

## **SUPERCONDUCTIVITY OF $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_8$ CERAMICS PREPARED VIA CO-PRECIPIATION METHOD**

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### **ABSTRACT**

In this paper, synthesis of  $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  superconductors via co-precipitation route is reported. Acetates of thallium, bismuth, strontium, calcium, yttrium and copper were mixed according to required stoichiometric ratios and reacted to form oxalates precipitates. The precipitates were subjected to various heating conditions for best conversion to oxides and carbonates. The co-precipitated powders were placed in an open crucible (CPR2 sample), in a closed crucible (CPR1 sample) and pressed into pellet form (CPR3 sample) before calcination at 600°C. CPR4 sample was prepared using excess thallium acetate in the starting solution composition and CPR5 sample was prepared by direct addition of  $Tl_2O_3$  powder to the co-precipitated powder before sintering. All the samples were sintered at 980°C for 5 minutes in flowing oxygen. Temperature dependent electrical resistance (dc) measurements showed semiconductor-like normal state behavior for CPR1, CPR2 and CPR3 with  $T_{conset}$  between 94 K – 108 K and  $T_{c\ zero}$  between 29 K – 70 K. Addition of 10 wgt% excess  $Tl_2O_3$  (CPR5 sample) increased  $T_{c\ zero}$  to 74 K and showed semiconductor-semimetallic normal state behavior. CPR4 which was prepared with excess thallium acetate showed metallic normal state behavior and  $T_{c\ zero}$  of 80 K. The values of transport critical current density ( $J_c$ ) of the samples determined by four-point-probe measurement using the  $1\mu Vcm^{-1}$  criterion are reported. X-Ray diffraction analysis showed formation of dominant 1212 phase in all co-precipitated samples. The effects of preparation procedures and addition of extra thallium in the starting composition on superconducting properties and Tl1212 phase formation are discussed.

### **INTRODUCTION**

Several synthesis routes are being used to produce Cu-O based superconducting ceramic materials. These include conventional solid state reaction, sol-gel, freeze drying and co-precipitation, to name a few.<sup>(1-3)</sup> Although solid state reaction is the most commonly employed synthesis procedure, solution based procedures have a fundamental advantage over conventional solid state route as they start with a homogeneous mixture of cations. Moreover, solution based procedures are usually time saving and less costly.<sup>(4)</sup>

Co-precipitation is a solution based reaction which is based on simultaneous precipitation of soluble components with a precipitating agent. Cations of either nitrates, carbonates, hydroxides, acetates and oxalates are precipitated as oxalates with oxalic acid or citrates with citrate acid as the precipitating agent. Despite the advantages, synthesizing superconducting ceramic materials via co-precipitation reaction is complicated. The process needs to be carefully monitored to get the desired composition ratio of the intended superconducting material.

TlSr1212 is an interesting compound in Tl-based family of superconducting cuprates and is analogous to the Y123 system.<sup>(7)</sup> Although quite a number of work has been done on TlSr1212 via the solid state route, similar report on TlSr1212 using co-precipitated method is limited. This is probably due to difficulty of controlling the stoichiometry of precipitated cations due to volatility of thallium oxide. On the other hand, numerous elemental substitutions have been reported for TlSr1212. Substitutions of Bi and Y at Tl and Ca sites, respectively have been reported to improve superconducting properties of the compounds.<sup>(5,6)</sup> At present, to our knowledge there is no report on synthesis of  $(\text{Tl}_{0.8}\text{Bi}_{0.2})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_7$  via the co-precipitated method.

In this paper, we report the effect of different preparation conditions and addition of excess thallium on co-precipitated  $(\text{Tl}_{0.8}\text{Bi}_{0.2})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_7$  superconductors. The normal and superconducting state behaviors of the co-precipitated superconducting materials were compared to similar composed material prepared via the conventional solid-state reaction. Transport critical current densities ( $J_c$ ) of the superconducting materials from both synthesizing routes are also reported.

## EXPERIMENTAL

The co-precipitated process used was in general similar to that described in Ref. [8]. Reagent-grade thallium, bismuth, strontium, calcium, yttrium and copper acetates with stoichiometric ratios of 0.8:0.2:2:0.8:0.2:2 were dissolved in 200 ml of glacial acetic acid. Appropriate amount of oxalic acid was separately dissolved in 200 ml of glacial acetic acid. The former solution was added slowly to the latter while maintaining solution pH of around 1.8 using 25 % ammonium hydroxide. The mixing was done under vigorous stirring to ensure complete precipitation process. The mixture containing oxalates precipitates was kept overnight and was filtered via vacuum filtration. The sky blue precipitates were dried at 80°C for 24 hours and were ground to powdery state. The calcination for co-precipitated samples was at 600°C for a duration of 20 hours in air. Before calcination, for CPR3 sample, the oxalate powder was put in a 13 mm-diameter Specac die and pelletized under a pressure of around 5000 kg/cm<sup>2</sup>. For CPR2 the oxalate powder was placed in an open crucible while for CPR1 the oxalate powder was placed in a covered crucible. After heating the samples were reground and pressed into pellets before sintering at 980°C for 5 minutes in flowing O<sub>2</sub>.

