

A Diffusion Reaction Technique for the Preparation of Thick Films of Cuprate Superconductors*

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Abstract

Liquid- and vapour-phase diffusion have been used to fabricate thick films of Y-based, Bi-based, and Tl-based ceramic superconductors. Solid substrates are coated with slurries of complementary compositions and sintered at low temperatures for short times to give dense adherent films that are principally single-phase. This technique can be used to produce reproducible materials of simplified fabrication.

1. Introduction

This work reports the use of a liquid- or vapour-diffusion growth technique to make Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, Bi-Pb-Sr-Ca-Cu-O, Tl-Pb-Sr-Ca-Cu-O, Tl-Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O superconductors. While the production of materials in the system Y-Ba-Cu-O is relatively simple (Easterling *et al.* 1988), Bi-based materials require very narrow processing conditions (Dou *et al.* 1988*b*), and Tl-based materials exhibit high (toxic) vapour pressures at temperatures above $\sim 700^\circ\text{C}$, which require specialised encapsulation techniques (Dou *et al.* 1988*a*; 1989*a*). While some work on liquid-solid reactions has been reported (Hermann and Sheng 1987), the present liquid-solid and vapour-solid diffusion reaction techniques involving substrates and reactant coatings permit more simplified and controlled processing routes that can overcome some of these difficulties to produce adherent thick films.

2. Experimental Procedure

Samples to be used as substrates with starting compositions corresponding to Y_2BaCuO_5 (211), $\text{SrCaCu}_2\text{O}_4$ (0112), $\text{SrCaCu}_4\text{O}_6$ (0114), $\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{7.5}$ (0.5/223), $\text{Bi}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{7.75}$ (0.5'/223), and $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ (0223) were prepared from suitable solid precursors by standard ceramic processing routes: mixing, calcining, grinding, pressing, and sintering, as shown in Table 1. Prior to reaction, the substrates were polished on 1200 grit SiC paper.

The reactant coatings consisted of (nominal composition) $\text{Ba}_3\text{Cu}_5\text{O}_8$, Bi_2O_3 , $3\text{Bi}_2\text{O}_3+2\text{PbO}$, and Tl_2O_3 . In the case of slurry formation, pre-reacted $\text{Ba}_3\text{Cu}_5\text{O}_8$, Bi_2O_3 , and $3\text{Bi}_2\text{O}_3+2\text{PbO}$ were mixed with polyethanol as a medium. The

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substrates were coated with the appropriate slurries, dried for 6 h at 180°C, and sintered for 40 h at 950°C for samples of the Y-Ba-Cu-O system and for 10–40 h at 800–880°C for the Bi-Sr-Ca-Cu-O and Bi-Pb-Sr-Ca-Cu-O systems. In the case of vapour-phase formation from vaporised powders, Tl_2O_3 powder was added to the appropriate substrates and pressure sealed in a silver tube. The samples were then sintered for 3–12 h at 800–890°C for the Tl-Pb-Sr-Ca-Cu-O, Tl-Bi-Sr-Ca-Cu-O, and Tl-Ba-Ca-Cu-O systems. The reaction systems are summarised in Table 2.

Table 1. Substrate sintering parameters

Material	Time (h)	Temperature (°C)
211	20	1000
0112	12	980
0114	12	1000
0·5/223	15	900
0·5'/223	15	900
0223	12	890

Table 2. Diffusion reaction systems

System	Substrate	Reactant coating	Nature of coating
Y-Ba-Cu-O	Y_2BaCuO_5 (211)	$\text{Ba}_3\text{Cu}_5\text{O}_8$	Slurry
Bi-Sr-Ca-Cu-O	$\text{SrCaCu}_2\text{O}_4$ (0112)	$0\cdot5\text{Bi}_2\text{O}_3$	Slurry
	$\text{SrCaCu}_4\text{O}_6$ (0114)	$0\cdot5\text{Bi}_2\text{O}_3$	Slurry
Bi-Pb-Sr-Ca-Cu-O	$\text{SrCaCu}_2\text{O}_4$ (0112)	$0\cdot125(3\text{Bi}_2\text{O}_3+2\text{PbO})$	Slurry
	$\text{SrCaCu}_4\text{O}_6$ (0114)	$0\cdot125(3\text{Bi}_2\text{O}_3+2\text{PbO})$	Slurry
Tl-Pb-Sr-Ca-Cu-O	$\text{Pb}_{0\cdot5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{7\cdot5}$ (0·5/223)	$0\cdot25\text{Tl}_2\text{O}_3$	Powder
Tl-Bi-Sr-Ca-Cu-O	$\text{Bi}_{0\cdot5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{7\cdot75}$ (0·5'/223)	$0\cdot25\text{Tl}_2\text{O}_3$	Powder (vaporised)
Tl-Ba-Ca-Cu-O	$\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ (0223)	Tl_2O_3	Powder (vaporised)

The electrical resistivity (voltage drop) was measured by the standard four-probe d.c. technique. Electron microscopy was performed with a JEOL JXA-840 scanning electron microscope (SEM) equipped with a Link Systems energy dispersive spectrometer (EDS).

