

## Effect of cationic size in $\text{Hg}(\text{Tl}/\text{Bi})\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ on superconducting and microstructural characteristics

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**Abstract.** In this paper we have reported investigations on the effect of simultaneous substitution of Bi and Tl at the Hg site in the oxygen deficient  $\text{HgO}_d$  layer of  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$  cuprate superconductor. Bulk polycrystalline samples have been prepared by the two-step solid state reaction process (precursor route). It has been observed that the as grown  $\text{HgBi}_{0.2-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$  (with  $x = 0.00, 0.05, 0.10, 0.15, 0.20$ ) corresponds to the 1223 phase. It has been found that the  $T_c$  varies with the average cationic size  $\langle R_d \rangle$  of the dopant cations. The optimum  $T_c$  of  $\sim 131$  K has been found for the composition  $\text{HgBi}_{0.15}\text{Tl}_{0.05}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ . This composition leads to the average dopant cation size of  $\sim 1.108$  Å which is very close to the size of  $\text{Hg}^{2+}$  ( $\sim 1.11$  Å). The microstructure for  $\text{HgBi}_{0.15}\text{Tl}_{0.05}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$  has been found to be most dense and this phase exhibits the highest stability. The  $J_c$  of the optimum material  $\text{HgBi}_{0.15}\text{Tl}_{0.05}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$  is found to be  $\sim 1.29 \times 10^3$  A/cm<sup>2</sup> at 77 K.

**Keywords.** HTSC; XRD; cationic size;  $T_c$ .

### 1. Introduction

To date,  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  represents the most interesting homologues series out of all known high temperature cuprate superconductors. Undoubtedly the primary reason for this is the high critical transition temperature exhibited by this series. Thus the phase with  $n = 3$  i.e. Hg-1223 exhibits the highest ambient condition critical temperature of 130–135 K (Putlin *et al* 1993; Sastry *et al* 1998b; Fujii *et al* 1999). This HTSC has significant practical importance since wires and tapes corresponding to this phase can be easily operated at 77 K. The other reason for Hg based HTSC phases being interesting is the fact that the anisotropy of these HTSC phases is in between Y and Bi bearing cuprates and they are therefore, expected to show effective flux pinning and microstructure exhibiting good texturing of grains. However, inspite of these advantages their use is not yet as widespread as other HTSC materials e.g. Y-123. This is due to considerable difficulty experienced in the synthesis of Hg bearing HTSC phases including Hg-1223 because of their extreme sensitivity towards contamination from humidity and carbon dioxide. The Hg-1223 samples are known to degrade rapidly after synthesis. In view of this, significant efforts have recently been made to improve the stability of the Hg bearing HTSC phases, particularly the Hg-1223 phase.

It is now known that the most effective way to improve the stability of the Hg-1223 phase is through suitable cationic substitution for Hg. Typically suited cations are those having oxidation states higher than that of Hg i.e. greater than + 2. They bring in more oxygen in the oxygen deficient  $\text{HgO}_d$  layer leading to phase stability. The higher oxidation state cations also lead to hole optimization in the hole deficient as grown Hg-1223 phase, thus producing optimum critical transition temperature ( $T_c$ ). A variety of cationic substitution such as Bi, Tl, Mo, Re, Sn, Pb etc have been attempted (Sun *et al* 1994; Shao *et al* 1994; Meng *et al* 1996; Balchev *et al* 1997; Chmaissem *et al* 1997; Li *et al* 1998, 1999; Sastry *et al* 1998a; Fujii *et al* 1999). Even though all of them lead to enhanced chemical stability, the influence of different cationic substitutions on the superconducting properties are different. As for example whereas Tl substitution has been found to easily optimize hole concentration and hence  $T_c$  (Sun *et al* 1994; Pandey *et al* 1998), the substitution of Re has been found to lead to enhancement of  $B_{irr}$  (Fujii *et al* 1999). It may be pointed out that the specific substituted cationic characteristics taken into account generally concerns the oxidation number. However, the influence of another important dopant cationic parameter i.e. the cationic size, has not been studied in detail. The dopant cation size is likely to influence some important characteristics. The  $T_c$  will depend on the size of the dopant ions, since mismatch of dopant ions sizes with native Hg ions will produce local pressure. Also band overlap will change on substitution of

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cation of different sizes and this may also lead to change in  $T_c$ . The other characteristics which will be influenced by the cationic size will be the degree of stability and microstructure through the strain they produce in the HgO layer.

