

Short Communication

Formation of $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ (Tl-1212) Superconducting Phase Using Cr_2S_3

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Received: 1 March 2013 / Accepted: 4 May 2013 / Published: 1 June 2013

The use of Cr_2S_3 to prepare the $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ (Tl-1212) superconductor phase is discussed. Samples with nominal starting composition $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ (Tl-1212) for $x = 0.05, 0.10, 0.15, 0.20, 0.25$ and 0.30 were prepared by the solid state reaction method. Cr_2S_3 with lower melting point than the normally used Cr_2O_3 was employed for the Cr source. The samples were studied by powder X-ray diffraction method and electrical resistance versus temperature measurements. The samples with $x = 0.05$ and 0.10 showed a single Tl-1212 phase. A higher amount of Cr ($x > 0.10$) showed the Tl-1201 as a minor phase. The onset transition temperature ($T_{c \text{ onset}}$) was between 90 K and 105 K. Sample with $x = 0.15$ showed the highest $T_{c \text{ onset}}$ (105 K) and the lowest normal state electrical resistivity although it contained the Tl-1201 impurity phase. Our results showed that Cr_2S_3 could be effectively used to prepare a high purity and high quality Tl-1212 superconducting phase.

Keywords: Electrical properties; superconductors; thallium-based; Cr_2S_3

1. INTRODUCTION

The $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ (Tl-1212) is an interesting superconducting material. It was initially identified in the Tl-Ba-Ca-Cu-O system [1]. The Tl-1212 superconductor is not easy to prepare in pure form [2, 3] because of the high the formal Cu valence (2.5+). Substitution with metallic elements of higher valences decreases the formal valence of Cu, improves the superconducting properties and stabilizes the Tl-1212 phase [2-6]. Partial substitution of Bi, Pb or Cr can stabilize the Tl-1212 superconducting phase [2, 7-9]. Substitution of rare-earth elements (R) into the Sr^{2+} site [10-14] and Ca^{2+} site [10-13] can also facilitate the formation of the Tl-1212 phase. $\text{TlSr}_2(\text{Ca,R})\text{Cu}_2\text{O}_7$ with transition temperature (T_c) of 90 K have been reported [6, 15]. Partial replacement of Tl^{3+} by Bi^{3+} [7, 8], Pb^{4+} [2, 8] or Cr^{3+} [9, 16] facilitates the formation of the Tl-1212 phase. Pb substitution results in the $(\text{Tl, Pb})\text{Sr}_2\text{CaCu}_2\text{O}_7$ phase with T_c up to 85 K [2, 4, 8, 15].

There have been several reports on the effect of Cr on the superconductivity and formation of the Tl-1212 phase [17]. Substitution of Cr for Tl or Ca site improves the superconducting behavior and stabilizes the Tl-1212 phase [9, 17-20]. It was found that Cr substitution improves T_c to above 100 K [17]. The formation of the Tl-1212 phase using ultrafine co-precipitated powder of less than 1 μm has also been reported [21]. In those studies, the usual source of Cr is Cr_2O_3 .

In this paper, we report effectiveness of Cr_2S_3 as a starting material for the formation of the $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ superconductor for $x = 0.05, 0.10, 0.15, 0.20, 0.25$ and 0.30 . Previous works used Cr_2O_3 (melting point $2329\text{ }^\circ\text{C}$) as the Cr source, however in this work we used Cr_2S_3 with much lower melting point ($1350\text{ }^\circ\text{C}$) as the starting material. Results from electrical resistance (dc) measurements using four-point-probe method and structural investigation using powder X-ray diffraction (XRD) are presented. Our results showed that Cr_2S_3 led to the formation of highly pure Tl-1212 phase with $T_{c\text{ onset}}$ of more than 100 K for low Cr content.

2. EXPERIMENTAL DETAILS

Samples with nominal starting composition $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ ($x = 0.05, 0.10, 0.15, 0.20, 0.25$ and 0.30) were prepared using the solid-state reaction method. High purity ($\geq 99.99\%$) SrO, CaO and CuO were mixed in appropriate amounts and ground before being calcined at $900\text{ }^\circ\text{C}$ for over 48 h with several intermittent grindings to obtain a uniform black powder. Then appropriate amounts of Tl_2O_3 and Cr_2S_3 were 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. In order to compensate for the thallium loss during heating, excess 10 % Tl_2O_3 was added. The pellets were heated at around $1000\text{ }^\circ\text{C}$ for 4 min in flowing O_2 followed by furnace cooling.

The dc electrical resistance measurements were carried out with the four point probe method using silver paste contacts. A CTI Cryogenics Closed Cycle Refrigerator Model 22 and Lake Shore Temperature Controller Model 340 were used for temperature-dependent measurements. $T_{c\text{ zero}}$ is defined as the temperature where the electrical resistance becomes zero and $T_{c\text{ onset}}$ is defined as the temperature where the resistance begins to drop sharply. The Van der Pauw method was used to determine room-temperature resistivity.

