

## **SYNTHESIS OF $Tl_{0.85}Cr_{0.15}Sr_2CaCu_2O_{7-\delta}$ SUPERCONDUCTOR FROM COPRECIPIATION Tl-FREE PRECURSOR**

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### **ABSTRACT**

In this study, high purity Tl1212 superconductor samples were successfully synthesized from  $Tl_{0.85}Cr_{0.15}Sr_2CaCu_2O_{7-\delta}$  nominal starting composition by a two-step solid-state reaction method using Tl-free precursor powder prepared from coprecipitation method. The effect of using two different excess amount of precipitating agent (case I and case II) to react with metal oxalates in precursor preparation by coprecipitation method was investigated. XRD pattern of all samples sintered at 1000 °C for 4 minutes essentially showed formation of high purity 1212 phase. The results of samples' zero resistance critical temperature,  $T_{c\ zero}$  were between 98-99 K and bulk critical current density,  $J_c$  measured at 40 K in zero magnetic fields were around 5-9 A/cm<sup>2</sup>. SEM investigation on the sample derived from case I and II revealed distinctly different sample morphology. The synthesized high purity sample can be useful as starting material for high temperature superconductor tapes fabrication.

### **INTRODUCTION**

The most common method to synthesize high temperature superconductor (HTSC) is the conventional solid state method. In this method, the precursor powder was prepared from high purity metal oxides and/or carbonates that are mixed and ground, often being ball-milled to enhance mixing, and to reduce powder particle sizes. The mixed powders are then heated at high temperature to allow inter-diffusion of solid particles. However, in the case of solid state synthesis of Tl-based superconductors, it is often difficult to get high-purity samples, as the melting point of  $Tl_2O_3$  is 717 °C at atmospheric pressure and it evaporates quickly at higher temperatures [1]. This has resulted in very few reports on the characterization of these compounds. The effort to improve the quality of the compound/ material is important in order to obtain good performance of the material as well as its application in technology can be realized.

Amongst Tl-based superconductors, Tl1212 and its derivatives are potential compounds for application in magnetic fields. The presence of single Tl-O insulating layer in the compounds' structure was suggested to lead to stronger coupling between adjacent Cu-O planes [2]. For single elemental substitution into Tl1212, the Cr-doped Tl1212 is of particular interest because they show high transition temperature. The (TlCr) $Sr_2CaCu_2O_7$  in particular, was found to super conduct at around 100 K [3] and this is higher than either (TlBi) $Sr_2CaCu_2O_7$  [4] or (TlPb) $Sr_2CaCu_2O_7$  [5] superconductors. Cr doping of around 10% to 20% has been found to give the optimum

transition temperature [3,6]. Several works have reported the synthesis of Cr-substituted Tl1212 using the solid state [7] and coprecipitated Tl-containing [8] precursor method. However, while solid state diffusion of oxides and/or carbonates needs extensive heating at high temperature for inter-diffusion of solid particle, the use of coprecipitated Tl-containing precursor is expected to cause unavoidable Tl-loss during both calcination and sintering stages. Therefore, the use of coprecipitated Tl-free precursor in a rapid sintering process is recommended to achieve higher purity samples as the loss of thallium is only limited to the sintering stage.

In this paper, we describe the synthesis of a high purity (TlCr)Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>7</sub> superconductor from coprecipitated Tl-free precursor. Results of phase characterization using powder X-ray Diffraction (XRD), zero resistance critical temperature ( $T_c$ ), transport critical current density ( $J_c$ ) at 40 K and scanning electron microscope (SEM) investigations are presented and discussed.