3. Results and Discussion

Fig. 1 shows the voltage drop versus temperature curve for a single-phase thick film of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (123) formed from $\text{Y}_2\text{BaCuO}_5+\text{Ba}_3\text{Cu}_5\text{O}_8$; the sample showed a temperature of zero resistivity T_0 of 86 K.

While bulk materials in the Bi-Sr-Ca-Cu-O system usually show a strong transition at 80 K and only a slight resistivity drop at 110 K, diffused films in this system showed an enhanced transition at 110 K, although the 80 K transition was still present (Dou *et al.* 1989*b*).

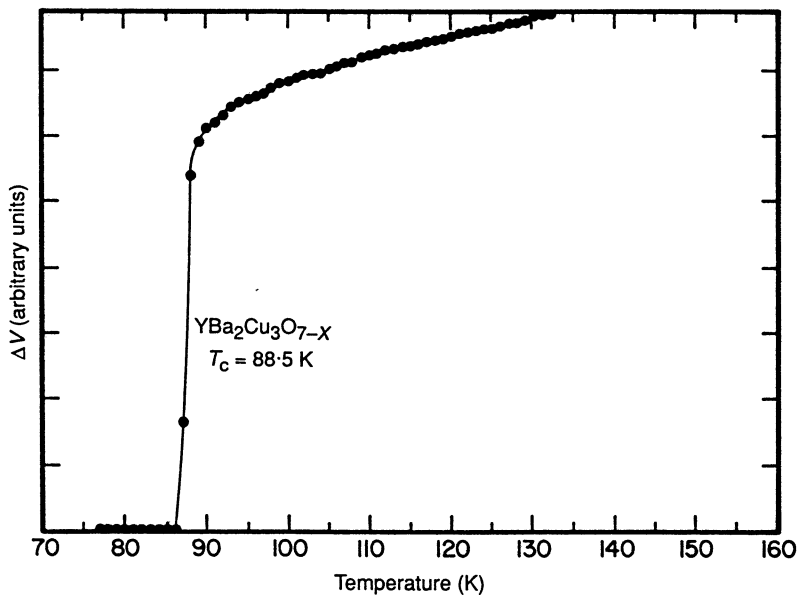


Fig. 1. Dependence of voltage drop on temperature for a thick film of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

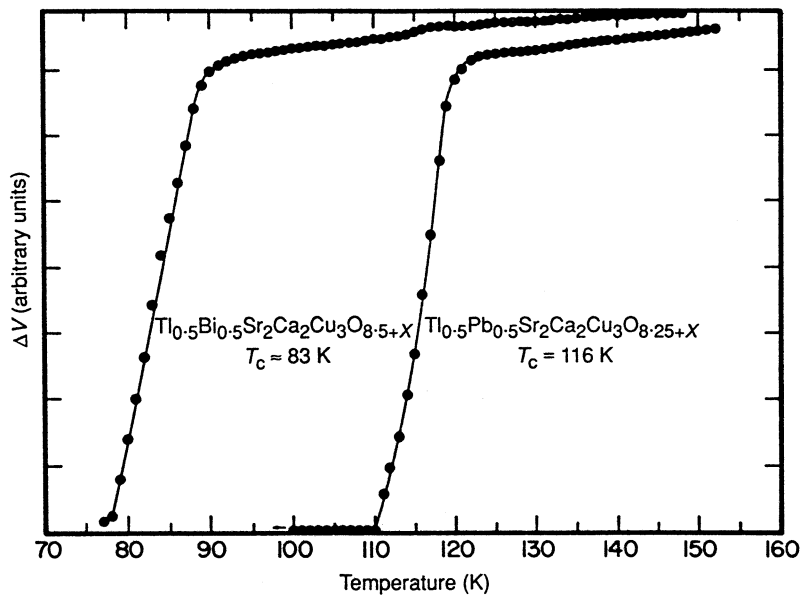


Fig. 2. Dependence of voltage drop on temperature for thick films produced from nominal compositions $\text{Tl}_{0.5}\text{Bi}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.5+x}$ and $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.25+x}$.

With Pb doping of this system, the use of substrates of 0112 and 0114 plus slurries of $3\text{Bi}_2\text{O}_3 + 2\text{PbO}$ gave materials with a single transition at 110 K, with T_0 values of 103 and 101 K respectively (Dou *et al.* 1989b). These materials consisted principally of $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ (2223) with impurities of $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (2212).

Fig. 2 shows typical curves for two-phase $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.25+x}$ and multiphase $\text{Tl}_{0.5}\text{Bi}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.5+x}$ (nominal compositions) with T_c (midpoint of 10–90% transition sigmoid) values of 116 and ~ 83 K respectively.

In the absence of Pb, Bi, and Sr, the system $\text{Tl}-\text{Ba}-\text{Ca}-\text{Cu}-\text{O}$ gave nearly single-phase $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ (2'223), with T_c and T_0 as high as 123 and 118 K respectively (Dou *et al.* 1988a).

