Preparation of Tl-2212 Cr-Substituted (Tl$_{2-x}$Cr$_x$)Ba$_2$CaCu$_2$O$_{8-\delta}$ Superconductor

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Abstract. We have prepared Tl$_{2-x}$Cr$_x$Ba$_2$CaCu$_2$O$_{8-\delta}$ (Tl-2212) for x=0.0-0.4 by standard solid state reaction with carbonate precursor and Cr$_2$O$_3$ as a source of Cr. The role of Cr substitute the Tl-sites in Tl-2212 superconductor system has been studied. The dc electrical resistance was determined using four point probe and the phase occurrence was studied by X-ray diffraction method. The transition temperature showed metallic normal state behavior for all samples. It was found that the addition of 0.2% mole Cr enhanced the Tc zero for 3.22%, whereas T$_{\text{conset}}$ was enhanced up to 10.47%. The effectiveness substitution of Tl-sites by Cr was achieved in the series of x < 0.2%. Most of the samples were in 14/mmm space group.

1. Introduction

Starting from the discovery of high Tc superconductivity by Bednorz and Muller until now, a great amount of researches contribute to superconductivity. Several workers around the world not only explored several precursor materials but also have studied several systems. It has been known that Thallium system is the most promising material in the improvement of critical temperature. Sheng and Hermann [2] discovered high temperature superconductivity (HTSC) in the Tl-Ba-Ca-Cu-O system. As a consequence, many new superconducting systems and phases have been reported [1]. The Tl-Ba-Ca-Cu-O system high temperature superconductor is one of the most promising candidates in terms of critical temperature since its high Tc [1-7]. Several techniques such as: the preparation of precursor [2-4], the role of the doping [5,6,7,8,10] and the modification of sintering temperature [11,12] have been applied to the superconducting material in order to increase the transition temperature.

The basic structure of Tl-Ba-Ca-Cu-O superconducting phases contains (Tl-O)$_2$ bilayers or (Tl-O) monolayer separated by BaO-CuO$_2$-Ca- CuO$_2$-BaO layers [3]. The transition temperature for Tl-Ba-Ca-Cu-O system is in the range of 85K-125K [1] has been reported.

In this paper we study the (Tl-O)$_2$ bilayers with the formula of Tl$_{2-x}$Cr$_x$Ba$_2$CaCu$_2$O$_{8-\delta}$ (x= 0.0 - 0.4) by solid state reaction. Z Y Chen et al. [13] and Z Z Sheng et al. [14] reported that Cr atom has an ability to improve the phase formation. All of them reported the enhancement of formation Tl-1201 phase and Tl-1212 phase respectively by Cr substitution. However, little information about Tl-2212 phase. Cr-substituted TlSr$_2$CaCu$_2$O$_{7-\delta}$ compounds are commonly synthesized via the conventional solid-state method, as the reaction proceeds by diffusion in the solid state, it requires mixing and grinding of high purity powders of oxides and/or carbonates for long hours before heating the mixtures at high temperature [11]. The high temperature processing of the Tl superconductors is further complicated by the volatility of Tl$_2$O$_3$, which as a result produced superconducting oxides that are
highly porous and of low density [1]. Whereas M ASubramaniam et al. [15] reported that the highest transition temperatures was observed when the samples were partially melted at > 900°C. They also reported that Tc zero of 110K and Tc onset of 112K were achieved. Faizah et al. [7] reported that Tc zero=95K and Tc onset 112K and samples showed existence of dominant Tl-2212 phase along with small impurity phases. They also reported that the addition of Ag showed little effect on Tc values and showed a lowering of Tc to around 70K.

2. Methods
Samples with the nominal starting composition of \((\text{Tl}_{2-x}\text{Cr}_x)\text{Ba}_2\text{CaCu}_2\text{O}_8\) with \(x = 0.0, 0.1, 0.2, 0.3\) and 0.4 were prepared by the solid state reaction method. An appropriate amounts of high purity (>99.99%) BaCO\(_3\), CaO and CuO were mixed completely using an agate mortal to obtain a homogeneous mixture. The precursor powders were heated at 900°C for 24h with twice intermittent grinding. An appropriate amounts of Tl\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) according to mole% were then added to the precursor and completely mixed before being pressed into pellets form of 1.3 cm in diameter and 0.2 cm in thickness under 7 ton/cm\(^2\) of pressure and then first heated at 900°C in the flowing oxygen for 4 minutes, followed by furnace cooling to room temperature. In order to compensate thallium loss during heating, excess of 10% Tl\(_2\)O\(_3\) were added in to accomplish pellet samples. The dc electrical resistance measurements in a range of 300K-30K were carried out using the four-point method with silver paste contact in conjunction with a closed cycle refrigerator from CTI Cryogenic Cycle Refrigerator Model 22 and a temperature controller from Lake Shore Temperature Controller Model 340 for temperature-dependent measurements. A constant current source between 1 and 100mA was used throughout the measurements. The powder X-ray diffraction (XRD) patterns were recorded using a Bruker model D8 Advance diffractometer with CuK\(_\alpha\) radiation.

3. Results and Discussion
A typical temperature dependence of electrical resistance for the pellet samples is shown in Figure 1. It can be seen that at their normal state, all of samples show metallic behavior until the transition temperature was reached. The resistance of samples decrease gradually and at a certain temperature, called Tc\(_{\text{onset}}\), the resistances start to drop abruptly. The temperature at which superconductivity occurs is called Tc\(_{\text{zero}}\).