In the solid state route (SSR sample), the same stoichiometric ratios of high purity (99.995%) oxides and carbonate were ground into homogenized powder. The powder was calcined in an exposed crucible at 900°C for 48 hours, with an intermittent grinding. The heated powder was then ground and made into pellets prior to sintering process.

Co-precipitated sample prepared from the same acetates as above but with stoichiometric ratios of 0.96:0.2:2:0.8:0.2:2 (CPR4 sample) was similarly calcined at the same temperature as sample CPR2 and was also made into pellets for the sintering process. Another co-precipitated sample (CPR5) was prepared from stoichiometric ratios of 0.8:0.2:2:0.8:0.2:2 and calcined at the same temperature as sample CPR2 but was directly added with 10 wgt% of high purity (99.995%) thallium oxide powder before being pelletized for the sintering process. All samples were sintered in oxygen at 980°C for 5 minutes followed by controlled furnace cooling to 700°C and slow cooling to room temperature. The oxygen was kept flowing until the temperature reached below 300°C.

Electrical resistance (dc) measurements were carried out using the standard 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. Room temperature resistivity was investigated using the Van der Pauw technique. The phase characterization was done by powder x-ray diffraction (XRD) using Siemens D5000 diffractometer with Cu-K $\alpha$  source. Transport critical current densities ( $J_c$ ) were measured in zero magnetic field using electric field criterion of 1  $\mu\text{Vcm}^{-1}$ .

## RESULTS AND DISCUSSION

The dependence of electrical resistance on temperature of the co-precipitated samples which are subjected to various heating conditions, are shown in Fig. 1. The values of  $T_{c\text{ onset}}$ ,  $T_{c\text{ zero}}$ , transition width ( $\Delta T_c$ ), resistivity (300 K),  $J_c$  and normal state behavior of CPR1, CPR2 and CPR3 samples are tabulated in Table 1. The resistance of the CPR1, CPR2 and CPR3 samples with temperature showed semiconductor-like normal state behavior with  $T_{c\text{ onset}}$  ranging from 94 K to 108 K. The CPR2 sample which is calcined in an exposed crucible, displayed the highest  $T_{c\text{ onset}}$  of 108 K and  $T_{c\text{ zero}}$  of 70 K. The result suggests that the best conversion process from oxalates to oxides and carbonates is in ambient air. Although different heating conditions are applied to the oxalates powder, no large variations are observed on the samples  $T_{c\text{ onset}}$  values. However, heating the powder in an exposed condition improved the materials normal state behavior. The semiconductor-like normal state behaviors of CPR1, CPR2 and CPR3 samples in contrast to the metallic normal state behavior of SSR sample indicates that the composition of the oxalate precipitate may be different from the original solution composition. Stoichiometric composition of precipitates depends on the pH of the solution, which can affect metals solubility and metals complexations, in particular the copper complexation.<sup>(9)</sup> In addition, this could be due to thallos oxide evaporation during the sintering since solid thallium oxide is easily converted to gaseous thallos oxide at temperatures between 750°C and 775°C.<sup>(10)</sup>

Figure 2 shows the temperature dependence of electrical resistance for three samples; CPR4, CPR5 and SSR. Co-precipitated  $\text{Tl}_{0.96}\text{Bi}_{0.2}\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_7$  (CPR4) has a  $T_{c\text{ onset}}$  of 102 K and  $T_{c\text{ zero}}$  of 80 K whereas co-precipitated  $\text{Tl}_{0.8}\text{Bi}_{0.2}\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_7$  with additional 10 wgt%  $\text{Tl}_2\text{O}_3$  (CPR5) ) has a

