

## **SUPERCONDUCTIVITY AND TRANSPORT CRITICAL CURRENT DENSITY IN Tl<sub>1-x</sub>Pb<sub>x</sub>Sr<sub>1.8</sub>Sb<sub>0.2</sub>CaCu<sub>2</sub>O<sub>7</sub> CERAMICS**

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### **ABSTRACT**

Superconducting properties of Tl<sub>1-x</sub>Pb<sub>x</sub>Sr<sub>1.8</sub>Sb<sub>0.2</sub>CaCu<sub>2</sub>O<sub>7</sub> ( $x = 0.1 - 0.6$ ) ceramics prepared using solid-state synthesis have been investigated. Tl<sub>1-x</sub>Pb<sub>x</sub>Sr<sub>1.8</sub>Sb<sub>0.2</sub>CaCu<sub>2</sub>O<sub>7</sub> ( $x = 0.1 - 0.5$ ) showed metallic normal state behavior and an increase in  $T_{c\ zero}$  from 26 K at  $x = 0.1$  to a maximum value of 80 K at  $x = 0.5$ . Further substitution of Pb to  $x = 0.6$  caused a decrease in  $T_{c\ zero}$  to 27 K. The transport critical current density,  $J_c$  measured in zero magnetic field for Tl<sub>1-x</sub>Pb<sub>x</sub>Sr<sub>1.8</sub>Sb<sub>0.2</sub>CaCu<sub>2</sub>O<sub>7</sub> ( $x = 0.2 - 0.4$ ) between 20 K and 80 K was determined by the four-point probe measurement using the  $1\mu\text{Vcm}^{-1}$  criterion.  $J_c$  increases when the temperature is reduced for all samples ( $x = 0.2 - 0.4$ ). The results of the electrical measurements and powder X-ray diffractions analysis are presented. The significance of each elemental substitution at different atomic sites are suggested. Effects of Pb and Sb substitution are discussed in terms of average Cu valence. Behavior of transport critical current density  $J_c$  with temperature was explained using a self-field approximation.

### **INTRODUCTION**

Elemental substitution in cupric oxide superconductors has been an important experimental attempt in the study of high- $T_c$  superconductivity. It is well known that substitution of rare earth elements of higher valence in the TlSr<sub>2</sub>CaCu<sub>2</sub>O<sub>7</sub> (Tl1212) may reduce the average Cu valence to an optimum value. Such substitution can also stabilize the 1212 phase and improve the superconducting behavior [1-3]. The substitution of Pb [4] or Bi [5] into Tl-sites in TlSr<sub>2</sub>CaCu<sub>2</sub>O<sub>7</sub> results in the stabilization of the 1212 structure and induced bulk superconductivity with  $T_c$  up to 80 K. A combination substitution of Pb and Y into the Tl and Ca sites, respectively produced Tl<sub>0.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>Ca<sub>0.8</sub>Y<sub>0.2</sub>Cu<sub>2</sub>O<sub>7</sub> with a  $T_c$  up to 110 K [6].

It is interesting to investigate further the effect of Pb substitution together with Sb on the superconductivity and formation of the Tl1212 phase. In this paper we report superconducting properties of double-substituted Tl<sub>1-x</sub>Pb<sub>x</sub>Sr<sub>1.8</sub>Sb<sub>0.2</sub>CaCu<sub>2</sub>O<sub>7</sub> ( $x = 0.1 - 0.6$ ). We present results from electrical resistance (dc) measurements, powder X-ray diffraction (XRD) and transport critical current density  $J_c$ . The superconducting properties are discussed according to the concept of average Cu valence.

## EXPERIMENTAL PROCEDURE

### *Samples preparation*

Appropriate amounts of high purity ( $\geq 99.99\%$ ) powders of  $\text{SrCO}_3$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{CuO}$  were mixed and ground in an agate mortar. The well-mixed oxides were then calcined in air at around  $900\text{ }^\circ\text{C}$  for 48 hours with several intermittent grindings to prepare the precursor. Appropriate amounts of  $\text{Tl}_2\text{O}_3$  and  $\text{PbO}$  were then mixed with the precursor to form mixtures with the nominal composition  $\text{Tl}_{1-x}\text{Pb}_x\text{Sr}_{1.8}\text{Sb}_{0.2}\text{CaCu}_2\text{O}_7$  ( $x = 0 - 0.6$ ). The mixtures were then pressed into pellets with diameter of 13 mm and thickness of around 2 mm under a load of 4-5 tons using a hydraulic press. The pellets were then placed in a ceramic boat and heated in a tube furnace at  $1005\text{ }^\circ\text{C}$  in flowing oxygen for 6 minutes followed by furnace cooling to room temperature. To investigate the role of Sb, Sb-free  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_7$  was prepared using a similar procedure.