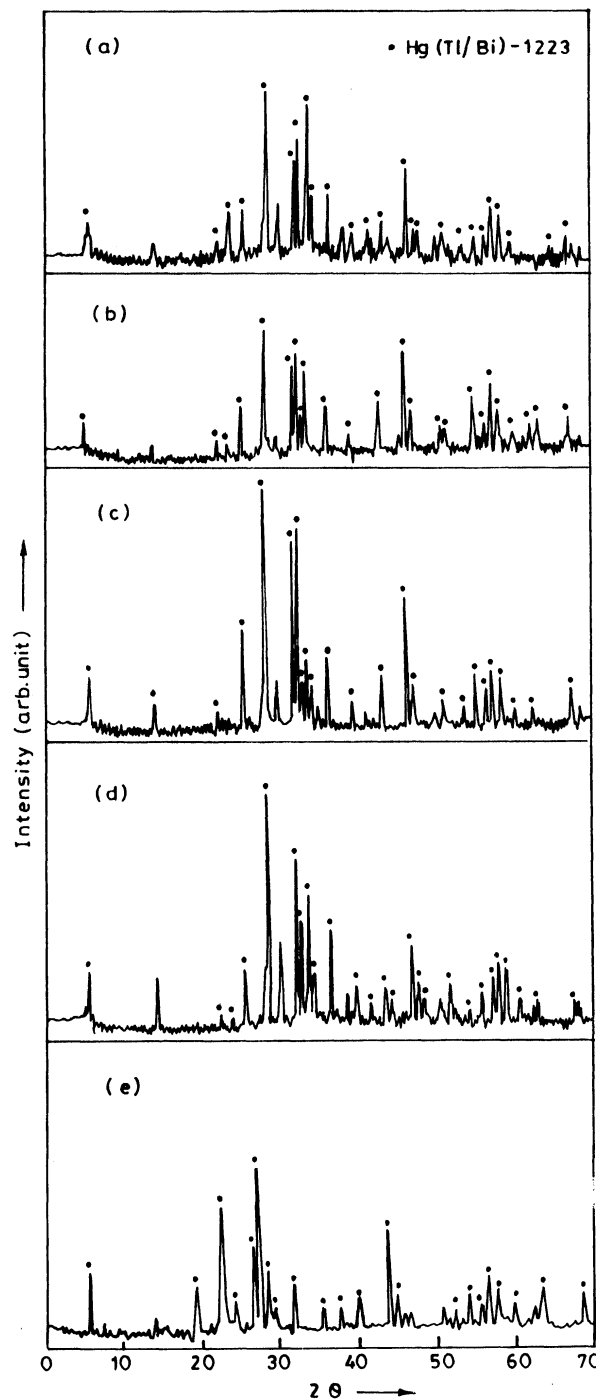
Keeping the above said aspects in view, we have investigated the influence of the cationic size on the superconducting characteristics and stability of Hg-1223 phase. We have doped Hg-1223 with both Bi and Tl taken together in varying concentrations. In view of the fact that in most of the recent studies the total effective concentration of Hg vs dopant cations M are taken as  $\text{HgM}_{0.2}$  (Sastry *et al* 1998b; Fujii *et al* 1999), we have investigated the  $\text{HgBi}_{0.2-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ . It may be mentioned that both Bi and Tl have individually been previously successfully employed for doping the Hg-1223. However, to the best of our knowledge the effect of simultaneous doping of Bi and Tl in Hg based copper-oxide superconductors have not been reported in the past. The cationic size of  $\text{Bi}^{3+}$  (the state which is thought to be effective in HTSC materials) is 1.16 Å and that of  $\text{Tl}^{3+}$  is 0.95 Å. The effective size of the dopant has been taken by us to be represented by average dopant radius  $\langle R_d \rangle$  and this varies with the concentration of Bi and Tl. We have found that the maximum  $T_c$  of ~131 K which is representative of undoped Hg-1223 is obtained for  $\text{Hg}(\text{Bi}_{0.15}\text{Tl}_{0.05})$ -1223 where  $\langle R_d \rangle$  1.108 Å, a value which is very close to that of Hg (~1.11 Å). Yet another result obtained is that the microstructure for the  $\text{Hg}(\text{Bi}_{0.15}\text{Tl}_{0.05})$ -1223 phase is most dense and this phase exhibits highest stability.