The powder X-ray diffraction method was used to determine the resultant phases. A Bruker model D8 Advance diffractometer with CuK_α source was used. The volume fraction of the Tl-1212 and Tl-1201 phase was estimated from the strongest diffraction line of each phase i.e. the (103) reflection of the 1212 phase and the (102) reflection of the 1201 phase. The lattice parameters were calculated by employing at least 15 diffraction peaks.

3. RESULTS AND DISCUSSION

Figure 1 shows the powder X-ray diffraction patterns of $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ for $x = 0.05, 0.10, 0.15$ and 0.20 samples. The patterns indicated a single Tl-1212 phase with tetragonal unit cell (space group, P4/mmm) for samples with $x = 0.05$ and 0.10 . The Tl-1201 impurity peaks were

observed in the $x = 0.15, 0.20, 0.25$ and 0.30 samples. The lattice parameters for $x = 0.05$ sample were, $a = 3.782 \text{ \AA}$ and $c = 12.056 \text{ \AA}$ while the lattice parameters for $x = 0.10$ sample were, $a = 3.785 \text{ \AA}$ and $c = 12.059 \text{ \AA}$.

The electrical resistance versus temperature curves of the $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ samples for $x = 0.05, 0.10$ and 0.15 are shown in Figures 2(a) and 2(b) show the curves for $x = 0.20, 0.25$ and 0.30 . All samples showed metallic normal-state behaviour. Sample with $x = 0.15$ showed the highest $T_{c \text{ onset}}$ (105 K). This sample also showed the lowest normal state electrical resistance (Figure 3). To examine the changes in T_c with x , we plotted $T_{c \text{ onset}}$ and $T_{c \text{ zero}}$ as a function of x (Figure 3). $T_{c \text{ onset}}$ increased for $x \leq 0.15$ and decreased for $x > 0.15$. The highest $T_{c \text{ onset}}$ was observed at $x = 0.15$ indicating an optimal doping level and consistent with previous report [9]. This also coincided with the lowest normal state resistivity (at 300 K) which indicated that the highest charge carrier concentration resulted in the optimal superconducting transition.

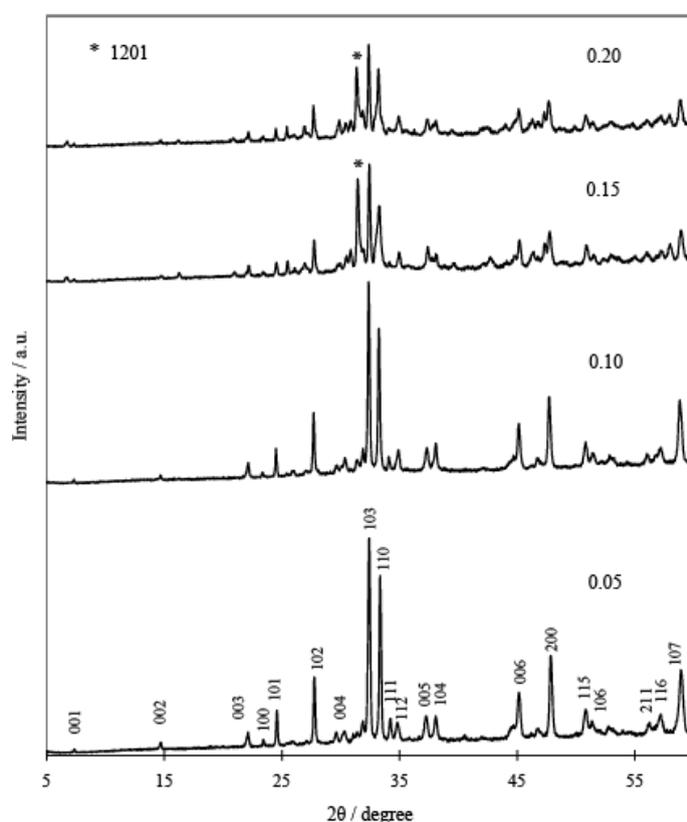


Figure 1. Powder X-ray diffraction patterns of samples with nominal starting composition $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ for $x = 0.05, 0.10, 0.15$ and 0.20 . (*) indicates the Tl-1201 phase

A single Tl-1212 phase can be obtained for $x \leq 0.10$ and for $x > 0.10$, peaks from the Tl-1201 phase were observed. This may be due to the effect of the ionic radii of the elements involved and certain values are preferred. When the amount of the smaller Cr ions (with radius equal or less than 0.063 nm) was increased and the larger Tl^{3+} (0.095 nm) was decreased, the average radius decreased and became too small to participate in the formation of 1212 phase.