## METHODOLOGY

The coprecipitated Tl-free precursor was derived from reaction between reagent-grade Sr, Ca, Cu acetates solution having stoichiometric ratios of 2:1:2 and a slight excess solution of oxalic acid (case I). The use of a large excess of precipitating agent was also investigated (case II). The precipitation of the precursors (P1 of case I and P2 of case II) were carried out under monitored condition of pH 2 and at a temperature of 2 °C. After filtering and drying of the precipitate overnight at 80 °C, the powder was calcined at 850 °C for 20 hours in air at heating and cooling rates of 1 °C/min. Appropriate amounts Tl<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> of 99.995% purity were later added to the calcined powder according to nominal starting composition of Tl<sub>0.85</sub>Cr<sub>0.15</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>7</sub>. The mixture was completely ground and pressed into pellets. The pellets were sintered at 1000 °C for 4 minutes in flowing O<sub>2</sub> followed by furnace cooling to room temperature (S1 of case I and S2 of case II).

Electrical resistance (dc) measurements for the S1 and S2 samples 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. The phase characterization was done by powder XRD using PANalytical model Xpert PRO MPD diffractometer with Cu-K<sub>α</sub> source. The 1212 lattice parameters of all samples were calculated using computer fittings of observed  $d$  values from peak positions determined from the XRD data. The volume fractions of 1212 and 1201 phases were estimated from the intensities of major phase, minor phase peaks and other peaks observed, as used by Driessche *et al.* [9] and Matsuhita *et al.* [10] namely, the Eq. 1 and 2 below;

$$\text{Tl1212\%} = \frac{\sum I_{1212}}{\sum I_{1212} + \sum I_{1201} + \sum I_{\text{others}}} \times 100\% \quad (1)$$

$$Tl_{1201}\% = \frac{\sum I_{1201}}{\sum I_{1212} + \sum I_{1201} + \sum I_{\text{others}}} \times 100\% \quad (2)$$

Where,

I = Peak intensity of the present phase.

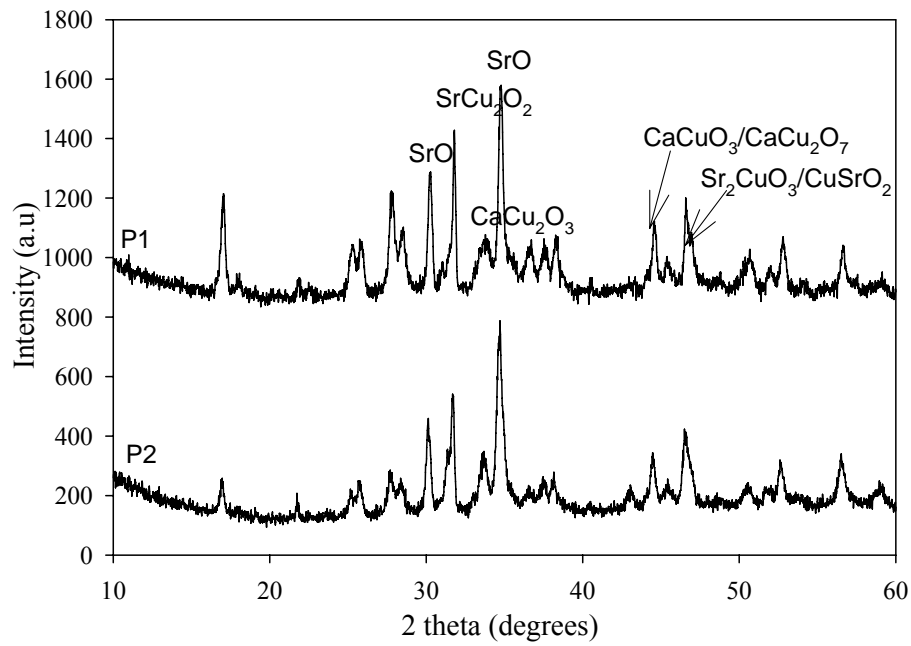
Transport critical current,  $I_c$  was determined from the I-V characteristic at 40 K using electrical field criterion of  $1\mu\text{V}/\text{cm}$ . The transport critical current density,  $J_c$  of the bar shaped sample with cross sectional dimension of 1.5 mm x 2.5 mm was calculated by dividing  $I_c$  with the corresponding cross sectional area. Scanning electron micrographs of the S1 and S2 samples were recorded using LEO 982 Gemini scanning electron microscope.