Although the cationic substitution of  $\text{HgO}_d$  site leads to stabilization, it also affects the superconducting properties,  $T_c$  and  $J_c$ . The exercise of stabilization will be only useful, if the superconducting properties remain as good as the unsubstituted Hg-1223 or better than that. The superconducting properties are known to be dependent on substituted cationic properties and structural/microstructural characteristics. The central aim of the present study is to report results of investigations seeking to bring out the dependence of superconducting characteristics on the effective cationic size of the substituted cations, which varies with their concentrations. The inter-relationship between stabilization and cationic size as well as structural characteristics has also been explored.

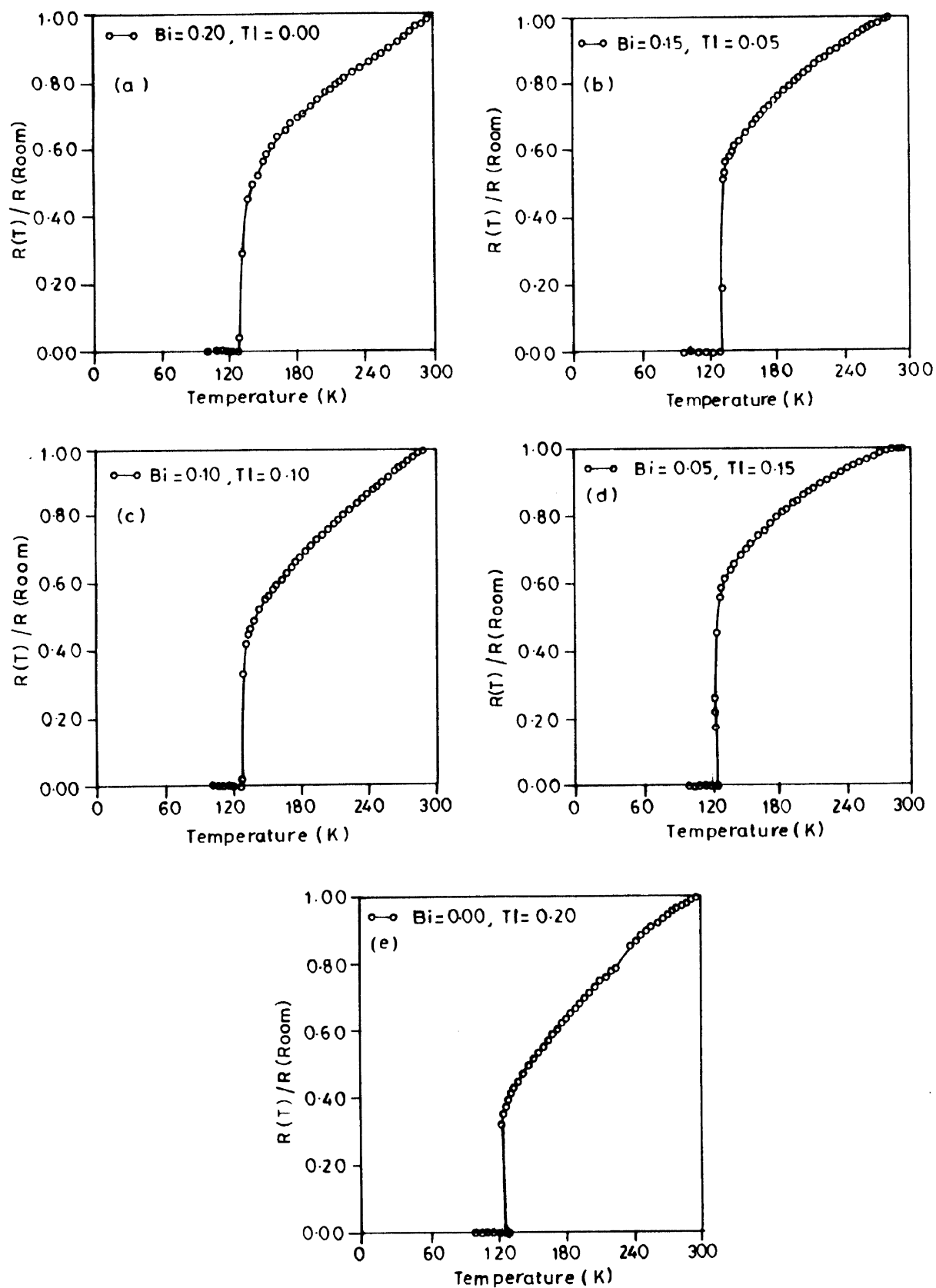
## 2. Experimental

In the present study the synthesis of Bi and Tl doped  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$  high temperature cuprate superconductor has been carried out by two-step method. In the first step, highly pure (3N) powders of  $\text{Ba}(\text{NO}_3)_2$ , CaO and CuO were mixed in the stoichiometric ratio ( $\text{Ba}/\text{Ca}/\text{Cu} = 2/2.2/3.2$ ) and ground in an agate mortar. The resultant mixture was heated in flowing oxygen with three intermediate grindings at 925°C for 48 h. In the second step, the Ba–Ca–Cu–O precursor was mixed with HgO,  $\text{Bi}_2\text{O}_3$

and  $\text{Tl}_2\text{O}_3$  to obtain the nominal composition  $\text{HgBi}_{0.2-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ , where  $x = 0.0, 0.05, 0.1, 0.15, 0.2$ . All the intermediate grindings and final mixing/grinding have been carried out in a glove box containing  $\text{P}_2\text{O}_5$ , NaOH and nitrogen atmosphere. After the final grinding the Hg(Bi,Tl)–Ba–Ca–Cu–O powder was pelletized at a