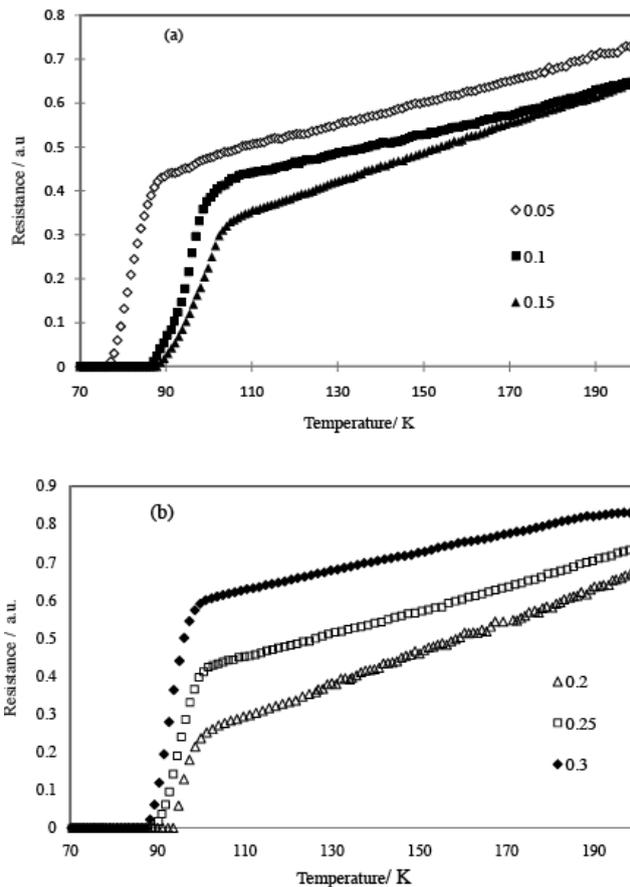


Figure 2. Electrical resistance versus temperature curves of $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ for $x = 0.05, 0.10$ and 0.15 and (b) electrical resistance versus temperature curves of $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ for $x = 0.20, 0.25$ and 0.30

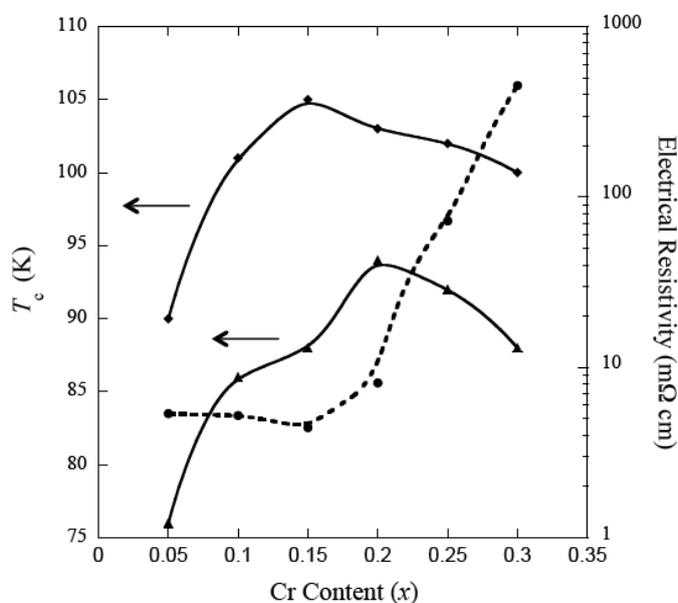


Figure 3. Normal state electrical resistivity (\bullet) at 300 K and the variation of $T_{c \text{ onset}}$ (\blacklozenge) and $T_{c \text{ zero}}$ (\blacktriangle) as a function of x for $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$

The rare-earth (R) substituted $\text{TlSr}_2(\text{Ca}_{1-x}\text{R}_x)\text{Cu}_2\text{O}_7$ [22, 23] showed optimal T_c for a higher rare-earth content (i.e. $x = 0.5$). For the Cr substitution, a smaller value ($x = 0.15$) showed the optimal T_c (as shown in this work). This can be due to the fact that R with valence 3+ replaces lower valence Ca^{2+} is able to optimize the charge carrier concentration. It is generally known that the optimum valency of Cu in the 1212 phase is between 2.2+ and 2.3+. This shows that in our samples the valence state of Cr at the Tl site is higher than 4+. $\text{Cr}^{>4+}$ is able to occupy the thallium layers because of its smaller size compared to Tl^{3+} , due to the Jahn Teller nature of Cu which allows a high flexibility of the Cu-O apical distance making it possible for Cr with very high valency to occupy the Tl^{3+} site [16]. It is interesting to note that in this work where Cr_2S_3 was employed, sulfur does not show any detrimental effect on the superconducting properties of the Tl-1212 phase. This was also found to be the case for F and Cl-doped Tl-1212 phase [5].

In conclusion, samples with nominal starting composition $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CaCu}_2\text{O}_7$ have been prepared and studied by dc resistivity and X-ray powder diffraction method. The Cr substituted sample exhibited the highest $T_{c \text{ onset}}$ at $x = 0.15$ indicating the optimal doping level. The $x = 0.05$ and 0.10 samples exhibited a single Tl-1212 phase. The lower melting point of Cr_2S_3 compared to Cr_2O_3 also facilitated the formation of the Tl-1212 phase. This work showed that Cr_2S_3 was effective for the formation of the Tl-1212 phase and provided another method to synthesis high quality Cr doped Tl-1212 superconductor. Sr does not degrade the superconducting properties of the Tl-1212 phase.

ACKNOWLEDGEMENTS

This work has been supported by the Ministry of Higher Education of Malaysia under grant no.: ERGS/1/2011/STG/UKM/01/25 and Universiti Kebangsaan Malaysia under grant no.: UKM-DLP-2011-018.

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