

CHANGES IN DOPING STATE AND TRANSPORT CRITICAL CURRENT DENSITY OF (Tl,Pb)(Sr,Yb)₂CaCu₂O₇ CERAMICS

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ABSTRACT

Two series of samples with nominal compositions of $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.1 - 0.6$) and $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0 - 0.6$) were synthesized using solid-state method and characterized by electrical resistance (dc) measurements and powder X-ray diffraction analysis. Temperature dependent electrical resistance measurements on $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.1 - 0.5$) showed metallic normal state behaviors and increase in $T_{c\ zero}$ from 61 K at $x = 0.1$ to a maximum value of 101 K at $x = 0.5$. At $x = 0.6$ the normal state behavior remained metallic but $T_{c\ zero}$ slightly decreased to 98 K. Substitution of Yb at Sr-site of $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ for $y = 0 - 0.2$ caused an increase in $T_{c\ zero}$ from 62 K ($y = 0$) to a maximum value of 93 K ($y = 0.2$). However, further substitution of Yb caused $T_{c\ zero}$ to decrease from 64 K at $y = 0.3$ to 34 K at $y = 0.5$. Superconductivity was not observed down to 16 K for $y = 0.6$. Results of transport critical current density measurements and powder X-ray diffraction are presented. The effects of Pb and Yb substitutions on superconductivity of Tl1212 are discussed in terms of ionic radius of elements, Tl 1212 phase formation and the concept of average Cu valence.

INTRODUCTION

Tl-based cuprates form a large family of high- T_c superconductor with critical temperature ranging from 0 K to 130 K [1]. However, the un-substituted Tl-based 1212-type phase $TlSr_2CaCu_2O_7$ is difficult to synthesized in a pure form because of high average Cu valence and overdoping of hole carriers [1–3]. Substitution of rare earth elements of higher valence in $TlSr_2CaCu_2O_7$ may reduce the average copper valence. These substitutions stabilized the 1212 phase and improved the superconducting behavior [4-5]. It has been reported that partial substitution of Tl by Pb and Ca by Y promotes the formation of the high- T_c phase up to 108 K in the $Tl_{0.5}Pb_{0.5}Ca_{0.8}Y_{0.2}Sr_2Cu_2O_y$ system [6].

In this paper we report superconducting properties and transport critical current density of $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.1 - 0.6$) and $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0 - 0.6$) ceramics. We present results of electrical resistance (d.c) measurements, powder X-ray

diffraction (XRD) and the variation of J_c with temperature in zero magnetic field. The superconducting properties are discussed according to the concept of average Cu valence.

EXPERIMENTAL PROCEDURE

Samples preparation

Samples with nominal compositions $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.1 - 0.6$) and $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0 - 0.6$) were prepared using solid state reaction and the precursor method. Appropriate amounts of high purity ($\geq 99.99\%$) powders of $SrCO_3$, Yb_2O_3 , CaO and CuO were mixed and ground in an agate mortar. The precursor powders were then calcined in air at around $900^\circ C$ for 48 hours with several intermittent grindings. Appropriate amounts of Tl_2O_3 and PbO were then added to the precursor and completely mixed. The powders 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 three-zone tube furnace at $1005^\circ C$ in flowing oxygen for 5-6 minutes followed by furnace cooling to room temperature.

Samples characterization

The samples were examined by powder X-ray diffraction method using Bruker D8 Advance diffractometer with $Cu-K_\alpha$ radiation. 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 lattice parameter of the samples was obtained from the computer fittings of observed d values of diffractograms for individual sample. 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 temperature sensor used was a TG-120P GaAlAs diode. The onset of superconductivity, $T_{c\ onset}$ was taken as the temperature at which the tangent of the resistance versus temperature curve intersects with the tangent of the part where resistance dropped abruptly. $T_{c\ zero}$ is defined as the temperature at which the electrical resistance readings reached zero. The transport critical current density was measured using the $1\ \mu Vcm^{-1}$ criterion.

RESULTS AND DISCUSSION

Powder X-ray diffraction patterns for $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.1 - 0.6$) showed all samples consist of dominant 1212 phase with tetragonal unit cell (space group $P4/mmm$) and 1201 minor phase. Figure 1 shows X-ray diffraction patterns for $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.5$) which consists mainly of 1212 phase. The peaks due to the 1201 phase are marked with *. The volume fraction of 1212 phase was found to increase with Pb content (Table 1). Substitution of Pb at Tl-site promotes formation of the Tl1212 phase in agreement with previous report [7-8].

