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Superconductivity behaviour of screen-printed $LnBa_2Cu_3O_7$ ($Ln = Eu$, Y) films

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Abstract. Thick films of the high T_c superconducting oxides, $LnBa_2Cu_3O_7$, Ln = Eu, Y, have been fabricated by screen printing on alumina and $SrTiO_3$ substrates. Conditions for optimum superconductivity behaviour of the films have been established. T_c^{onset} varies from 90–94 K for all the films but zero resistance was observed only in a few cases.

Keywords. High temperature superconductors; screen printed films; LnBaCuO

1. Introduction

Rare earth and yttrium-barium-copper-oxides of the formula $LnBa_2Cu_3O_7$, exhibit superconductivity at ~90 K and have been extensively investigated in the last one year in the form of polycrystalline pellets, single crystals and thin and thick films (Cava *et al* 1987; Rao *et al* 1987; Rao 1988; Proceedings 1987). Screen printing affords an easy and valuable technique for obtaining thick films of $LnBa_2Cu_3O_7$ materials on suitable substrates for practical applications. However, optimization of the coating parameters, film adherence and heat treatment is always necessary to obtain good films. Earlier, Koinuma *et al* (1987) reported results on screen printed films of Yb-Ba-Cu-O oxide, which was multiphasic but exhibited high T_c. Presently we report on the fabrication and testing of superconductivity behaviour of the screen-printed films of $LnBa_2Cu_3O_7$, Ln = Eu and Y on Al_2O_3 and $SrTiO_3$ substrates. Our preliminary results have been presented elsewhere (Varadaraju *et al* 1987).

2. Experimental

Polycrystalline powders of the pure $LnBa_2Cu_3O_7$, Ln = Eu and Y have been synthesized (10–25 g batches) by the high temperature solid state reaction (950°C) of the constituent high purity oxides/carbonate. Detailed optimized procedure has been described elsewhere (Subba Rao 1987). The essential step is the oxygen annealing at 600°C for 24 h and slow cooling to room temperature which ensures the high T_c orthorhombic 123 phase. Four-probe electrical resistivity on pressed and sintered pellets employing ultrasonically soldered indium contacts showed superconductivity with a zero resistance (T_c^{zero}) of 90 and 91 K respectively for Ln = Eu and Y. The $LnBa_2Cu_3O_7$ powder was sieved and particle size range 37–93 μm were used for screen printing.

Alumina (recrystallized Al_2O_3; 99·9%; 30–40 mm dia; 5–6 mm thick, Thermal Synd., UK) and strontium titanate ($SrTiO_3$ powder; 99·9% pure, Ventron, USA) have been used as substrates. Discs of $SrTiO_3$ (30–35 mm dia; 2–3 mm thick) were cold pressed with a binder and sintered in air at 1350°C for 5 h. The substrates were polished, cleaned and dried before use. The following parameters were used for screen printing: screen characteristics: silk, 180 mesh with standard aperture around 94 μm; carrier liquid: octyl alcohol; size of the coated film: 1·8 × 1·8 cm square; 100–200 μm thick (two wet coatings). The as-coated films were dried in an oven at 150°C for a few hours and heated in air at 950°C for periods ranging from 0·5 to 24 h. After optimization, subsequent annealing of the films was carried out in flowing oxygen gas at 600°C for periods ranging from 1 to 6 h.

X-ray diffraction (Phillips, CuK_α radiation) was used to characterize the $LnBa_2Cu_3O_7$ powder and screen-printed films. SEM (Cambridge Stereoscan 180 UK) and optical microscope (Leitz, W. Germany) were used at magnifications 50–2000 for checking the adherence and texture of the films. Four-probe d.c. resistivity measurements (with In-contacts) were made on the films in the temperature range 85–300 K for checking the superconductivity.

3. Results and discussion

A total of 20–30 films have been fabricated and tesfed in the present study. Good adherent films of $LnBa_2Cu_3O_7$, Ln = Eu and Y, have been obtained after sintering in air at 950°C for 6 h on both Al_2O_3 and $SrTiO_3$ substrates. These exhibited good superconductivity transitions after O_2 annealed at 600°C for 6 h. SEM photographs and electrical resistivity measurements indicated good texture and continuity of the film. X-ray diffraction indicated the desired orthorhombic 123 phase for Eu and Y (trace impurities of Y_2BaCuO_5 and CuO, for the latter).

Film adherence was not good at lower temperatures of heat treatment, whereas the room temperature resistivity ($\rho_{300\,K}$) of the films was higher for smaller times of heat treatment (at 950°C).

Treatment upto 24 h at 950°C did not significantly affect the adherence and $\rho_{300\,K}$ for Y and Eu compounds on both the Al_2O_3 and $SrTiO_3$ substrates. Temperatures above 1000°C (and longer times) for heat treatment are not advisable due to the possibility of substitution of Al or Ti (from substrates) at the copper site in $LnBa_2Cu_3O_7$ thereby producing deleterious effects.