### *Samples characterization*

Powder X-ray diffraction analysis was carried out using Bruker D8 Advance diffractometer with  $\text{Cu-K}_\alpha$  radiation. The electrical resistance measurements between 16 K to 300 K were carried out using the four-point probe method with silver paint contacts in a Janis model CCS 350ST cryostat in conjunction with a closed cycle refrigerator from CTI Cryogenics model 22. The transport critical current density was measured using the  $1\text{ }\mu\text{Vcm}^{-1}$  criterion in zero magnetic field.

## RESULTS AND DISCUSSION

Powder X-ray diffraction patterns of samples with nominal composition  $\text{Tl}_{1-x}\text{Pb}_x\text{Sr}_{1.8}\text{Sb}_{0.2}\text{CaCu}_2\text{O}_7$  ( $x = 0 - 0.6$ ) showed 1212 major phase for  $x = 0.2 - 0.5$  with 1201 as minor phase. For samples with  $x = 0, 0.1$  and  $0.6$  1201 is the major phase. Figure 1 shows the X-ray diffraction patterns for  $x = 0.2$  and  $0.3$ . The 1212 peaks were indexed based on a tetragonal unit cell with space group  $P4/mmm$ . The volume percent of the 1212 and 1201 phases in the samples were estimated by assuming that the amounts of 1212 phase and 1201 phase are proportional to the intensity of their strongest diffraction line i.e. the (103) peak for 1212 phase and (003) peak for 1201 phases. The peaks due to the 1201 phase are indicated by (\*) in the X-ray diffraction pattern. The lattice parameter of the samples was obtained from the computer fittings of observed  $d$  values of diffractograms for individual sample.

Table 1 lists the results of 1212:1201 phase ratio and 1212 lattice parameters for  $\text{Tl}_{1-x}\text{Pb}_x\text{Sr}_{1.8}\text{Sb}_{0.2}\text{CaCu}_2\text{O}_7$  ( $x = 0 - 0.6$ ). The sample with  $x = 0$  exhibits the 1201 phase along with an unidentified phase. Substitution of Pb at  $x = 0.1$  promotes formation of 1212 minor phase alongside the 1201 major phase. Further substitution of Pb at  $x = 0.2$  caused the 1201 phase to decrease and the 1212 phase to increase. For  $x > 0.2$  the 1212 phase decreased with increasing  $x$ . At  $x = 0.6$ , 1201 was the major phase.

