Thick REBaCuO Films for Power Applications Planted on Silver Tapes

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Abstract. We report on a novel technique of growing highly c-axis oriented ErBa$_2$Cu$_3$O$_y$ (Er-123) thick films on commercial silver substrates, starting from Er$_2$BaO$_4$, BaCuO$_2$, and CuO powders mixed in an Er-rich Er-123 ratio. Thick films are prepared by the screen-printing technique, being then processed in Ar-1% O$_2$ atmosphere. Using a three-step annealing, we obtain good quality films, with $T_c$ (onset) 92 K. From x-ray diffraction (XRD) patterns, mainly the (0 0 l) reflections from the Er-123 films are observed. Formation of large flat grains, more than 100 µm in size, was observed by scanning electron microscope. The critical current density ($J_c$) value at 77 K and 0 T, estimated by magnetization measurements, is 32 kA/cm$^2$. The present results indicate that the large-area superconducting thick films produced by the novel technique within a short processing time, possess good electromagnetic properties. As the technology is relatively cheap, the films are appropriate for commercial applications.

1. Introduction
Major part of the emphasis in the field of high-$T_c$ superconductor technology is now oriented towards development of high quality, low cost, and high performance superconducting tapes for production of power cables operating at 77 K [1]. After the Bi-based silver-sheath tapes and cables, the RE-Ba$_2$Cu$_3$O$_y$ (RE=rare earth) coated conductors “CC” represent the second generation of superconducting wires, considered at present as the most perspective ones [2]. Besides the basic requirement of the lowest possible production cost the major problem is a precise alignment and connectivity of grains in the typically polycrystalline thin films. This point receives an increasing importance with increasing film thickness required for power applications. While in thin films biaxial texturing helps to increase grain size and connectivity, the affectivity of biaxial texturing drops with increasing layer thickness. Up to date, the maximum thickness, above which the critical current dramatically drops, is around 1.5 micrometers. Production of thicker layers by traditional techniques is mostly ineffective, moreover time-consuming. To overcome the present problems, we introduced a simple and cheap process, very useful for commercial applications.

It was recently found that good quality melt-processed RE-Ba$_2$Cu$_3$O$_y$ bulks could be produced using RE$_2$BaO$_4$, BaCuO$_2$, and CuO as a starting mixture [3]. In this process, the Ba-Cu-O melts around 840°C, which is crucial for obtaining highly dense large-size bulks more than 14 cm in diameter. On the other hand, recent quench experiments clarified that RE-123 phase could develop fairly well bellow melting temperature of silver, 961°C [4]. Development of a two-step heating process and the processing condition control led finally to production of good quality Er-123 thick films on
commercial silver substrates [5]. However, the scanning electron microscopy (SEM) with the electron probe micro-beam analysis (EPMA) revealed formation of BaCuO$_2$ precipitates in the final 123 films. It is well known that RE-rich admixture can help to control the transformation of liquid phases into the 123 phase [6], resulting thus in homogeneity and quality improvement of the 123 films. Although, one can get also only Cu and 211 rich phases in the final composition. Furthermore, the lower melting temperature of the material gives more space for working with the silver substrate. Therefore, to improve quality of the newly developed Er-123 films, the films were prepared with Er-rich Er-123 ratios and processed in Ar-1% O$_2$ atmosphere. In this paper, we report on using the Er$_2$BaO$_4$ and liquid phases as a starting material with Er-rich admixture for producing thick films with high $J_c$ at 77 K in a shorter time.