**Figure 1.** Representative X-ray diffraction pattern of  $\text{HgBi}_{0.2-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$  with (a)  $x = 0.00$ , (b)  $x = 0.05$ , (c)  $x = 0.10$ , (d)  $x = 0.15$  and (e)  $x = 0.20$ , as synthesized samples at 850°C for various compositions using  $\text{CuK}_\alpha$  radiation.



**Figure 2.** Normalized resistance  $[R(T)/R(300)]$  vs temperature for various compositions of as grown  $\text{Hg}(\text{Bi},\text{Tl})\text{Ba}-\text{Ca}-\text{Cu}-\text{O}$ : (a)  $\text{HgBi}_{0.2}\text{Tl}_{0.0}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ , (b)  $\text{HgBi}_{0.15}\text{Tl}_{0.05}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ , (c)  $\text{HgBi}_{0.10}\text{Tl}_{0.10}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ , (d)  $\text{HgBi}_{0.05}\text{Tl}_{0.15}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$  and (e)  $\text{HgBi}_{0.00}\text{Tl}_{0.20}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ .

pressure of 3.5 tons/cm<sup>2</sup>. The pellets were filled in a platinum box, which was then put into a quartz tube. The quartz tube was evacuated up to 10<sup>-5</sup> torr and sealed. For safety purposes the sealed tube was encased in a steel tube filled with sand and tightly closed. Thereafter steel tube was inserted into a programmable Heraeus tube type furnace. The temperature of the furnace was raised at a rate of 200°C/h up to 600°C and thereafter at a rate of 100°C/h up to 850°C and held at this temperature for 10 h. Finally the furnace was cooled at the rate of 100°C/h to room temperature. All the samples in the present investigation were subjected to gross structural characterization by X-ray diffraction (XRD, Philips PW 1710, CuK<sub>α</sub>), electrical transport characterization by four-probe technique (Keithley resistivity-Hall setup), surface morphological characterization by scanning electron microscope (SEM, Phillips XL20) and cationic composition was investigated by energy dispersive analysis (EDAX; DX4, PV9400/08).