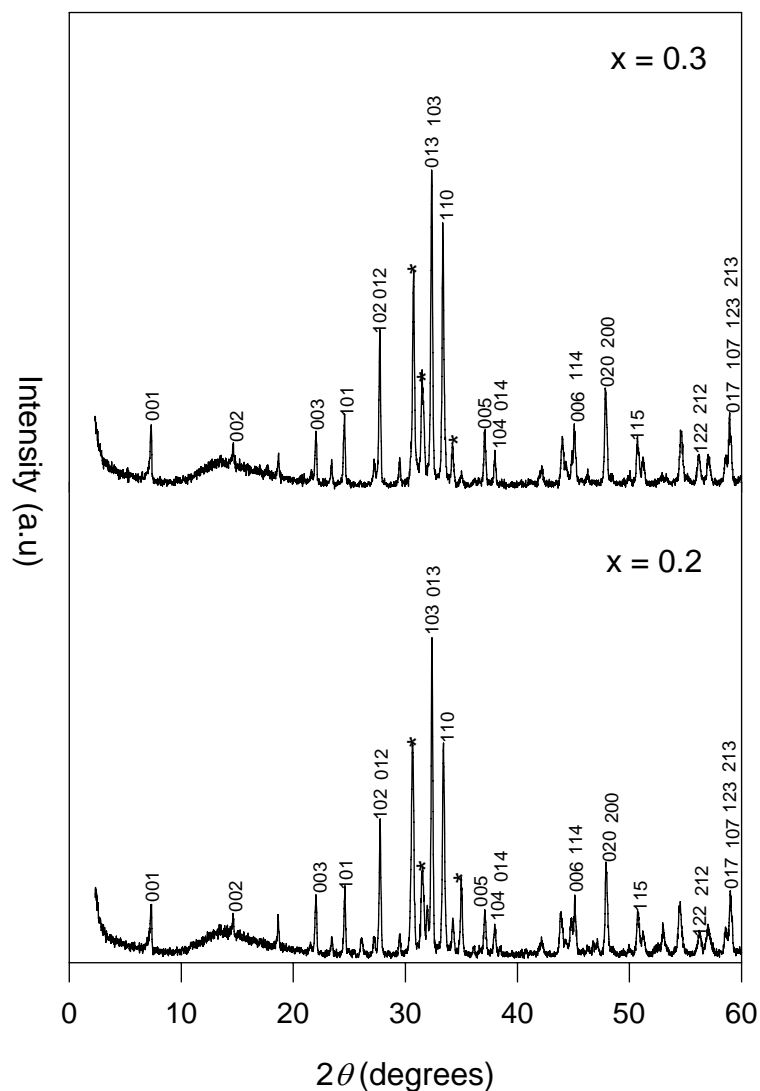


Figure 1: Powder X-ray diffraction patterns for  $Tl_{1-x}Pb_xSr_{1.8}Sb_{0.2}CaCu_2O_7$  ( $x = 0.2 - 0.3$ ). Peaks identified as 1201 phase are marked with \*

Table 1: 1212:1201 phase ratio and 1212 lattice parameters for  $Tl_{1-x}Pb_xSr_{1.8}Sb_{0.2}CaCu_2O_7$  ( $x = 0.0 - 0.6$ ) samples

Sample	1212	1201	1212 Unit cell	
	phase ratio	Vol (%)	$a$ (Å)	$c$ (Å)
$x = 0$	1201 (+an unknown phase)		-	-
$x = 0.1$	42 : 58		3.795	12.122
$x = 0.2$	60 : 40		3.797	12.116
$x = 0.3$	59 : 41		3.800	12.114
$x = 0.4$	54 : 46		3.801	12.112
$x = 0.5$	52 : 48		3.802	12.106
$x = 0.6$	35 : 65		3.805	12.104

For  $\text{Tl}_{1-x}\text{Pb}_x\text{Sr}_{1.8}\text{Sb}_{0.2}\text{CaCu}_2\text{O}_7$  ( $x = 0.1 - 0.6$ ),  $a$ -lattice was observed to increase with increasing  $x$  while  $c$ -lattice decrease with increasing  $x$  (Table 1). The increase in  $a$ -lattice can be explained in terms of the concept of the average Cu valence. When  $\text{Pb}^{4+}$  is substituted for  $\text{Tl}^{3+}$ , the average Cu valence is decrease, since  $a$ -lattice depends mainly in CuO plane, the decreasing of average Cu valence caused expansion of the CuO framework and increased the  $a$ -lattice. The decrease of  $c$ -lattice is may be due to the following reason: considering the ionic radius of  $\text{Pb}^{4+}$  (0.915 Å) which is smaller than  $\text{Sr}^{2+}$  (1.18 Å) and  $\text{Ca}^{2+}$  (0.99 Å), it is also possible that some  $\text{Pb}^{4+}$  may substitute for  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  causing a decrease in  $c$ -lattice.