2. Experimental

High purity commercial powders of Er$_2$BaO$_4$, BaCuO$_2$, and CuO were mixed in a nominal composition of Er$_{1-x}$Ba$_2$Cu$_3$O$_y$ (x = 0, 0.05, 0.1, 0.2, and 0.3) and ball milled in acetone. The ball-milling process was carried out for 4 hours, in order to reduce particle size to < 100 nm. These powders were air-dried, then vacuum dried at 200°C for 6 hours, and finally pre-treated in pure oxygen at 500°C for 24 hours. Then 35mol% of ErBa$_2$Cu$_3$O$_y$ powder made by solid-state reaction was added to the pre-treated ball-milled powders to improve the density and shrinkage of the final thick films. A mixture of alpha-terpineol and 2-ethyl acetate was used as a solvent to which the powder mixture was added and grinded several hours to form a highly dense paste. A thick film was prepared by spreading the paste on a commercial silver substrate (0.2 mm thick) by means of a screen-printing technique through a 165-mesh screen. The thermal stability of these samples was analyzed by differential thermal analysis (DTA) in 1% O$_2$ + Ar atmosphere. DTA experiments were carried out in Pt cups with a MAC SCIENCE TG-DTA 2000S with a gas flow rate of 50 ml/min and heating rate of 5°C/min. The phase transition temperature was determined as the onset temperature in the DTA peak in the final heating process. For the film growth, the covered silver substrates were placed into tube furnaces and heated at various temperatures in Ar-1% O$_2$ atmosphere. The film was heated up within 3 hours to a maximum temperature between 920 and 935°C and held there for 10 minutes. Then it was rapidly cooled down to 880°C and held there for 1 hours and subsequently held at 875°C for 2 hours. Finally, the samples were slowly cooled to room temperature within 18 hours.

3. Results and discussion

3.1.1 Differential Thermal Analysis (DTA)

To determine the exact temperature for processing the thick films on silver substrates, a 100 nm sized Er-rich powder mixture based on Er-210, BaCuO$_2$, CuO was studied by the differential thermal
analysis (DTA) in Ar-1% O₂ atmosphere. The results are presented in Fig. 1. One can see two endothermic peaks on the DTA curves, at 810 to 845 (P1) and at 930 to 937°C (P2). The higher and

Figure 1. DTA curves in 1% O₂ + Ar for Er₁₊ₓBa₂Cu₃O₇ with x = 0.05, 0.10, 0.2, and 0.3.

Figure 2. X-ray diffraction patterns of Er₁₊ₓBa₂Cu₃O₇ films grown on commercial silver substrates in Ar-1% O₂ atmosphere. Note that only the (0 0 l) reflections from the films were observed.
the lower peaks indicate the peritectic decomposition of Er-123 phase and the melting of unreacted Ba-Cu-O, respectively. Both temperatures decrease with increasing Er content in Er-123 system. The melting temperature of is well below silver melting temperature, which enabled us to prepare thick Er-123 films.

3.1.2 X-ray diffraction
Figure 2 shows a typical X-ray diffraction patterns of the Er_{1-x}Ba_2Cu_3O_y films, with x ranging between 0.05 and 0.30, grown on commercial Ag substrates at 930°C in Ar-1% O_2 atmosphere. An examination of Fig. 2 reveals that the prominent peaks can be indexed to the (0 0 l) reflections of Er-123 phase. The intensity of the (0 0 l) reflections increases with increasing content of Er in the Er-123 system. On the other hand, samples with x = 0.2 and 0.3 show a weak ErBaCO (200) peak, demonstrating presence of small amounts of a-axis oriented grains. We also tried to grow films above and below 930°C, however found 930°C to be the optimum temperature for a good quality thin films with a minimum content of secondary and liquid phases. These results indicate that c-axis oriented Er-123 thick films can be grown on commercial silver substrates using as the starting material combination of Er-210 and liquid phases.

3.1.3 Microstructure analysis
The SEM micrograph in Figure 3 shows the top surface of Er_{1-x}Ba_2Cu_3O_y thick film processed in Ar-1% O_2 atmosphere on a commercial silver substrate. It is interesting to note that (i) all the samples show formation of very large flat Er-123 grains, more than 100 µm in size, (ii) the grains are closely connected one to the other, (iii) the amount of liquid phase (some of it indicated by L) decreases with increasing Er content in the Er-123 system, up to x = 0.2, and (iv) for x>0.2 the liquid and 211 phases appear again in the Er-123 matrix. The microstructure analysis illustrates nicely that highly oriented large-size plate-like Er-123 grains can be produced on commercial silver substrate, similarly as the grains in the Bi-2212 system.