## RESULTS AND DISCUSSION

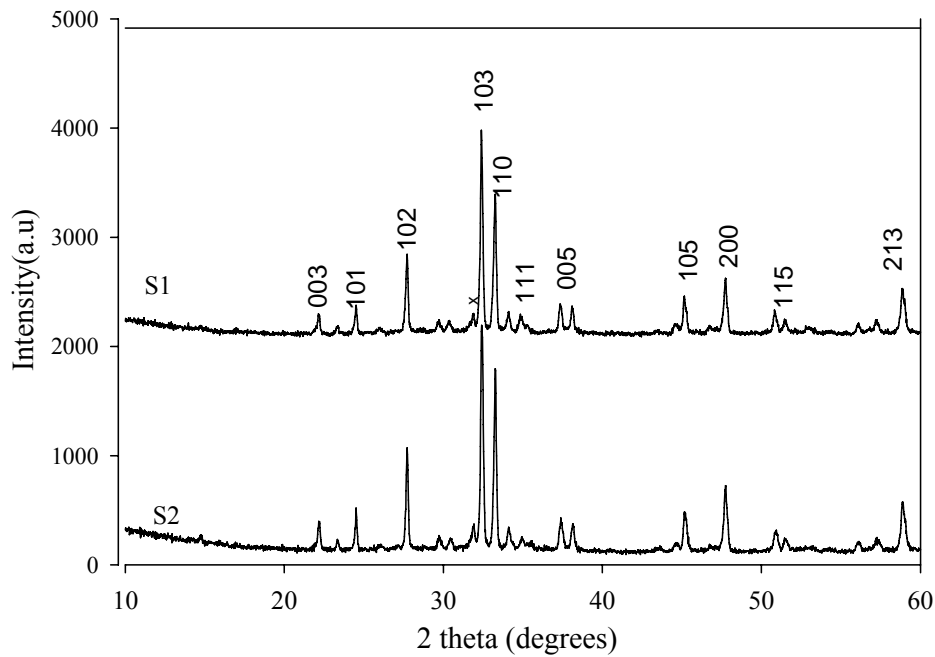
Figure 1(a) and 1(b) shows the XRD patterns of the precursors (P1 and P2) and sintered  $Tl_{0.85}Cr_{0.15}Sr_2CaCu_2O_7$  samples (S1 and S2), respectively. In Figure 1(a), XRD of both calcined precursors P1 and P2 indicate presence of various forms of oxide such as SrO,  $CaCu_2O_3$  and  $SrCu_2O_2$ . The formation of these oxides at this particular stage is crucial as full conversion of oxalates into oxides and not carbonates will ensure samples of higher purity after sintering process. In Figure 1(b), the diffractograms essentially showed peaks due to the 1212 phase that were indexed based on tetragonal unit cell with space group P4/mmm. Peaks representing minor 1201 phase were also identified and marked as an asterisk (\*) in the diffractograms. The non-existence of  $SrCO_3$  impurity peaks in the diffractograms of the sintered S1 and S2 samples indicates  $SrCO_3$ -free form of  $Tl_{0.85}Cr_{0.15}Sr_2CaCu_2O_7$  samples. This is unlike our previous work on  $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$  using coprecipitated Tl-containing precursor where rapid sintering at a high temperature produced sample with mixed 1212:1201 phase and  $SrCO_3$  impurity [11]. Table 1 lists onset critical temperature ( $T_{c \text{ onset}}$ ), zero resistance critical temperature ( $T_{c \text{ zero}}$ ), resistivity values at 300 K and 1212:1201 volume % ratio for S1 and S2 samples.

