

Growth of high T_c Bi–Sr–Ca–Cu–O thick films

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Abstract. Thick films of Bi–Sr–Ca–Cu–O were deposited on (100) MgO substrates by screen-printing technique with the starting composition 1112. To attain the superconducting state, the films were subjected to two-step heat-treatment. R–T and XRD have been studied for films annealed at different durations of the second step. Initially T_c ($R = 0$) increased from 77 to 103 K as the annealing duration was increased after which T_c decreased. Kinetics of the growth of high T_c phase is discussed in the light of our results.

Keywords. Superconducting thick films; high T_c phase; Bi–Sr–Ca–Cu–O film; screen printing.

1. Introduction

Bi–Sr–Ca–Cu–O system is known to exist in three phases. The tetragonal unit cell with orthorhombic distortion in the structure of these phases differs in the number of CuO_2 planes (n) in the Bi–Sr–Ca–Cu–O system. For $n = 1, 2$ and 3 the length of the c -axes are approximately 24.6, 30.7 and 37.1 Å respectively with T_c values of < 20, 85 and 110 K respectively (Tarascon *et al* 1988a). While low T_c phase (2212) is easy to obtain in single phase, the high T_c phase (2223) is always observed in multiphase mixtures. There have been several reports on attempts to obtain single-phase high T_c material starting with different compositions (Huang *et al* 1989; Shi *et al* 1989a; Tsuchiya *et al* 1989). However they always lead to multiphase growth. For understanding the growth of high T_c phase, a more systematic study is necessary. In this paper we report the growth of high T_c phase in Bi–Sr–Ca–Cu–O screen-printed thick films when the films were subjected to long annealing durations.

2. Experimental

The powders for screen-printing technique were prepared by solid-state reaction between Bi_2O_3 , SrCO_3 , CaCO_3 and CuO taking 1112 composition. The stoichiometric mixture was thoroughly grounded and doubly calcined at 820°C for 12 h and then slowly cooled to room temperature. The resultant compound was pulverized to fine powders and passed through 350 mesh screen. The powders were subsequently converted into a paste by thoroughly mixing in cyclohexanol for screen printing of the films on (100) MgO substrates. The films were first annealed at 880°C for 45 min followed by slow cooling to 864°C. In the second step the films were retained at this temperature for different durations up to 104 h and later furnace-cooled. R–T was measured using the standard four-probe technique. X-ray diffraction patterns of the films were recorded using CuK_α radiation.

3. Results and discussion

Figure 1 shows R–T curves for films 1 to 4 and table 1 summarizes the heat-treatment conditions. T_c (offset) values were found to increase from 77 K to 103 K as the duration of the second-step annealing was increased to 80 h. However when the duration of this heat-treatment was kept to 104 h, T_c (offset) was found to decrease. R–T curves reported in figure 1 are measured for $10\ \mu\text{A}$ current. T_c (offset) decreased when the current through the film was increased. For film 3, T_c (offset) was 103 K, 100 K and 99 K for currents $10\ \mu\text{A}$, $100\ \mu\text{A}$ and $1\ \text{mA}$ respectively.

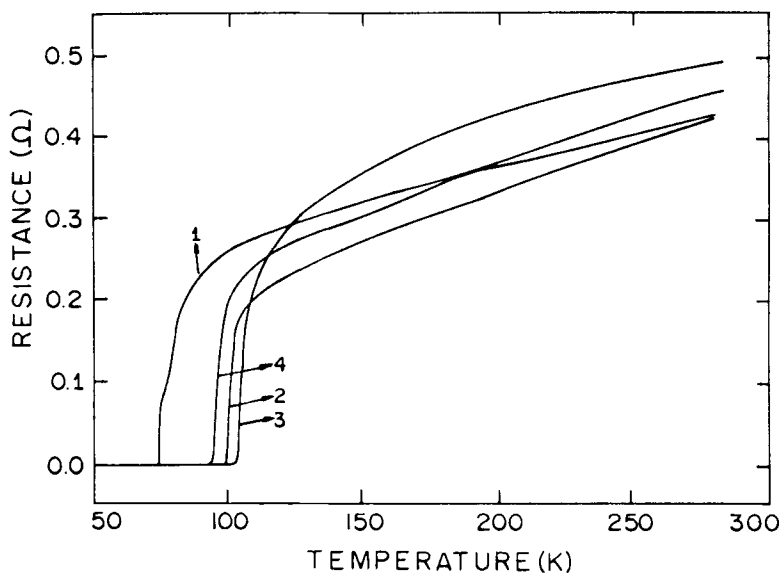


Figure 1. R–T curves for Bi–Sr–Ca–Cu–O screen-printed films 1–4 (for annealing conditions see table 1).