Oxygen treatment of the 950°C sintered films of $LnBa_2Cu_3O_7$ at 600°C for periods ranging from 1 to 6 h has been found to be beneficial for optimum behaviour of the films, especially those on the $SrTiO_3$ substrate. The values of $\rho_{300\,K}$ varied from 0·05–2·0 Ω cm for all the films. The ρ-T behaviour showed clear onset of superconductivity characterized by significant departure from normal high temperature behaviour in all the films. The T_c^{onset} varied from 90 to 94 K (figures 1 and 2). However, zero resistance was achieved only in films of $YBa_2Cu_3O_7$ (on Al_2O_3 and $SrTiO_3$ substrates; T_c^{zero} = 85·5 K and 84 K respectively; figure 1). $EuBa_2Cu_3O_7$ films (on both the substrates) did not show zero resistance upto 85 K, the lower limit of our measurement. However, as can be seen from figure 2, T_c^{zero} will lie between 75 and 85 K in these films. It may be pointed out that in the present study T_c^{zero} values obtained on the screen printed films are lower than those obtained on bulk pellets. Similar observations were made in general by others in films coated using various techniques (Zhao *et al* 1987; Hammond *et al* 1987; Ogale *et al* 1987; Hong *et al* 1987; Koinuma *et al* 1987). The reasons for the above are not clear.

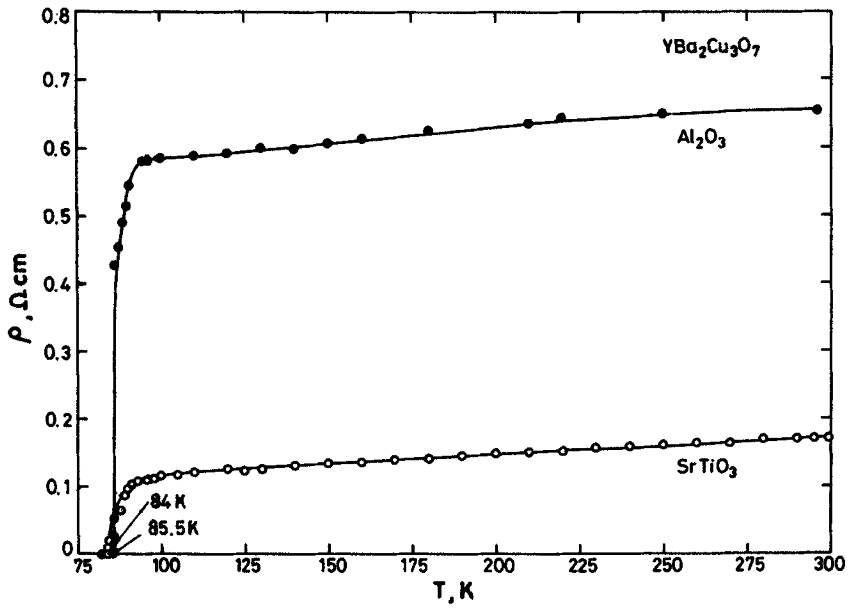

Figure 1. Resistivity vs temperature curves for $YBa_2Cu_3O_7$ screen printed films on Al_2O_3 and $SrTiO_3$ substrates (950°C, 6 h, air; 600°C, 6 h, O_2).

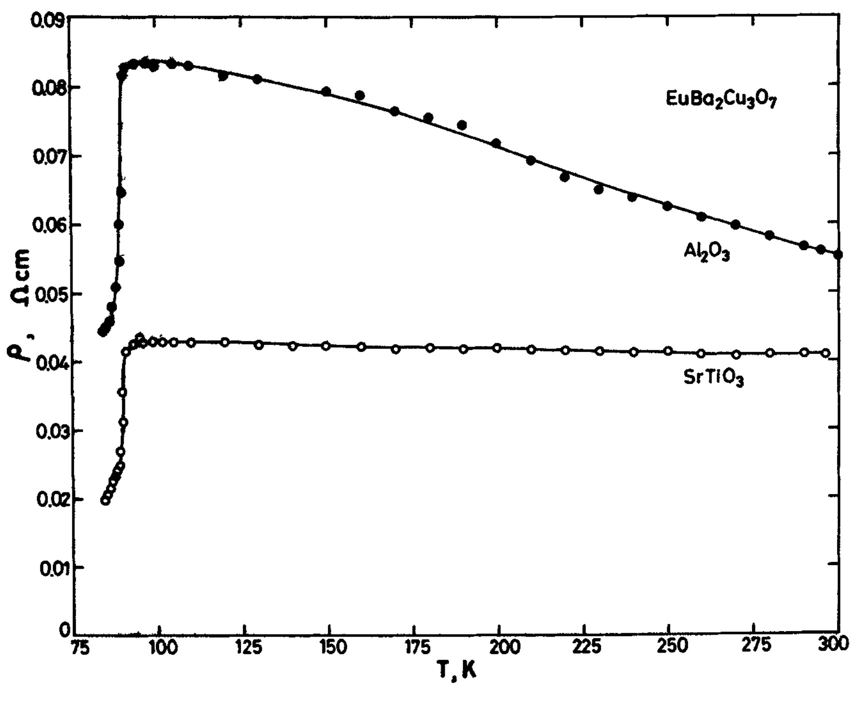

Figure 2. Resistivity vs temperature curves for $EuBa_2Cu_3O_7$ screen-printed films on Al_2O_3 and $SrTiO_3$ substrates (950° C, 6 h, air; 600° C, 6 h, O_2).

Preliminary studies have shown that the films are fairly stable towards exposure to air and moisture. However, long term stability is to be established and protective coatings can possibly be applied for increased stability.

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