### 3. Results and discussion

The as grown samples having various Bi and Tl concentrations were subjected to gross structural characterization employing the X-ray diffraction (XRD) technique. The XRD data collected from various samples show that all the samples are polycrystalline and correspond to Hg(Bi/Tl)-1223 phase. The XRD also shows some impurity phases with vanishingly small concentrations. The representative XRD patterns are shown in figure 1. The lattice parameters have been estimated using *d*-values and (*hkl*) reflections of the observed X-ray diffraction pattern through the software program of S Sivasankaran (Crystal Growth Centre, Anna University, Chennai) and the values are shown in table 1. As regards the stoichiometry corresponding to various compositions it was verified through EDAX, employing EDAX (DX4, PV9400/08) micro-analysis system, attached to the EM-CM200 electron microscope, at CAT Indore, India. The observed stoichiometry through EDAX is broadly in conformity with the envisaged stoichiometry.

The variation of resistance with temperature of the as synthesized HgBi<sub>0.2</sub>Tl<sub>x</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+d</sub> HTSC samples was

measured by the standard four-probe technique. The normal state resistance of all the samples shows metal like behaviour with respect to temperature. A plot of the normalized resistance [*R*(*T*)/*R*(295K)] vs temperature (*R*-*T*) behaviour of samples with various Bi and Tl concentrations are shown in figure 2. The values of critical transition temperature (*T*<sub>c</sub>) for as grown HgBi<sub>0.2</sub>Tl<sub>0.00</sub>-1223, HgBi<sub>0.15</sub>Tl<sub>0.05</sub>-1223, HgBi<sub>0.10</sub>Tl<sub>0.10</sub>-1223, HgBi<sub>0.05</sub>Tl<sub>0.15</sub>-1223 and HgBi<sub>0.00</sub>Tl<sub>0.20</sub>-1223 HTSC phases are 127 K, 131 K, 126 K, 124 K and 125 K, respectively. In view of the quality characterization provided by Kirschner *et al* (1996), it can be categorically stated that our samples are of 'good quality'. Since one of the central aim of the present investigation was to study the critical transition temperature as a function of effective size (radius) of the cations, the *T*<sub>c</sub>s for various cation sizes (radii) were evaluated. The effective dopant radii was changed by varying the concentration of Tl and Bi cations. The effective cation radii was taken to be the average radius of the cations and this was defined as

$$\langle R_d \rangle = \frac{N_{\text{Bi}}^{3+} r_{\text{Bi}}^{3+} + N_{\text{Tl}}^{3+} r_{\text{Tl}}^{3+}}{N_{\text{Bi}}^{3+} + N_{\text{Tl}}^{3+}},$$

where  $N_{\text{Bi}}^{3+}$  and  $N_{\text{Tl}}^{3+}$  represent the concentrations of Bi and Tl cations and  $r_{\text{Bi}}^{3+}$  and  $r_{\text{Tl}}^{3+}$  are the radii of Bi and Tl cations. The ionic radii of Hg, Tl and Bi, i.e.  $r_{\text{Hg}}^{2+}$ ,  $r_{\text{Tl}}^{3+}$  and  $r_{\text{Bi}}^{3+}$  are 1.11 Å, 0.95 Å and 1.16 Å, respectively.