Figure 1. Electrical resistance history of \((\text{Tl}_{2-x}\text{Cr}_x)\text{Ba}_2\text{CaCu}_2\text{O}_{8.8}\) for \(x = 0.0, 0.1, 0.2, 0.3\) and 0.4 at a temperature range of 300K-30K.
Based on Figure 1, it is clear that all samples displayed metallic characteristics above the onset transition temperature. For x=0.0 (sample without Cr addition), a small fluctuation occurred. This is due to the contact problem and normal for the resistance measurement using cryogenics. From the graph, it can be seen that the addition of 0.1% mole of Cr increased either Tc_zero (1K) or Tc_onset (5K) of the sample. When 0.2% mole Cr was added-in, a significant enhancement in both Tc_zero (3K) and Tc_onset (11K) was achieved. If the content of Cr was increased to 0.3% mole, it was observed that the Tc_zero decreased to 92K and the Tc_onset decreased to 110K. For the next composition where the content of Cr was increased up to 0.4% mole, it was observed that the Tc_zero decreased to 75K, whilst the Tc_onset decreased to 79K. These results implied that the strength of the coupling between grains is still high in the composition of x > 0.2% samples. The highest Tc in this experiment was 96K achieved, whereas the highest Tc for Tl-2212 system is around 105K [1]. The difference may be due to the sample preparation method. However this system is reasonable to be developed by using a higher purity of precursor. Figure 2 shows normal state electrical resistivity at room temperature for (Tl_2-xCr_x)Ba_2CaCu_2O_8-δ. As it can be seen from Figure 2, the resistivity of all samples are inversely proportional to critical temperature. It is clear and in a good agreement with the theory [5,7].

![Figure 2](image.png)

**Figure 2.** Normal state electrical resistivity at room temperature and variation of Tc as a function of Cr content for (Tl_2-xCr_x)Ba_2CaCu_2O_8-δ.

Table 1 shows the lattice parameter calculation with Cr content based on the XRD pattern (not shown). As it can be seen, the highest critical temperature was achieved with the highest c-lattice parameter value (29.3880Å). The smallest value of c-lattice parameter, 12.6800 Å can be seen in Tl_1.6Cr_0.4Ba_2CaCu_2O_8-δ sample. It can be noted that this composition has the lowest Tc. However, all of samples can be classified as a high temperature superconductor [1,7]. As such, the decrease in c-lattice parameter value, the volume of the cell will also be changed prior to the change of the space group.
Table 1. Lattice parameter of five pellets with nominal composition (Tl$_{2-x}$Cr$_x$)Ba$_2$CaCu$_2$O$_8$

| Series          | Tc(K)  | Lattice parameter | Space group |
|-----------------|--------|-------------------|-------------|
|                 | zero   | onset             | a (Å)       | b (Å)       | c (Å)       |             |
| Tl$_{2}$Ba$_2$CaCu$_2$O$_8$-$δ$ | 93     | 105               | 3.85430     | 3.85430     | 29.294      | 14/mmm     |
| Tl$_{1.9}$Cr$_{0.1}$Ba$_2$CaCu$_2$O$_8$-$δ$ | 94     | 110               | 3.8558      | 3.8558      | 29.2596     | 14/mmm     |
| Tl$_{1.8}$Cr$_{0.2}$Ba$_2$CaCu$_2$O$_8$-$δ$ | 96     | 116               | 3.86        | 3.86        | 29.3880     | 14/mmm     |
| Tl$_{1.7}$Cr$_{0.3}$Ba$_2$CaCu$_2$O$_8$-$δ$ | 92     | 110               | 3.85200     | 3.85200     | 29.2100     | 14/mmm     |
| Tl$_{1.6}$Cr$_{0.4}$Ba$_2$CaCu$_2$O$_8$-$δ$ | 75     | 79                | 3.8330      | 3.8330      | 12.6800     | P4/mmm     |

The occurrence of P4/mmm system was noted at x=0.4. The transition of space group has a significant effect to both of critical temperature: Tc zero as well as Tc onset. From table 1 above, it can be seen that the onset transition temperature (Tc$_{onset}$) was in the range of 79K and 105K. In the previous work on Tl$_{1.2}$Ba$_2$CaCu$_2$O$_7$ system, it was found that the superconductivity arose at about 80 K [13] when Cr was substitution at various metal sites, the transition temperature of Tl$_{1.8}$Sr$_2$CaCu$_2$O$_7$ was found to increase up to 110 K [14]. We can report that in this study, the optimum composition to improve the Tc onset was found in Tl$_{1.8}$Cr$_{0.2}$Ba$_2$CaCu$_2$O$_8$-$δ$ system. This is clear since the highest Tl$_{2212}$ phase was achieved with this composition. This also related to the highest charge carrier concentration as can be confirmed from normal state resistivity at room temperature (Figure 2).

4. Conclusion
We can conclude that the Cr substitute the Tl-sites in Tl$_{2212}$ system to be effective only with a small amount x< 0.2. The overdoped sample was found in x=0.4. Most of the samples were in 14/mmm space group. All the samples were in high temperature superconductor class, and showed a metallic-like behavior.

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