Figure 2 shows the normalized resistance versus temperature curve for  $\text{Tl}_{1-x}\text{Pb}_x\text{Sr}_{1.8}\text{Sb}_{0.2}\text{CaCu}_2\text{O}_7$  ( $x = 0.1 - 0.5$ ). The onset temperature ( $T_{c \text{ onset}}$ ) and zero-resistance ( $T_{c \text{ zero}}$ ) for each sample are listed in Table 2. Substitution of Pb in place of Tl ( $x = 0 - 0.5$ ) showed metallic normal state behaviors and an increase in  $T_{c \text{ zero}}$  from 26 K at  $x = 0.1$  to a maximum of 80 K at  $x = 0.5$ . Further substitution of Pb at  $x = 0.6$  caused  $T_{c \text{ zero}}$  to decrease to 27 K. The room-temperature resistivity (Table 2) was observed to decrease from 0.11 mΩ.cm ( $x = 0.1$ ) to 0.03 mΩ.cm ( $x = 0.6$ ) with Pb. The variation in room temperature resistivity of the samples with Pb content indicates increase in hole carrier concentration. Sb-free  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_7$  also showed metallic normal state behavior but with lower  $T_{c \text{ zero}}$  (62 K) and  $T_{c \text{ onset}}$  (70 K) compared to  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_{1.8}\text{Sb}_{0.2}\text{CaCu}_2\text{O}_7$ . The room temperature resistivity for Sb-free sample is 1.2 mΩ.cm and is higher than the Sb-substituted sample. This indicates that substitution of Sb at the Sr-site significantly affects superconducting properties of the material.

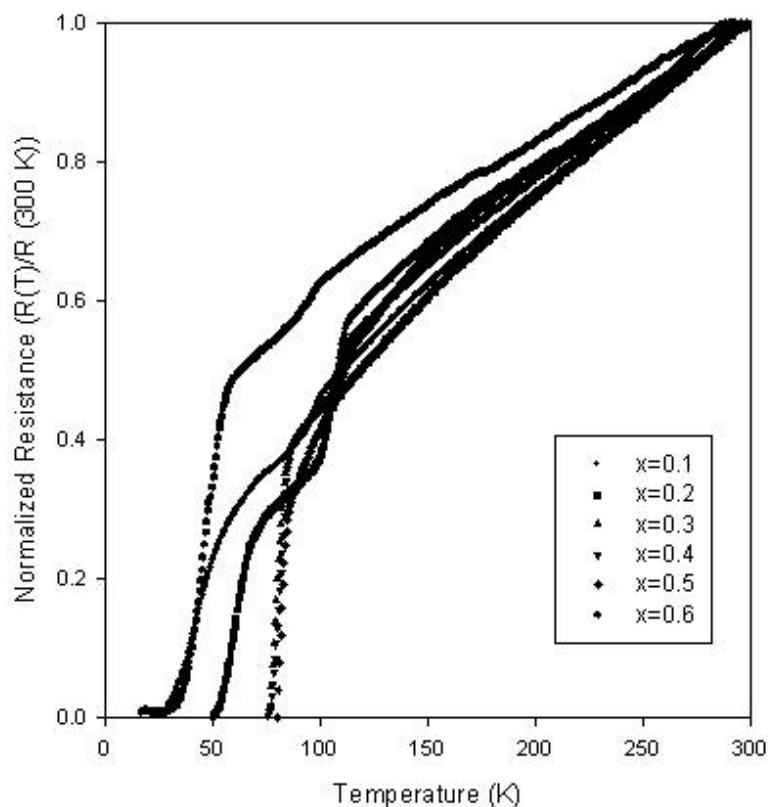


Figure 2: Normalized resistance versus temperature curve for  $\text{Tl}_{1-x}\text{Pb}_x\text{Sr}_{1.8}\text{Sb}_{0.2}\text{CaCu}_2\text{O}_7$  ( $x = 0.1 - 0.6$ ) samples.

Table 2:  $T_{c\ onset}$ ,  $T_{c\ zero}$ , resistivity (at 300 K) and  $J_c$  for  $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$  ( $x = 0.1 - 0.6$ ) samples

Sample	$T_{c\ onset}$ (K)	$T_{c\ zero}$ (K)	Resistivity at 300 K $\rho$ (m $\Omega$ .cm)	$J_c$ (A/cm $^2$ )	
				20 K	50 K
$x = 0.1$	54	26	0.11	-	-
$x = 0.2$	71	50	0.10	16.38	0.39
$x = 0.3$	85	75	0.08	19.10	13.12
$x = 0.4$	86	76	0.07	15.64	10.59
$x = 0.5$	86	80	0.05	-	-
$x = 0.6$	56	27	0.03	-	-