Table 1 :  $T_{c \text{ onset}}$ ,  $T_{c \text{ zero}}$ ,  $\Delta T_c$ ,  $J_c$ , (40K) and 1212:1201 vol. % for  $Tl_{0.85}Cr_{0.15}Sr_2CaCu_2O_7$  samples prepared using different methods

Reference / Method	$T_{c \text{ onset}}$ (K)	$T_{c \text{ zero}}$ (K)	$\Delta T_c$ (K)	$J_c$ , (40K) (A/cm <sup>2</sup> )	1212:1201 (vol. %)
This work (Coprecipitation Tl-free with slight excess of precipitating agent) S1	102	99	3	5	99:1
This work (Coprecipitation Tl-free with large excess of precipitating agent) S2	102	98	4	9	99:1
[8] (Coprecipitation Tl-containing)	118	100	18	-	-
[7] (Solid state)	104	-	-	-	90:10



(a)



(b)

Figure 1: Powder X-ray diffraction patterns for (a) calcined P1 and P2 precursors and (b) sintered S1 and S2  $Tl_{0.85}Cr_{0.15}Sr_2CaCu_2O_7$  samples. Peak identified as 1201 phase is marked with an asterisk (\*).

Normalized resistance versus temperature curve of the sintered S1 sample is shown in Figure 2. The sample showed metallic normal state behavior with  $T_{c\ onset}$  and  $T_{c\ zero}$  of 102 K and 99 K, respectively. Likewise are the  $T_{c\ onset}$  and  $T_{c\ zero}$  of S2 sample which are tabulated in Table 2. Based on the magnitude of the  $T_{c\ onset}$  value, it is suggested that superconductivity in the S1 and S2 samples is due to the Tl1212 phase [12]. The appearance of a single and sharp transition to  $T_{c\ zero}$  as shown in Figure 2 is another factor that further supports this result. The sharp transition was also retained in the case of the S2 sample. Although there is presence of a small volume of minor 1201 phase in both the S1 and S2 samples, it does not affect its superconductivity as the observed  $T_{c\ onset}$  of Tl1201 was reported to be below 50 K [13]. In addition, the transition width ( $\Delta T_c$ ) for the samples prepared in this work is the smallest compared to the  $\Delta T_c$  of samples prepared using other preparation methods (Table 1). This suggests that the purity of  $Tl_{0.85}Cr_{0.15}Sr_2CaCu_2O_7$  sample can be enhanced by using coprecipitation derived Tl-free precursor method described in this work.