The phase diagram for the system $\text{BaO}-\text{CuO}_x$ (Roth *et al.* 1987) shows a eutectic at 900°C at the composition corresponding to $\text{Ba}_3\text{Cu}_5\text{O}_8$ (the slurry). Y_2BaCuO_5 (the substrate) has been reported (Roth *et al.* 1988) to melt at $>1200^\circ\text{C}$. Since these samples were processed at 950°C , it is clear that $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ formed through a liquid–solid reaction.

In the system $\text{Bi}-\text{Sr}-\text{Ca}-\text{Cu}-\text{O}$, Bi_2O_3 (the slurry) melts at 820°C (Weast 1966). The substrates $\text{SrCaCu}_2\text{O}_4$ and $\text{SrCaCu}_4\text{O}_6$ have been observed to melt at 1000°C and 1020°C respectively. Since the processing temperatures for these samples were $800\text{--}880^\circ\text{C}$, again, a liquid–solid reaction resulted in the formation of the superconducting phases $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ (110 K) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (80 K).

In the system $\text{Bi}-\text{Pb}-\text{Sr}-\text{Ca}-\text{Cu}-\text{O}$, the slurry consisted of $3\text{Bi}_2\text{O}_3 + 2\text{PbO}$. The phase diagram for the system $\text{Bi}_2\text{O}_3\text{--PbO}$ (Levin and Roth 1964) is incomplete, but a eutectic may be inferred to exist at $\sim 700^\circ\text{C}$ at the approximate composition $7\text{Bi}_2\text{O}_3 \cdot 2\text{PbO}$. This is verified by the observation that the slurry formed a melt at $\sim 700^\circ\text{C}$. Consequently, with processing temperatures of $800\text{--}880^\circ\text{C}$, a liquid–solid reaction was responsible for the precipitation of platelets of $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ as the majority phase.

In the systems containing thallium, sintering temperatures and atmospheres are critical because Tl_2O_3 melts at 717°C and decomposes at 875°C (Weast 1966). While the substrates used all had melting points $>900^\circ\text{C}$, the processing temperatures of $800\text{--}890^\circ\text{C}$ ensured that Tl_2O_3 formed a vapour phase and generated the product phases through a vapour–solid reaction, probably preceded by a liquid–solid reaction. This technique is safe because no weight losses were observed for these reactions.

4. Conclusions

The techniques of liquid–solid and vapour–solid diffusion reactions can be used to produce superconductors from the Y-based, Bi-based and Tl-based systems. These methods offer advantages in the production of thick films on bulk substrates because equilibrium between the two different phases is attained considerably more quickly than through solid-state reactions during sintering. Further, relatively pure samples, with the possibility of preferred orientation, can be produced. In the case of toxic materials such as Tl_2O_3 and PbO , vaporisation losses can be reduced through the use of sealed silver tubes, thus providing greater control over stoichiometry and reducing toxic emissions.

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References

- Dou, S. X., Liu, H. K., Bourdillon, A. J., Tan, N. X., Savvides, N., Andrikidis, C., Roberts, R. B., and Sorrell, C. C. (1988a). *Supercond. Sci. Tech.* **1**, 83-7.
- Dou, S. X., Liu, H. K., Bourdillon, A. J., Tan, N. X., Savvides, N., Zhou, J. P., and Sorrell, C. C. (1988b). *Supercond. Sci. Tech.* **1**, 78-82.
- Dou, S. X., Liu, H. K., Bourdillon, A. J., Tan, N. X., Savvides, N., Andrikidis, C., Roberts, R. B., and Sorrell, C. C. (1989a). In 'Advances in Superconductivity', Proc. First Int. Symp. on Superconductivity (ISS. 88) (Eds K. Kitazawa and T. Ishiguro), pp. 813-8 (Springer: Tokyo).
- Dou, S. X., Liu, H. K., Bourdillon, A. J., Tan, N. X., and Sorrell, C. C. (1989b). *Physica C* **158**, 93-6.
- Easterling, K. E., Sorrell, C. C., Bourdillon, A. J., Dou, S. X., Sloggett, G. J., and Macfarlane, J. C. (1988). *Mater. Forum* **11**, 30-42.
- Hermann, A. M., and Sheng, Z. Z. (1987). *Appl. Phys. Lett.* **51**, 1854-6.
- Levin, E. M., and Roth, R. S. (1964). *J. Res. Nat. Bur. Stand.* **68A**, 189-95.
- Roth, R. S., Davis, K. L., and Dennis, J. R. (1987). *Adv. Ceram. Mater.* **2**, 302-12.
- Roth, R. S., Rawn, C. J., Beech, F., Whitler, J. D., and Anderson, J. O. (1988). In 'Research Update, 1988: Ceramic Superconductors II' (Ed. M. F. Yan), pp. 13-26 (Am. Ceramic Soc.: Westerville, Ohio).
- Weast, R. C. (Ed.) (1966). 'CRC Handbook of Chemistry and Physics', 47th edn (Chemical Rubber Company: Cleveland, Ohio).

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