Table 1. T_c variation of Bi–Sr–Ca–Cu–O screen printed films with different annealing treatments.

Film No.	Annealing conditions	T_c (onset)	T_c (offset)(R = 0)
1.	1) 880°C for 45 min 2) no treatment at 864°C, furnace-cooled to room temperature	85 K	77 K
2.	1) 880°C for 45 min 2) 864°C for 35 h, furnace-cooled to room temperature	103 K	98 K
3.	1) 880°C for 45 min 2) 864°C for 80 h, furnace-cooled to room temperature	110 K	103 K
4.	1) 880°C for 45 min 2) 864°C for 104 h, furnace-cooled to room temperature	100 K	94.5 K

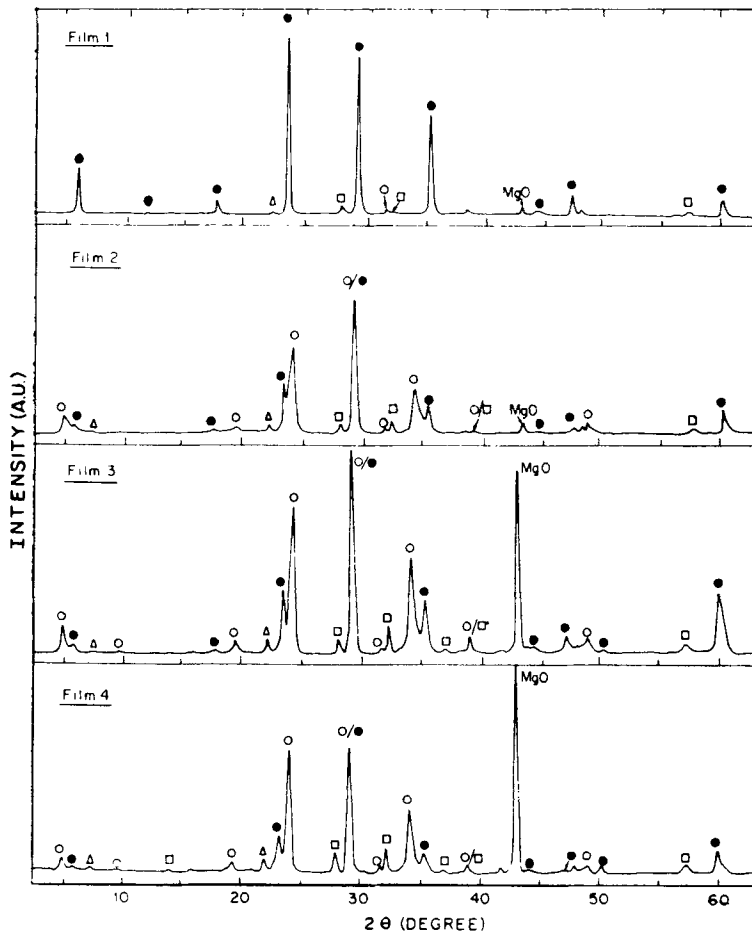


Figure 2. XRD patterns for Bi-Sr-Ca-Cu-O screen-printed film 1-4 (for annealing conditions see table 1).