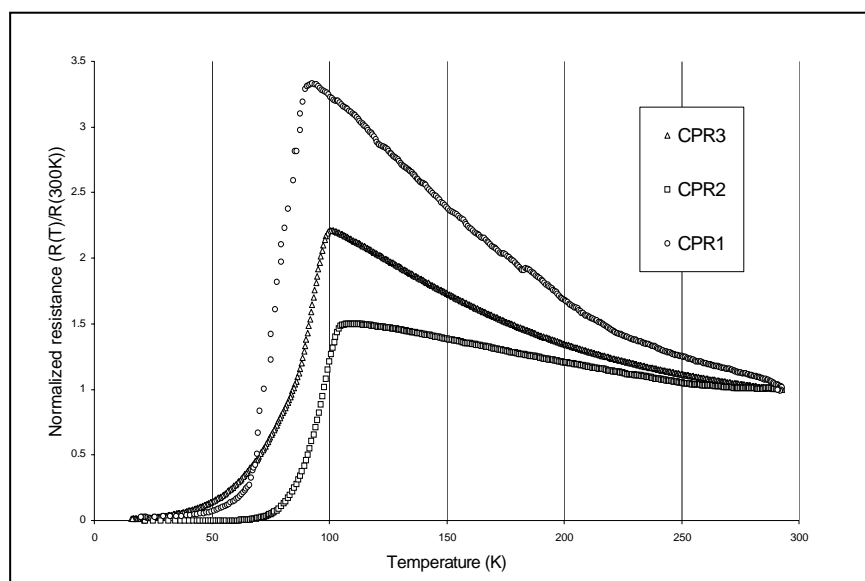


Figure1 : Normalized resistance versus temperature curve for co-precipitated  $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  under different heating conditions

lower  $T_{c\ onset}$  of 97 K and a lower  $T_{c\ zero}$  of 74 K. Another sample (SSR) which is derived via the solid state route has a  $T_{c\ onset}$  of 109 K and a  $T_{c\ zero}$  of 93 K. From the results, it is interesting that additional thallium acetate in the starting solution composition of the co-precipitated sample increased its zero transition temperature as well as caused its normal state behavior to change from semiconductor-like to metallic behavior. Additional thallium acetate also reduced the superconducting transition width from 38 K to 22 K. This indicates that the thallium content in the starting composition is responsible for variations in the electrical properties of the material. Further investigation is needed to improve the superconducting quality of the co-precipitated materials. The resistivity values at 300 K (Table 1) indicate variation in charge carrier concentration with sample preparation and starting stoichiometry.

Figure 3 shows the X-ray diffraction (XRD) patterns for co-precipitated  $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  (CPR2 sample), co-precipitated  $Tl_{0.96}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  (CPR4 sample), co-precipitated  $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  with additional 10 wgt%  $Tl_2O_3$  (CPR5 sample), and  $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  prepared by solid state route (SSR sample). The Tl1212 peaks are indexed as tetragonal unit cell with space group P4/mmm. The SSR sample consists essentially of single phased Tl1212. The XRD for co-

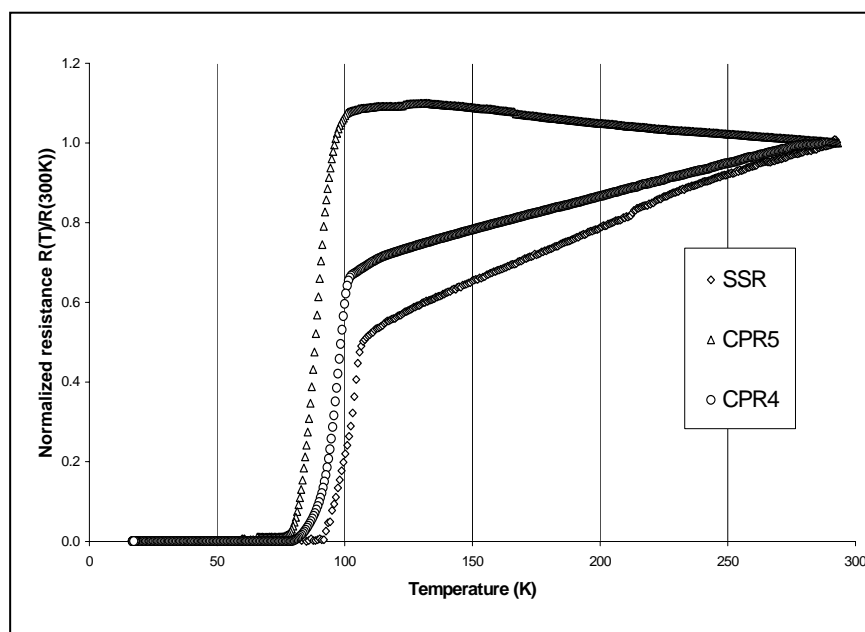


Figure 2 : Normalized resistance versus temperature curve for co-precipitated  $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  (CPR5), co-precipitated  $Tl_{0.96}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  (CPR4) and  $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  (SSR) prepared by conventional solid state route

Table 1 : Sample critical temperatures,  $T_c$ , transition width,  $\Delta T_c$ , room temperature resistivity,  $\rho$ , critical current densities,  $J_c$  and normal state behavior of the superconducting ceramics

