

## High Temperature Superconducting Materials and Device Structures\*

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### Introduction

The role-played by lead substitution in bismuth sites for the formation and stabilization of 2223 phase in the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  (BSCCO), system has been studied by many workers. We have studied this system,  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  via sol-gel technique and conventional solid stated route. Besides, this BSCCO system has three super conducting phases of 2201, 2212 and 2223 with  $T_c$  at 20K, 80K and 110K respectively. It is the role Ca and Cu that has changed its  $T_c$ . Investigation have been carried out by many workers on the effect of doping in Cu sites. However there are not many work were done on the effect of doping in Ca and Cu simultaneously. We have carried systematic studies on the doping of Sn on both sites. The effect of doping of elements of different ionic sizes and valencies such as Ba Sn, Zn, Y, V, Cr, Mg, Si, S, Dy, Pr, Gd, and Nd and Ca or/and Cu sites in  $\text{Bi}(\text{Pb})\text{-Sr-Ca-Cu-O}$  System have also been studied. From this work the role of the doping of rare earth magnetic elements and nonmagnetic elements on the super conducting properties of the system can be obtained. Another system that has been investigated is the  $\text{YBa}_2\text{Ca}_n\text{Cu}_{3+n}\text{O}_y$  system ( $n=1,2,3$ ), where we would like to know whether this system could exist as the BSCCO system.

### Materials and Methods

The ceramic samples of BSCCO and YBCO systems were prepared from appropriate mixtures of high purity oxides (e.g. Bi, Cu, Pb) and carbonates (e.g. Sr, Ca Ba). The mixtures were ball-milled for 24 hrs, calcined for 14 hrs and sintered for 150 hrs. at various temperatures. Another method of preparation is via sol-gel technique. The precursors were pure metal acetates of  $\text{Bi}(\text{CH}_3\text{COO})_3$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ,

$\text{Sr}(\text{CH}_3\text{COO})_2$ , and  $\text{Cu}(\text{CH}_3\text{COO})_2$ . Pure acetates were dissolved in acetic acid. The solution was hydrolyzed and polycondensed at room temperature by motorized stirring and maintaining pH at 5.5 by addition of ammonium hydroxide solution. By heating the hydrolyzed solution for 35 hr at 80C, the solution transformed to transparent gel. Further heating between 180-240C for 3-5 hrs converted the gel to solid bloating powders. These powders were then calcined and sintered. Pure acetates were also used to fabricate BSCCO via coprecipitation method. This method is able to produce high quality and quantity super conducting phase with a major reduction in processing time as compared to the previous methods. The electrical resistance was measured in the temperature range of 20-300 K by a standard four-point technique using a constant current source of 24 mA. Ac susceptibility measurements were performed in then temperature range of 20-120K using an Ac suseptometer (Lake shore Cryotronics- Model 7000). Identification of phases was done using a Siemens XRD machine with  $\text{Cu K}\alpha$  radiation. SEM observed the microstructure of the samples. Magnetic levitation studies of the materials were also carried out for temperature range 77-300K, using a self-designed automated system.

### Results and Discussion

The optimum doping of Pb in Bi was found to be between  $x = 0.2$  and  $0.3$ . This value is much lower than the reported value of  $0.4$  (Mohamed, 1999). Complex Ac susceptibility measurements showed that the nature of the grains, grain boundaries and coupling associated to the super conducting properties were superior in sol-gel samples due to fine powders of submicron size obtained through sol-gel process (Halim et al. 2000a).]. All doped samples showed decrease of zero re-

sistance with temperature. The dopants with bigger ionic radius than that of calcium showed better  $T_c$  zero (Malik et al. 1999; Mohamed 1999). Super conducting grains and grains connectivity differs for each doping. The Josephson coupling energy  $E_j = (h/4\pi e)I_0$ , where  $I_0 = 1.57 \times 10^{-8} T_c^2 / (T_c - T_{c0})$ , showed that the couplings are of the S-N-S type for dopant with bigger ionic radius and S-I-S types for dopants with smaller ionic radius (Halim et al. 1999b). Barium doped samples are least affected by compositional variation and the zero resistance values are higher than that of all the other doped samples (Halim et al. 1999d,e). The magnetic rare earth elements did not suppressed superconductivity drastically as observed in the magnetic transition elements. Hence it could be deduced that the 4f electrons have less effect than the 3d electrons on the electron pairing mechanisms.

The effect of Sn doping, either separately or simultaneously in Ca and Cu sites, showed that doping at Ca sites alone has the most drastic effect on  $T_c(\text{O})$  indicating the importance of the role of Ca in the pairing mechanism in the Cu-O planes (Azhan et al. 1999a; Halim et al. 2000b).

For coprecipitation samples the calculated Josephson current for pure sample is  $123 \mu\text{A}$ , which is higher than that obtained from samples prepared via conventional or sol-gel method. This is due to the submicron size of the starting materials and the good grains connectivity of the microstructures (Imad et. al 2001).

In the  $\text{YBa}_2\text{Ca}_n\text{Cu}_{3+n}\text{O}_y$  system ( $n=1,2,3$ ) the c-axis parameter remained unchanged despite the increase of Ca and Cu concentration and hence did not favors the formation of additional Cu-O planes as in the case of the BSCCO system. However the system is still super conducting with  $T_c(\text{zero})$

~64K (Azhan et al. 1999b; Halim et al. 2000b).

Magnetic levitation studies of the materials, carried out for temperature range 77-300K, using self-designed automated system showed microstructure dependence of the levitation force. The measurements showed hysteretic properties of the materials from which the magnetic stiffness and pinning effect could be deduced.

### Conclusions

The magnetic rare earth elements did not suppressed superconductivity drastically as observed in the magnetic transition elements. Hence it could be deduced that the 4f electrons have less effect than the 3d electrons on the electron pairing mechanisms. The effect of Sn doping, either separately or simultaneously in Ca and Cu sites, showed that doping at Ca sites alone has the most drastic effect on  $T_c(0)$  indicating the importance of the role of Ca in the pairing mechanism in the Cu-O planes (Azhan et al. 1999a; Halim et al. 2000b). In the  $YBa_2Ca_nCu_{3-n}O_y$  system ( $n=1,2,3$ ) the c-axis parameter remained unchanged despite the increase of Ca and Cu concentration and hence did not favour the formation of additional Cu-O planes as in the case of the BSCCO system. However the system is still superconducting with  $T_c(\text{zero}) \sim 64$ . Coprecipitation is a better preparation method for the fabrication of high  $T_c$  phase materials.

### Benefits from the study

Doping at Ca sites alone has the most drastic effect on  $T_c(0)$  indicating the importance of the role of Ca in the pairing mechanism in the Cu-O planes. The increase of Ca and Cu concentration did not favour the formation of additional Cu-O planes in the  $YBa_2Ca_nCu_{3-n}O_y$  system ( $n=1,2,3$ ) as in the case of the BSCCO system. However the system is still superconducting with  $T_c(\text{zero}) \sim 64$ K.

From the study, it could be deduced that the 4f electrons have less effect than the 3d electrons on the electron pairing mechanisms. Automated magnetic levitation equipment, designed in the laboratory enables the detailed studies of the levitation properties, such as magnetic stiffness and pinning effect of the materials for practical applications. Another benefit from this study showed that superior supercon-

ducting samples can be prepared via coprecipitation technique.

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