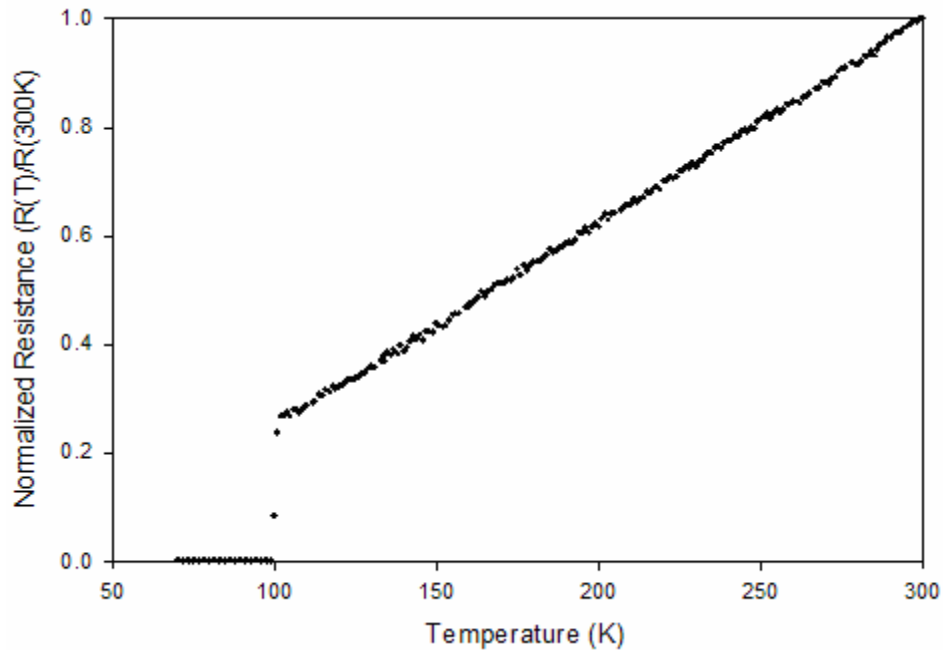
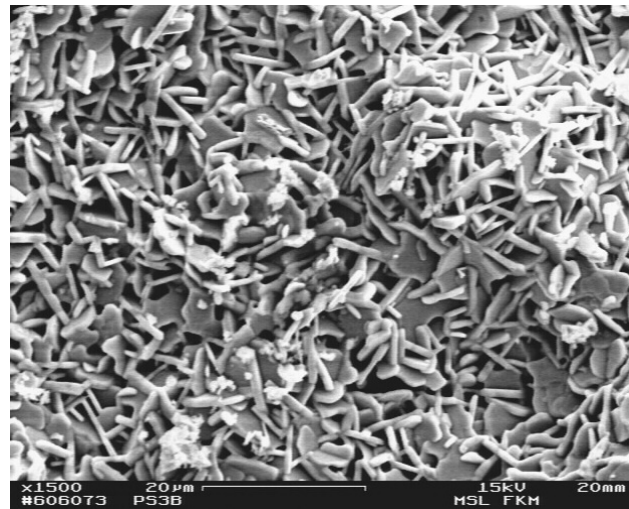


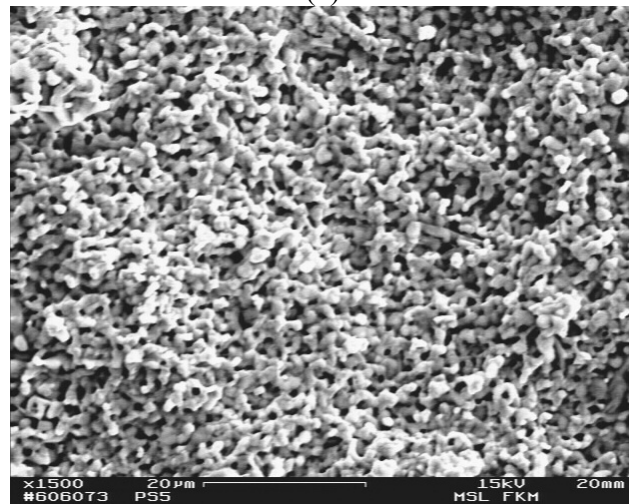
Figure 2: Typical normalized resistance versus temperature curve for  $Tl_{0.85}Cr_{0.15}Sr_2CaCu_2O_7$  sample synthesized from coprecipitated Tl-free precursor route.

Figure 3 (a) and (b) shows the SEM micrograph of the S1 and S2 samples, respectively. It can be observed that the morphology of the S1 sample is distinctly different from the S2 sample. As seen in Figure 3(a), the micrograph of S1 sample shows randomly oriented plate-like grains of approximately 5 – 8  $\mu m$  in grain sizes. For the S2 sample, using large excess of precipitating agent caused the grains to become rounded and are generally smaller with sizes around 2 – 3  $\mu m$  in addition to evidence of partially melted grains. From the microstructural observations, it is possible that the fine and partially melted grains of the S2 sample has lead to better inter-grains connection which may be