The highest  $T_{c\ zero}$  was observed for  $Tl_{0.5}Pb_{0.5}Sr_{2}Sb_{0.2}CaCu_2O_7$  and it is suggested to be the best superconducting behavior for the series. The possible valences of metallic ions in  $Tl_{1-x}Pb_xSr_{2-y}Sb_yCaCu_2O_7$  are  $Tl^{1+}/Tl^{3+}$ ,  $Pb^{2+}/Pb^{4+}$ ,  $Sr^{2+}$ ,  $Sb^{2+}/Sb^{3+}$ ,  $Ca^{2+}$  and  $Cu^{2+}/Cu^{3+}$ . Assuming that only copper is multivalent, Pb is in the 4+ [4] state, Tl and Sb are both +3 [7] in Tl1212 compounds, the average Cu valence can be computed. If an ideal stoichiometry is assumed, the average Cu valence for  $Tl_{1-x}Pb_xSr_{2-y}Sb_yCaCu_2O_7$  is  $2.5-(x+y)/2$ . Therefore, the optimal average Cu valence for  $x = 0.5$  and  $y = 0.2$  is 2.15+, in close agreement with previously reported optimum Cu valency for 1212 type phase [8].

Figure 3 shows critical current density ( $J_c$ ) versus temperature curve for  $Tl_{1-x}Pb_xSr_{1.8}Sb_{0.2}CaCu_2O_7$  ( $x = 0.2 - 0.4$ ). The transport critical current density,  $J_c$  decreases with temperature. The magnitude of  $J_c$  drops sharply with temperature for  $x = 0.2$ . The values of  $J_c$  ( $x = 0.3$ ) between 20 K – 80 K is consistently higher than  $J_c$  for  $x = 0.2$  and  $x = 0.4$ . The variation of  $J_c$  with temperature has been modeled by using a self-field approximation in terms of the mean grain size ( $R_g$ ) and the characteristic length ( $L_c$ ) which is related to the pinning force [9]. From this self-field model we suggest that for  $x = 0.3$  and  $x = 0.4$ ,  $R_g < L_c$ . Further discussion on the matter involving microstructural results will be reported elsewhere.

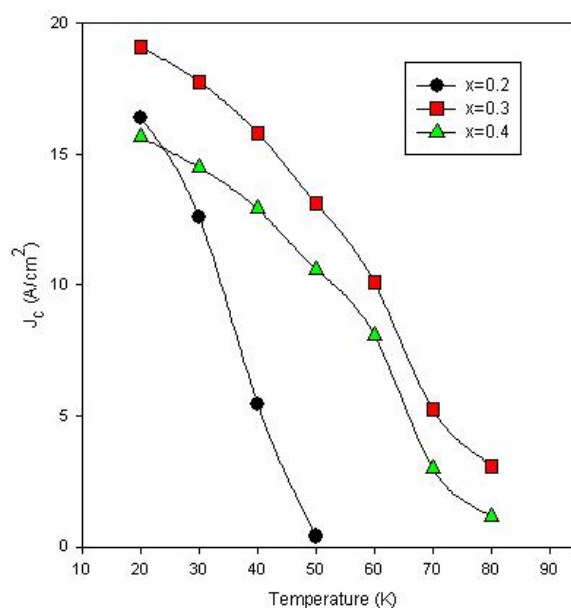


Figure 3: Temperature versus  $J_c$  in  $Tl_{1-x}Pb_xSr_{1.8}Sb_{0.2}CaCu_2O_7$  ( $x = 0.2 - 0.4$ ) samples.

## CONCLUSIONS

In conclusion, simultaneous substitution of Pb at Tl-site and Sb at Sr-site in  $Tl_{1-x}Pb_xSr_{1.8}Sb_{0.2}CaCu_2O_7$  promote 1212 phase formation and enhance superconducting properties. The highest  $T_{c\ zero}$  was observed for  $Tl_{0.5}Pb_{0.5}Sr_{1.8}Sb_{0.2}CaCu_2O_7$ . The optimal average Cu valence calculated for  $Tl_{0.5}Pb_{0.5}Sr_{1.8}Sb_{0.2}CaCu_2O_7$  is 2.15+. The transport critical current density  $J_c$  for  $x = 0.2 - 0.4$  was observed to decrease with temperature. The highest  $J_c$  was observed for  $x = 0.3$  between 20 K – 80 K.

## ACKNOWLEDGMENT

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