Sample	$T_c$ (K)		$\Delta T_c$ (K)	$\rho$ at 300K (m $\Omega$ .cm)	$J_c$ at 40K (A/cm <sup>2</sup> )	Normal state behavior
	Onset	Zero				
CPR1	94	42	52	-	-	semiconducting
CPR2	108	70	38	0.135	0.35	semiconducting
CPR3	99	29	70	-	-	semiconducting
CPR4	102	80	22	0.001	1.42	metallic
CPR5	97	74	23	0.053	0.27	semiconducting - semimetallic
SSR	109	93	16	0.003	2.14	metallic

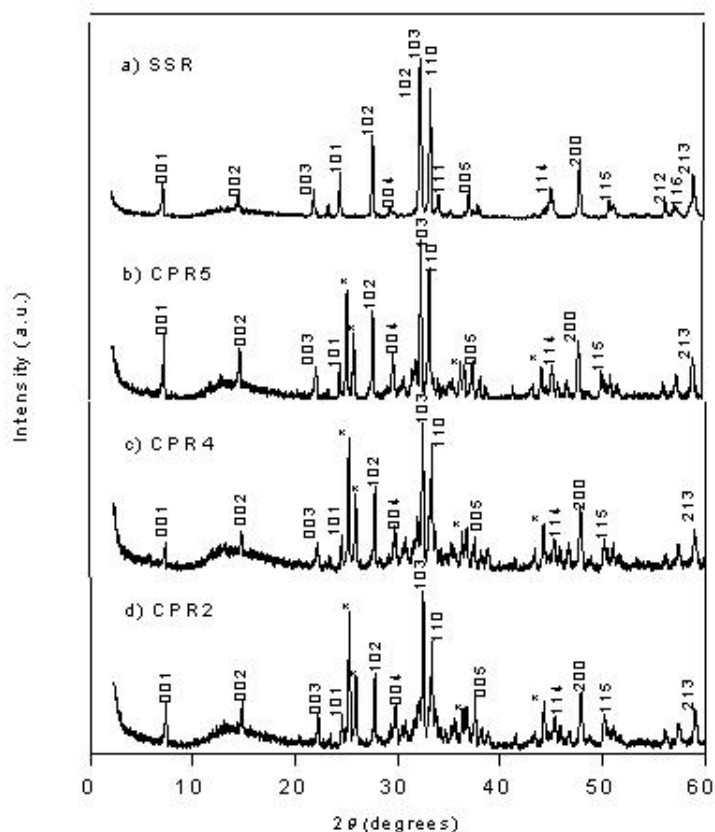


Figure 3 : X-ray diffraction pattern for CPR2, CPR4, CPR5 and SSR samples. The peaks identified as  $\text{SrCO}_3$  are indicated by \*

precipitated samples showed existence of Tl1212 phase and impurity peaks which are identified mainly as  $\text{SrCO}_3$  and are found in all the co-precipitated samples. The  $\text{SrCO}_3$  impurity peaks in Figure 3 are indicated by asterisk(\*). These peaks shows existence of unreacted  $\text{SrCO}_3$ . It is possible that since the calcination of the co-precipitated samples was done at a relatively low temperature of  $600^\circ\text{C}$  and the fact that conversion of  $\text{SrCO}_3$  to  $\text{SrO}$  takes place at higher temperatures,<sup>(8)</sup> some unreacted  $\text{SrCO}_3$  still remained in the sample. However, it is evident from the XRD that a considerable quantity of the co-precipitated material was successfully converted to Tl1212. Transport critical current density values at zero magnetic field for all samples are given in Table 1. The highest  $J_c$  for co-precipitated samples was observed for the CPR4 sample and it is comparable to the  $J_c$  for the SSR sample. Since excess thallium was observed to improved superconducting properties of the ceramics and XRD showed existence of significant amount of unreacted  $\text{SrCO}_3$ , synthesis of higher quality 1212 sample by co-precipitation may depend not only on starting composition but also on thermal treatment of the ceramics. Further work to improve sample quality is in progress.

## CONCLUSION

In conclusion, we have successfully synthesized Tl1212 from  $\text{Tl}_{0.8}\text{Bi}_{0.2}\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_7$  starting composition via co-precipitation method. However, XRD shows existence of unreacted  $\text{SrCO}_3$  in all samples. Excess thallium acetate in the starting

solution composition was found to improve normal state behavior and superconducting properties of the ceramics. The highest  $T_{c\ zero}$  of 80 K is achieved by co-precipitated CPR4 sampel. The value of transport critical current density ( $J_c$ ) of the co-precipitated CPR4 sample is comparable to the  $J_c$  value of the SSR sample synthesized by the conventional solid state route.

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