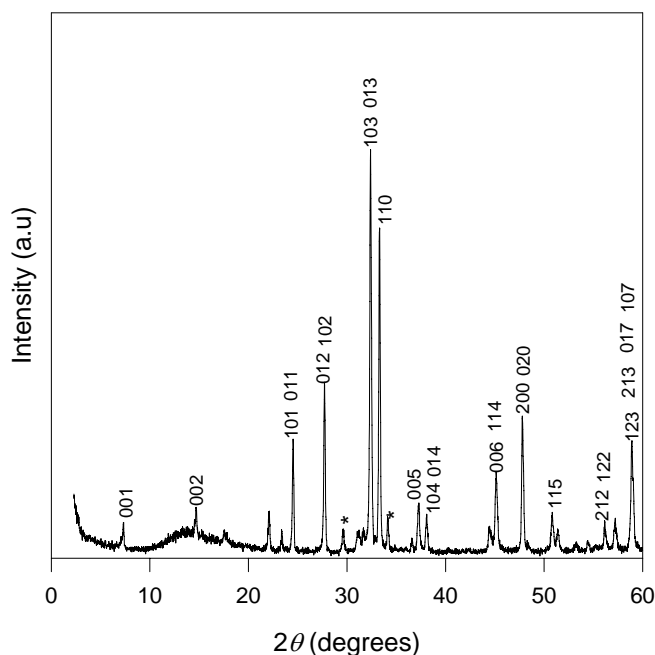


Figure 1: Powder X-ray diffraction patterns for $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.5$). Peaks identified as 1201 phase are marked with *

Table 1: $T_{c\ onset}$, $T_{c\ zero}$, resistivity (at 300 K), 1212:1201 phase ratio and lattice parameters 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 ρ (m Ω .cm)	1212 phase ratio Vol (%)	1201	1212 Unit cell a (Å) c (Å)
$x = 0.1$	92	61	4.05	82 : 18		3.791 12.004
$x = 0.2$	100	78	0.27	85 : 15		3.799 12.020
$x = 0.3$	102	89	0.07	88 : 12		3.798 12.022
$x = 0.4$	104	100	0.05	92 : 8		3.805 12.035
$x = 0.5$	105	101	0.04	94 : 6		3.806 12.036
$x = 0.6$	103	98	0.04	90 : 10		3.807 12.047

The calculated lattice parameters of the 1212 phase for $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.1 - 0.6$) are shown in Table 1. Both a - and c -lattice increased with increasing Pb content. When Pb^{4+} is substituted for Tl^{3+} , in order to satisfy charge neutrality requirement, smaller Cu^{3+} is converted to larger Cu^{2+} . Since a -lattice depends mainly on CuO plane the conversion from Cu^{3+} to Cu^{2+} caused expansion of CuO framework and increased the a -lattice.

Figure 2 shows normalized resistance versus temperature curve for $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.1 - 0.6$). Metallic normal state behaviors were observed for all samples. The onset temperature ($T_{c\ onset}$) and zero-resistance temperature ($T_{c\ zero}$) for each sample are listed in Table 1. Substitution of a higher valence Pb^{4+} for a lower valence Tl^{3+}

caused a increase in $T_{c\ zero}$ from 61 K at $x = 0.1$ to a maximum value of 101 K at $x = 0.5$. Further substitution of Pb at $x = 0.6$ caused a $T_{c\ zero}$ to slightly decrease to 98 K.