Figure 2 shows X-ray diffraction patterns of films numbered 1 to 4. The peaks are indexed in the usual way (Tarascon *et al* 1988a; Hazen *et al* 1988; Shi *et al* 1989b). Film 1, for which the duration of the second step was zero hour, contains predominantly low T_c 2212 phase with mostly (001) planes. Small peaks corresponding to Ca_2CuO_3 and $(\text{Sr,Ca})_3\text{Cu}_5\text{O}_y$ were also observed. When the duration of the second step was increased to 35 h (film 2), X-ray diffraction shows the growth of peaks corresponding to high T_c phase. Here again it is to be noted that growth of (001) planes of high T_c phase is more preferred. In the X-ray diffraction pattern of film 2, a small peak is also present at 7.3° which corresponds to the lowest T_c (2201) phase. This indicates that with longer annealing duration a small amount of lowest T_c phase also grows. As the duration of the second step was increased to 80 h, intensity of the peaks corresponding to high T_c phase increases. The ratio of the peaks of high T_c and low T_c phases corresponding to (002) plane was found to increase in comparison to film 2, when the duration of the heat-treatment was only 35 h. Some new peaks of 2212 phase also appear but they did not belong to (001) reflection planes. When the duration of the heat-treatment was increased to 104 h, intensity of the high T_c phase peak

corresponding to (002) plane decreased and there is a slight growth with lowest T_c phase peak for the (002) plane at (7.3°).

Electrical and X-ray diffraction studies of the thick Bi–Sr–Ca–Cu–O films suggest that the high T_c phase does not nucleate during the beginning of annealing. First the 2212 phase and impurity of Ca_2CuO_3 are formed and later the fraction of the high T_c phase increases gradually as the reaction time was increased. From films 1 to 3, as the duration of the second-step heat treatment is increased, the peaks corresponding to the high T_c phase grows more and T_c (offset) also shows an increase. The enhanced formation of the high T_c phase in the system is accompanied by decrease of the amount of low T_c phase. This suggests that the low T_c phase transforms into high T_c phase. The formation of 110 K phase involves adding of one more Ca–O and Cu–O planes in the 85 K phase unit cell structure through the syntactic intergrowth.

The 85 K phase has smaller unit cell, c -axis is 30.7 Å thus having relatively lower free energy compared with the 110 K phase ($c = 37.1$ Å). This is the main reason for the observed results that the 85 K phase crystallizes first. At 864°C, the temperature of the second-step high T_c phase is not thermodynamically and chemically stable (Shi *et al* 1989a). Therefore its decomposition into low T_c and lowest T_c phases occurs. In the XRD of film 2, for which the duration of second step was 35 h, a small peak of lowest T_c phase was observed and after 80 h annealing duration, the lowest T_c phase peak and some other peaks corresponding to the low T_c phase which did not belong to (001) planes were observed. After 104 h of heat-treatment the decrease in the peak height of the high T_c phase was found to accompany with increase in the peak height of the lowest T_c phase peak. These observations also support the view that the decomposition of high T_c phase starts even in the beginning when the rate of formation of high T_c phase was higher than the decomposition rate. After 80 h of annealing treatment in the present case, the decomposition rate is annulled by the formation rate. This is reflected in both T_c (offset) and XRD peaks corresponding to the high T_c phase of film 4. This deterioration of high T_c phase after a certain limit of heat treatment has been observed by other workers also (Shi *et al* 1989b). Variation T_c (offset) with the measuring current suggests that the high T_c phase dispersed in the film is filamentary in nature. Our observation agrees with the model proposed by Tarascon *et al* (1988b) and Shi *et al* (1989b).

4. Conclusion

Growth of high T_c phase in Bi–Sr–Ca–Cu–O screen-printed thick film is studied. Single high T_c phase in thick films cannot be obtained with the starting composition of 1112, the reason being extremely slow growth rate of high T_c phase and its inherent thermodynamic and chemical instability near the annealing temperature (864°C).

References

- Hazen R M *et al* 1988 *Phys. Rev. Lett.* **60** 1174
- Huang H S *et al* 1989 *IEEE Trans. Magn.* **MAG-25** 2017
- Shi D, Tang M, Boley M S, Hash M, Vandervoort K, Claus H and Lwin Y N 1989a *Phys. Rev.* **B40** 2247
- Shi D, Tang M, Vandervoort K and Claus H 1989b *Phys. Rev.* **B39** 9091
- Tarascon J M *et al* 1988a *Phys. Rev.* **B38** 8885
- Tarascon J M, LePage Y, Greene L H, Bagley B G, Barboux P, Hwang D M, Hull G W, McKinnon W R and Giroud M 1988b *Phys. Rev.* **B38** 2504
- Tsuchiya J, Endo H, Kijima N, Sumiyama A, Mizuno M and Oguri Y 1989 *Jpn J. Appl. Phys.* **28** L1918