the reason for the slightly higher transport critical current density,  $J_c$  of  $9 \text{ A/cm}^2$  compared to the S1 sample with  $J_c$  of  $5 \text{ A/cm}^2$ . Importantly, this result is consistent with previous report [14] that suggests  $J_c$  dependency on grains size. However, the plate-like microstructure of the S1 sample not only differs from the microstructure of the S2 sample but is also different from the microstructure of sample prepared using the Tl-containing precursor method in ref. (8). As such, it is suggested for  $\text{Tl}_{0.85}\text{Cr}_{0.15}\text{Sr}_2\text{CaCu}_2\text{O}_7$ , plate-like-grained microstructure can only be produced using coprecipitated Tl-free precursor route by using only a slight excess amount of precipitating agent. It has been shown, in the case of the Bi-based superconductor [15], that presence of plate-like superconductor grains are vital in enhancing texturization in superconductor tapes fabrication, yet the role of plate-like superconductor grains in Tl1212 superconductor has yet to be explored.



(a)



(b)

Figure 3 : Scanning electron micrographs for the S1 and S2 samples synthesized from coprecipitation Tl-free precursor route

## CONCLUSION

In conclusion, we are able to synthesize highly pure Tl1212 from  $Tl_{0.85}Cr_{0.15}Sr_2CaCu_2O_7$  starting composition using coprecipitation derived Tl-free precursor route. In this method, the precursor powder was first calcined at 850 °C followed by additions of appropriate amounts of  $Tl_2O_3$  and  $Cr_2O_3$  and was pressed into pellets and sintered at 1000 °C for 4 minutes. The result shows that using different excess amount of precipitating agent to react with metal oxalates in precursor preparation affect the microstructure of the resultant sample.

## ACKNOWLEDGMENT

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## REFERENCES

- [1]. R. Abd. Shukor (1993). *J. Mater. Sc. Lett.* **12**, 1428
- [2]. H. Kim, K.E. Gray, R.T. Kampwirth, R.T. Smoth, J.C. Richeson, T.J. Marks, J.H. Kang, J. Talvacchio and M. Eddy (1991). *Physica C* **177**, 431.
- [3]. F. Letouze, M. Hervieu, C. Martin, A. Maignan, B. Raveau, (1998) *Physica C* **296** 195
- [4]. S. Li and M. Greenblatt (1989). *Physica C* **157**, 365.
- [5]. Z.Z. Sheng, C. Dong, X. Fei, Y.H. Liu, L. Sheng and A.M. Hermann (1989). *Appl. Phys. Commun.* **9**, 27.
- [6]. Y. F. Lee, O. Chmaissem, Z. Z. Sheng. (1995) *Physica C* **248** 42
- [7]. R. Abd-Shukor and N. A. Nik Jaafar, (1999) *J. Mat Sc.: Mat. In Electronics*, **10** 677
- [8]. I. Hamadneh, W.K. Yeong, T.H. Lee and R. Abd-Shukor (2006). *Mat. Lett.* **60**, 734.
- [9]. I.V. Driessche, A. Buekenhoudt, K. Konstantinov, E. Bruneel and S. Hoste (1996). *Applied Supercond.* **4**(4), 185-190.
- [10]. T. Matsushita, A. Suzuki, T. Kishuda, M. Okude and H. Naito (1994). *Supercond. Sci. Technol.* **7**(4). 222-226.
- [11]. F. Md. Salleh, A.K. Yahya, H. Imad and M.H. Jumali (2005). *Physica C*. **426-431**, 319.
- [12]. J. Aponte, H.C. Abache, A. Sa-Neto, M. Octavio, (1989) *Phys. Rev. B* **39** 2233
- [13]. Z.Z. Sheng, Y.F. Li, D.O. Pederson, (1991), *Solid State Commun.* **80**, 913 – 915
- [14]. R. Maury, A.R. Fert, J.P. Redouless, J. Ayache, J. Sabras and C. Monty, (1990) *Physica C* **167**, 591
- [15]. L.C. Pathak, S.K. Mishra, D. Bhattacharya and K.L. Chopra, (1999) *J. Mat. Sc.* **34** 1619 – 1624