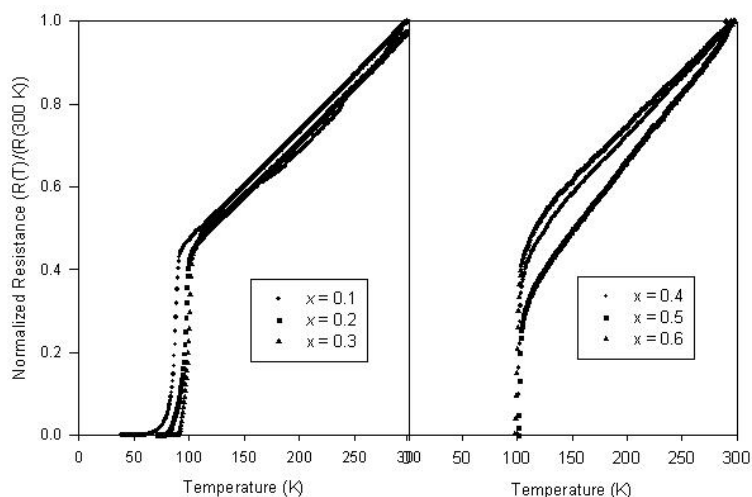


Figure 2: Normalized resistance versus temperature curve for $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.1 - 0.6$) samples.

To investigate the optimum Yb content, samples with nominal composition $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0 - 0.6$) were synthesized. Powder X-ray diffraction patterns of $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0 - 0.6$) showed a dominant 1212 phase with minor 1201 phase for Pb substituted samples ($y > 0$). Peaks for 1212 phase can be well indexed based on a tetragonal unit cell with space group $P4/mmm$. Figure 3 shows the X-ray diffraction patterns for $y = 0.5$.

Table 2 list the results of $T_{c\ onset}$, $T_{c\ zero}$, resistivity (at 300 K), 1212:1201 phase ratio and 1212 lattice parameters for $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0 - 0.6$). The sample with $y = 0$ consisted of 1201 major phase and 1212 minor phase. With a further increase in y , the 1201 phase decreased and the 1212 phase increased. The calculated lattice parameters of the 1212 phase for $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0 - 0.6$) showed a decrease of both a - and c -lattice with Yb content. The decrease in c -lattice for $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0 - 0.6$) (Table 2) suggests Yb^{3+} (ionic radius 1.008 Å) substitution for Sr^{2+} (ionic radius 1.18 Å).

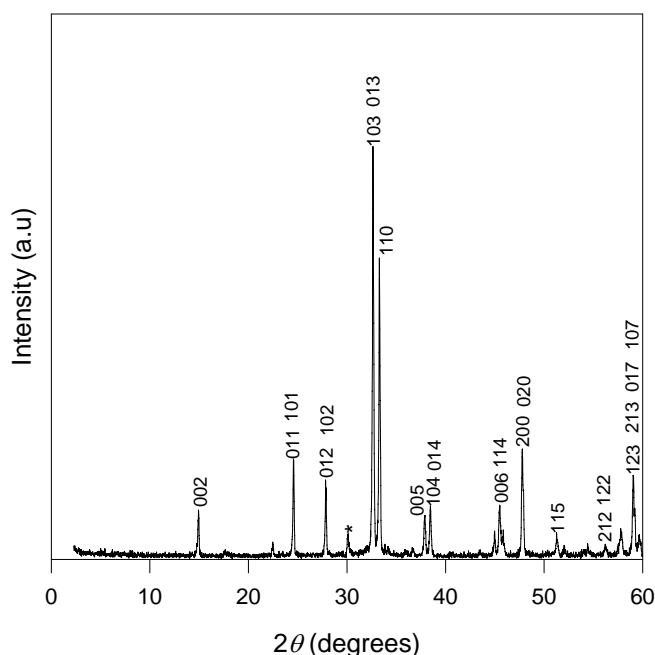


Figure 3: Powder X-ray diffraction patterns for $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O$ ($y = 0.5$). Peaks identified as 1201 phase are marked with *

Table 2 : $T_{c\ onset}$, $T_{c\ zero}$, resistivity (at 300 K), 1212:1201 phase ratio and lattice parameters for $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O$ ($x = 0 - 0.6$) samples

Sample	$T_{c\ onset}$ (K)	$T_{c\ zero}$ (K)	Resistivity at 300 K ρ (m Ω .cm)	1212 phase ratio Vol (%)	1201	1212 Unit cell a (Å) c (Å)
$y = 0$	70	62	1.20	35 : 65		3.805 12.054
$y = 0.1$	98	67	0.28	51 : 49		3.808 12.049
$y = 0.2$	105	103	0.10	85 : 15		3.806 12.036
$y = 0.3$	89	64	0.08	91 : 9		3.804 11.958
$y = 0.4$	70	55	0.07	96 : 4		3.800 11.894
$y = 0.5$	47	34	0.05	97 : 3		3.794 11.889
$y = 0.6$	36	-	0.04	93 : 7		3.790 11.868