The composition, the effective cationic size (average radius) and the corresponding *T*<sub>c</sub> are shown in table 1. A plot of effective cationic size and the transition temperature is shown in figure 3. A remarkable result as evidenced by table 1 and figure 3, relates to the fact that *T*<sub>c</sub> maximum of ~ 131 K is obtained for effective cationic size  $\langle R_d \rangle$  of 1.108 Å, which is almost the same as that of Hg<sup>2+</sup> (1.11 Å). This shows that *T*<sub>c</sub> is optimum when the effective cationic size is virtually the same as that of Hg<sup>2+</sup>. Since the maximum value of *T*<sub>c</sub> is expected to be for optimum hole doping, the concentration HgBi<sub>0.15</sub>Tl<sub>0.05</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+d</sub> would correspond to optimum level of hole doping. In order to verify this, the phase corresponding to HgBi<sub>0.15</sub>Tl<sub>0.05</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+d</sub> was annealed in oxidizing (oxygen) and reducing (argon and hydrogen

**Table 1.** Various compositions of HgBi<sub>0.2-x</sub>Tl<sub>x</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+d</sub>, their effective cationic size (Å), transition temperature (K) and lattice parameters.

Compositions	Effective cationic size $\langle R_d \rangle$ (Å)	Transition temperature (K)	Lattice parameter, <i>a</i> (Å)	Lattice parameter, <i>c</i> (Å)
HgBi <sub>0.2</sub> Tl <sub>0.0</sub> Ba <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8+d</sub>	$\langle R_{0.20,0.00} \rangle = 1.160$	127	3.849	15.923
HgBi <sub>0.15</sub> Tl <sub>0.05</sub> Ba <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8+d</sub>	$\langle R_{0.15,0.05} \rangle = 1.108$	131	3.848	15.843
HgBi <sub>0.1</sub> Tl <sub>0.1</sub> Ba <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8+d</sub>	$\langle R_{0.10,0.10} \rangle = 1.055$	126	3.846	15.834
HgBi <sub>0.05</sub> Tl <sub>0.15</sub> Ba <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8+d</sub>	$\langle R_{0.05,0.15} \rangle = 1.002$	124	3.845	15.833
HgBi <sub>0.0</sub> Tl <sub>0.2</sub> Ba <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8+d</sub>	$\langle R_{0.00,0.20} \rangle = 0.950$	125	3.849	15.794

mixture) ambient. Based on our previous work (Pandey *et al* 1998), the time and temperature for oxygen were 12 h and 500°C and for argon, hydrogen mixture (ratio 98 : 2) were 7 h and 300°C. It was found that the  $T_c$  decreased for both the oxidizing and reducing ambients. Thus,  $T_c$  dropped to 127 K for oxidizing and decreased to 128 K for reducing atmosphere, respectively. The  $HgBi_{0.15}Tl_{0.05}Ba_2Ca_2Cu_3O_{8+d}$  version of Hg-1223 was found to be highly reproducible and stable. There is very small decrease in  $T_c$  (~ 2 K) even after six months, for example,  $T_c$  of the optimum sample ( $HgBi_{0.15}Tl_{0.05}Ba_2Ca_2Cu_3O_{8+d}$ ) decreases to 129 K from 131 K after many cycles of measurements during a period of six months. The transport critical current density of all the samples has been measured by the four-probe technique using the criterion of 1  $\mu V/cm$ . The  $J_c$  value of the optimum composition at 77 K is  $\sim 1.29 \times 10^3 A/cm^2$ .

The microstructural features of all the as grown samples were studied by scanning electron microscopy (SEM) employing secondary electrons. The representative micrographs taken from the samples of various compositions are shown in figure 4. The morphological evaluation of  $HgBi_{0.2-x}Tl_xBa_2Ca_2Cu_3O_{8+d}$  samples reveals some interesting features which bear correlation with the average dopant radius. The samples in which average dopant radius  $\langle R_d \rangle$  differs significantly from  $Hg^{2+}$  radius (1.11 Å) exhibit discontinuous/porous microstructure. This is shown in figure 4a, which corresponds to  $HgBi_{0.2}Ba_2Ca_2Cu_3O_{8+d}$  ( $\langle R_d \rangle = 1.16$  Å) and in figure 4c which corresponds to  $HgTl_{0.2}Ba_2Ca_2Cu_3O_{8+d}$  ( $\langle R_d \rangle = 0.95$  Å). From these micrographs it is also clear that the grains are misaligned. In samples having the  $\langle R_d \rangle$  closer to that of  $Hg^{2+}$ , microstructure is dense, the grain alignment appears