**Figure 3.** Scanning electron micrographs of Er_{1-x}Ba_2Cu_3O_y films grown on commercial silver substrates in Ar-1% O_2 atmosphere. (a) x = 0.05, (b) x = 0.10, (c) x= 0.20, and (d) x= 0.30. Note the large plate-like Er-123 grain formation.
3.1.4 Magnetization measurements

Figure 4 (a) displays the temperature dependence of dc magnetic moment of the Er-rich Er-123 thick films measured at magnetic field of 1 mT. To disregard influence of different film thicknesses, we plotted the curves of magnetization, in emu/cm$^3$ units, instead of magnetic moment in emu. All the samples showed a similar $T_c$ (onset) around 92 K. Magnetization increased with increasing Er content up to $x=0.2$ and then decreased again. This can be explained by a decreasing liquid phase content in the final films, facilitated by the increasing Er excess up to the optimum content $x=0.2$, and the associated increase of the volume ratio of the superconducting and non-superconducting phases. For Er contents $x > 0.3$, magnetization of the samples decreased as a consequence of the decrease of volume fraction of Er-123 phase. The SEM micrographs supported this scenario. The critical current density, $J_c$, calculated from M-H curves at 77 K using the extended Bean model formula is shown in Figure 4 (b). The remanent state $J_c$ systematically increased with increasing Er content up to $x=0.2$, then decreased. The maximum critical current density in the remanent state of 32 kA/cm$^2$ at the self-field was recorded for $x = 0.2$.

![Figure 4(a)](image)

**Figure 4(a).** Temperature dependence of the magnetization for Er$_{1+x}$Ba$_2$Cu$_3$O$_y$ films grown on commercial silver substrates in Ar-1% O$_2$ atmosphere.

![Figure 4(b)](image)

**Figure 4(b).** $J_c(B)$ plots for Er$_{1+x}$Ba$_2$Cu$_3$O$_y$ films at 77 K and $B\parallel c$-axis. Note the relatively high critical current density of 32 kA/cm$^2$ at the self-field was recorded for $x = 0.2$.

As a whole, the results presented in this paper indicate that under ideal conditions, good quality large-flat-grain Er-rich Er-123 thick films can be produced with c-axis orientation on commercial silver substrates. With an optimized flux pinning and controlled grain size, the films can become the best candidate for silver sheath technology, which could be used at the liquid nitrogen temperature for high-temperature power applications.

4. Conclusions

We have developed technology for production of Er-rich Er-123 superconducting thick films on commercial Ag substrates using a mixture of Er$_2$BaO$_4$, BaCuO$_2$, and CuO as a starting material. The predominated c-axis orientation of the films was confirmed by XRD analysis. SEM microstructure analysis showed very large plate-like Er-123 grains. Magnetization and SEM by EPMA analyses
imply that the volume fraction of Er-123 phase increases with increasing Er content up to the optimum value $x=0.2$. The remnant $J_c$ of 32 kA/cm$^2$ was achieved at 77K for $B||c$ axis. The DTA analysis showed two endothermic peaks that shifted down with increasing Er content. Use of the mixture of Er$_2$BaO$_4$, BaCuO$_2$, and CuO in the Er-rich Er-123 ratio as a starting material brings several advantages. Ba-Cu-O melts at around 840°C, which is crucial for obtaining highly dense and $c$-axis oriented films on commercial Ag substrates. The excess of Er helps to minimize the liquid phase and Er-211 phase formation in the Er-123 films. This technology enables preparation of large-area superconducting thick films within a reasonably short processing time, relatively cheap and thus appropriate for commercial applications. Eventually, this process can transform into a silver-sheath technology for high field and high temperature applications.

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