Normalized resistance versus temperature curve of $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0 - 0.6$) are shown in Figure 4. Yb-free, $Tl_{0.5}Pb_{0.5}SrCaCu_2O_7$ showed metallic normal state behavior with $T_{c\ onset}$ of 70 K and $T_{c\ zero}$ of 62 K. Substitutions of Yb at Sr-site of $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$ ($y = 0.1 - 0.2$) showed metallic normal state behaviors and a increase in $T_{c\ onset}$ of 98 K and $T_{c\ zero}$ of 67 K at $y = 0.1$ to a maximum value in $T_{c\ onset}$ of 105 K and $T_{c\ zero}$ of 103 K at $y = 0.2$. Further substitution of Yb caused $T_{c\ zero}$ to decrease from 64 K at $y = 0.3$ to 34 K at $y = 0.5$. Metallic normal state behavior are observed for $y = 0.6$ with $T_{c\ onset}$ 36 K. However, zero resistance was not observed down to 16 K.

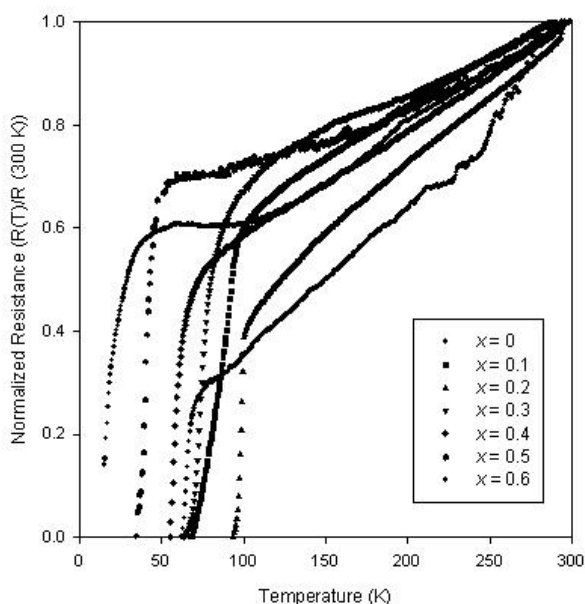


Figure 4: Normalized resistance versus temperature curve for $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O$ ($x = 0 - 0.6$) samples.

Considering $T_{c\ onset}$, $T_{c\ zero}$ and normal state behavior for serial samples, $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ and $Tl_{0.5}Pb_{0.5}Sr_{2-y}Yb_yCaCu_2O_7$, the sample with $x = 0.5$ and $y = 0.2$, respectively, is suggested to have showed the best superconducting behavior. The possible valences of metallic ions in $Tl_{1-x}Pb_xSr_{2-y}Yb_yCaCu_2O_7$ are Tl^{1+}/Tl^{3+} , Pb^{2+}/Pb^{4+} , Sr^{2+} , Yb^{2+}/Yb^{3+} , Ca^{2+} and Cu^{2+}/Cu^{3+} . However, Pb has been established to have definite valence state of 4+ at the Tl-site[2] while Tl was suggested to be in the 3+ state [9]. So, assuming that only Cu is multivalent, Pb is in the 4+ state, Tl and Yb are in 3+ state, if an ideal stoichiometry is assumed, the average Cu valence of $(Tl_{1-x}Pb_x)(Sr_{2-y}Yb_y)CaCu_2O_7$ is $2.5-(x + y)/2$. Therefore, the optimal average Cu valence for the above two series of samples is 2.15+ in close agreement with previously reported optimum Cu valence for Tl1212 type phase [10].

Figure 5 shows the temperature dependence of J_c in zero magnetic field for $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.3 - 0.6$). J_c increased with decreasing temperature as a consequence of thermal activated flux creep [11]. The magnitude of J_c drops abruptly with temperature in the range 40 – 70 K for $x = 0.3$. J_c varies as a parabolic function and a slightly drop occurs in the temperature range 60 – 90 K for $x = 0.4$ and 0.5. For $x = 0.6$ J_c varies as a linear function. This phenomenon has been modeled by using a self-field approximation in terms of mean grain size (R_g) and the characteristic length (L_c) which is related to the pinning force [11]. From this self-field model we suggest that for $x = 0.4$ and 0.5, $R_g > L_c$ and for $x = 0.3$, $R_g < L_c$. Microstructural investigation of samples will be performed and reported elsewhere.