better and grains are larger in size. This is clearly evident from figure 4b representing microstructures corresponding to  $HgBi_{0.15}Tl_{0.05}Ba_2Ca_2Cu_3O_{8+d}$  ( $\langle R_d \rangle = 1.108$  Å). Apparently the strain in  $HgO_d$  layer will get reduced when the average dopant radii approaches to that of  $Hg^{2+}$ .

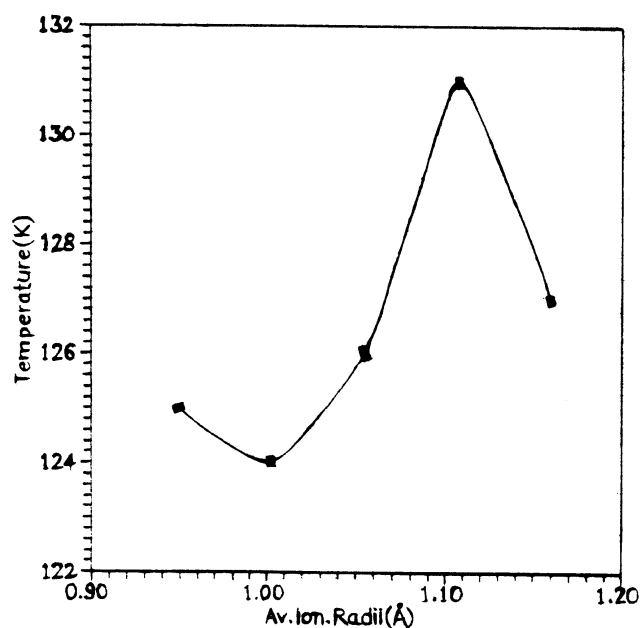


Figure 3. Variations in transition temperature with dopant average ionic radii.

Figure 4. SEM micrograph for various compositions of  $HgBi_{0.2-x}Tl_xBa_2Ca_2Cu_3O_{8+d}$  with (a)  $x = 0.00$ , (b)  $x = 0.05$  and (c)  $x = 0.20$ .

Consequently larger plate-like and more aligned grains are formed and the microstructure becomes denser. The densely packed and better aligned grains are conducive to higher critical current and this may be the reason that the sample with composition where  $\langle R_d \rangle$  is very close to  $\text{Hg}^{2+}$  radii has the highest transport  $J_c$  value of  $\sim 1.29 \times 10^3 \text{ A/cm}^2$  at 77 K.

#### 4. Conclusions

In the present study, we have investigated the effect of simultaneous doping of Tl and Bi in  $\text{HgO}_d$  layer of  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ . The as grown samples are dominantly  $\text{Hg}(\text{Bi/Tl})$ -1223 phasic. The transition temperature of as grown samples is found to be sensitive to the average dopant radius  $\langle R_d \rangle$  and it has been observed that maximum  $T_c$  (131 K) is achieved for  $\text{HgBi}_{0.15}\text{Tl}_{0.05}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$  where  $\langle R_d \rangle \approx 1.108 \text{ \AA}$ . This is nearly the same as that of ionic radius of Hg in +2 oxidation state (1.11  $\text{\AA}$ ). This phase does not need any additional post synthesis oxidation or reduction treatment and the as grown phase itself is optimally doped. This phase has been reproducibly produced and is very much stable with regard to moisture, carbon contamination and degradation in  $T_c$  is very small over a significant period. The microstructure for this phase is found to be most dense and the morphology of these samples shows plate-like layered microstructure. The  $J_c$  value of optimum composition at 77 K is  $\sim 1.29 \times 10^3 \text{ A/cm}^2$ .

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