. 4. All samples exhibit very wide hysteresis and the area of these hysteresis loops increases up to $x = 0.05\text{Rb}$, tending to decrease for higher Rb substitution. M - H data were used in

Eq. 2, proposed for cylindrical samples, in the well known critical Bean model [29].

$$J_c = 30 \frac{\Delta M}{d} \quad (2)$$

where $\Delta M = M^+ - M^-$ is measured in electromagnetic units per cubic centimeter, and d is the sample thickness. With this equation, the intragranular critical current density values, J_c , in ampères per square centimeter were calculated for all samples, and the results obtained at 10 K are presented in Fig. 5. These data clearly show that the $x = 0.05\text{Rb}$ sample possesses higher superconducting properties and has the largest J_c values ($2.2 \cdot 10^5 \text{ A/cm}^2$ at low fields), very close to that determined in the 0.025 Rb samples, which explicitly reduce when the magnetic field and the amount of Rb are raised. In this stage, it is possible to argue that the different type of secondary phases embedded in the crystal structure can reveal such a kind of results. According to the flux-pinning mechanism, those non-superconducting phases behave like very effective flux-pinning centers. Depending on the sizes of those secondary phases, the applied fields may diffuse into the sample, causing a decline in the critical current, J_c , values. The maximum J_c value obtained for the $x = 0.05\text{Rb}$ sample is almost twice larger than that given in literature for Na ($1.33 \cdot 10^5 \text{ A/cm}^2$) [14], and very similar to that obtained in Cs substituted materials ($2.5 \cdot 10^5 \text{ A/cm}^2$) [30]. This effect may be associated with the different cation sizes affecting the oxygen quantity and the number of charge carrier. In addition, in comparison with Na-doped materials, a possible slight charge carrier concentration enhancement can be arisen by the lower effective attraction of the external electrons in the Rb^+ cations than in smaller alkaline ones. It is well known that the flux-pinning force, F_P , is directly affected by the intrinsic properties of pinning centers as size, capability, stability, density, etc. In order to determine mechanism of vortex pinning, it will be useful to analyze the pinning forces by applying Eq. 3.

$$F_P = J_c \times \mu_0 H \quad (3)$$

where J_c is the critical current density calculated above, H is the applied field, and μ_0 is the permeability of vacuum ($4\pi \cdot 10^{-7} \text{ Wb/A m}$). The obtained results at 10 K are plotted in Fig. 6 for all samples. As can be observed, F_P values systematically go up for low fields and then sharply drop down above 8000 Oe,

for all samples. The F_{Pmax} values are presented in Table 1, where it can be observed that 0.05Rb samples reach the highest values ($8.5 \cdot 10^8$ Oe A/cm²). Moreover, the values determined in these samples are higher than the values of pure ones in the whole measured range.

In order to deeply understand the nature of pinning mechanism in the 0.05Rb sample, the experimental data have been used in the Dew-Hughes model [31]. The reduced pinning force F_P/F_{Pmax} with respect to reduced field $b = H/H_{max}$ is plotted in Fig. 7 and fitted using equation $f_P(F_P/F_{Pmax}) = b^p(1-b)^q$. Three theoretical models [32] are proposed for high- T_C bulk superconductors in order to determine the pinning mechanism, presented below as:

$$f_P(b) = 25 - 16b^{-1/2} (1-b/5)^2; \text{ normal surface pinning (4)}$$

$$f_P(b) = 9/4b(1-b/3)^2; \text{ normal point pinning (5)}$$

$$f_P(b) = 3b^2(1-2b/3); \Delta k \text{ pinning (6)}$$

As it can be observed in Fig. 7, the experimental results for this sample are well-matched with the normal point pinning in the limited scale.

4 Conclusions

In summary, an intensive research of structural, physical, and magnetic properties of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Rb}_x\text{Cu}_2\text{O}_{8+y}$ (where $x = 0.0, 0.025, 0.05, 0.075, 0.10$, and 0.125) textured materials has been performed. X-ray diffraction patterns indicate that all samples have nearly single Bi-2212 phase. SEM micrographs and EDX results have shown that Bi-2212 was major phase with minor amounts of $\text{Bi}_{2+x}(\text{Sr,Ca})_2\text{O}_{6+\delta}$, $(\text{Sr,Ca})\text{CuO}_2$, CuO_2 , and CaO secondary phases.

Very sharp diamagnetic transitions were observed when measuring magnetization versus temperature, typical for granular materials. The critical onset temperatures were nearly constant for all samples, independently of Rb content (about 92 K). M-H measurements have shown that the hysteresis loops are very large. In spite of the very close values determined in 0.025 and 0.05Rb-substituted samples, J_C of 0.05Rb sample is the highest one, around $2.2 \cdot 10^5$ A/cm². Moreover, the maximum pinning force has also been determined in 0.05Rb sample, $8.5 \cdot 10^8$ Oe A/cm² at 10 K, which is associated with normal point pinning nature.

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Table 1. T_c values deduced from the dc M-T measurement data, unit cell parameters, crystal size, maximum pinning force and critical current density of samples.

<i>Concent. x</i>	<i>T_c (K)</i>	<i>Unit-cell parameter a=b (Å)</i>	<i>Unit-cell parameter c (Å)</i>	<i>Cyrstal size L_{hkl} (Å)</i>	<i>F_{pmax} at 10 K (x10⁸ Oe*A/cm²)</i>	<i>Jc (x10⁴ A/ cm²)</i>
x=0	92.0	5.41	30.66	451	7.8	16.6
x=0.025	91.8	5.42	30.69	485	8.2	21.2
x=0.05	92.1	5.42	30.74	514	8.5	21.3
x=0.075	92.2	5.41	30.70	477	7.4	18.6
x=0.1	92.1	5.41	30.67	428	6.4	16.7
x=0.125	91.2	5.40	30.64	402	4.7	11.9

Figure captions

Figure 1. XRD patterns of samples. Peaks corresponding to the Bi-2212, Bi-2201, and CaCuO₂ phases are indicated by (*hkl*), **o**, and *, respectively.

Figure 2. SEM micrographs of the Bi₂Sr₂Ca_{1-x}Rb_xCu₂O_y samples with x = **a)** 0.0, **b)** 0.025, **c)** 0.05, **d)** 0.075 **e)** 0.10 and **f)** 0.125.

Figure 3. Magnetization against temperature, for the different Rb-content

Figure 4. *M-H* loops for all samples measured at 10 K.

Figure 5. Calculated critical current densities, *J_c*, of the samples, as a function of the applied magnetic field, at 10K.

Figure 6. Pinning Force versus applied field for samples, at 10K.

Figure 7. Reduced Pinning Force versus reduced applied field, for x=0.05Rb sample, at 10 K.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7