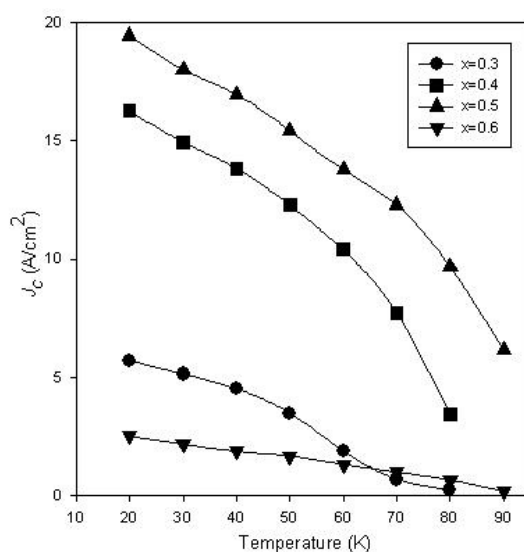


Figure 5: Temperature versus J_c in $Tl_{1-x}Pb_xSr_{1.8}Yb_{0.2}CaCu_2O_7$ ($x = 0.3 - 0.6$) samples.

CONCLUSIONS

In conclusion, double substitution of Pb at Tl-site and Yb at Sr-site in $(Tl_{1-x}Pb_x)(Sr_{2-y}Yb_y)CaCu_2O_7$ promote dominant 1212 phase formation. The average Cu valence for $Tl_{0.5}Pb_{0.5}Sr_{1.8}Yb_{0.2}CaCu_2O_7$ which showed the best superconducting behavior is 2.15+. J_c was observed to decrease with increasing temperature as a consequence of thermal activated flux creep. The highest J_c between 20 K – 90 K was observed for $x = 0.5$.

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REFERENCES

- [1] Z.Z.Sheng, A.M.Hermann, D.C.Vier, S.Schultz, S.B.Oseroff, D.J. Gerge and R.M.Hazen, *Phys.Rev.B* **38** (1988)7074
- [2] M.A. Subramaniam, C.C. Torardi, J.Gopalakrishnan, P.L Gai, J.C. Calabrese, T.R. Askew, R.B. Flippen and A.M. Sleight, *Science* **242** (1988) 249
- [3] T.Doi, K.Usami and T.Kamo, *Jpn J. Appl. Phys.***28** (1990)L57
- [4] Z.Z.Sheng, L.Sheng, X.Fei and A.M.Hermann, *Phys.Rev.B* **38** (1988) 2918
- [5] J.K Liang Y.L.Zhang G.H.Rao, X.R.Cheng, S.S.Xie and Z.X.Zhao, *Solid State Comm*, **70**, (1989) 661
- [6] R.S.Lui, J.M. Liang S.F.Wu, Y.T.Huang, P.T.Wu and L.J.Chen, *Physica* **C162** (1989) 869
- [7] Z.Z. Sheng, D.X. Gu, Y. Xin, D.O. Pederson, L.W. Finger, C.G. Hadidiacos and R.M. Hazen, *Mod. Phys Lett.* **B5** (1991) 635

- [8] R. S. Liu, J. M. Liang, Y.T.Huang, W.N. Huang, S.F. Wu, H.S. Koo, P.T.Wu and L. J. Chen, *Physica C* **162** (1989) 869
- [9] S.Nakajima, M.Kikuchi, Y.Syono, T.Oku, D.Shindo, K.Hiraga, N.Kobayashi, H.Iwasaki and Y.Muto, *Physica C* **158** (1989) 471
- [10] Z.Z Sheng Y.F.Li and D.O. Pederson, *solid state Comm.* **V80, N11** (1991)913.
- [11] Nasri A-hamid and R.Abd-shukor, *Supercond.Sci.Technol.***40** (2001)113.
- [12] A.Kilic, K.Kilic and S.Seoussi, *J.Appl.Phys* **84**, (1998) 3254