FORMATION OF Tl-1212 PHASE in Cr 
SUBSTITUTED (Tl\textsubscript{1-x}Cr\textsubscript{x}) Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7} SUPERCONDUCTOR

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ABSTRACT

Superconducting samples of (Tl\textsubscript{1-x}Cr\textsubscript{x}) Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7} for x = 0.0-0.7 have been prepared by a solid state reaction technique at normal pressure using high purity elements. The powder X-ray diffraction patterns have been studied for samples. All samples showed the Tl-1212 as the major phase and Tl-1201 as the minor phase. The superconducting transition temperature $T_c$ has been determined from the electrical resistivity measurements. The data of $T_c$, for (Tl\textsubscript{1-x}Cr\textsubscript{x}) Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7} show enhancement in its value from $104\;K$ to $112\;K$ as x (Cr-content) increases from 0.7 to 0.1. Our results shows the highest onset temperature for x = 0.2-0.3 and the lowest temperature for x = 0.7.

Keywords: Phase Formation, Tl-1212 Superconductor, Cr-Substitution, High $T_c$, Superconducting Transition, Diffraction Patterns, Reaction Technique, Solid State, Powder X-Ray

1. INTRODUCTION

The Tl-based cuprate high temperature superconductor continues to be an interesting family of material because it can form many phases. It is an ideal system to study the role of metal oxide and copper oxide layers in high temperature superconductivity. The studies of high temperature materials have been necessary to develop conductors for practical and also the studies of the phase formation can be useful to find out the crucial role of the oxygen partial pressure during the sintering process. The TlBaCaCuO (Tl/Ba) and TlSrCaCuO (Tl/Sr) make up the Tl-based cuprate superconductor. The Tl/Ba system can be written as Tl\textsubscript{2}Ba\textsubscript{2}Ca\textsubscript{n-1}Cu\textsubscript{n}O\textsubscript{z} with n = 1-4 and TlBa\textsubscript{2}Ca\textsubscript{n-1}Cu\textsubscript{n}O\textsubscript{z} with n = 1-5. The Tl/Sr system can be written as TlSr\textsubscript{2}Ca\textsubscript{n-1}Cu\textsubscript{n}O\textsubscript{z} with n = 1-3 (Lee, 2011). The three phases in the Tl/Sr system are TlSr\textsubscript{2}CuO\textsubscript{3} (Tl/Sr-1201), TlSr\textsubscript{2}CaCuO\textsubscript{3} (Tl/Sr-1212), TlSr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{10} (Tl/Sr-1223). But still not too many reports on Tl-Sr-1223 phase. There are some elements for raising the transition temperature of the Tl-1212 phase. Critical temperature around $100\;K$ of the Tl/Sr-1201 phase was reported (Eder and Gritzner, 1995). And several researches were studied on the effect of partial substitution of Ca with R (R = Y and rare-earths) in TlSr\textsubscript{2}CaCuO\textsubscript{7} (Kondo et al., 1991). Also transition temperature of TlSr\textsubscript{2}CaCuO\textsubscript{7} phase was found to increase up to $110\;K$ when Cr was substituted at different metal sites (Sheng et al., 1991). Therefore Tl-1234 superconducting phase was prepared by (Ihara et al., 1997) under the high pressure of 3.5 GPa at 850-9500°C for 2 h in a gold capsule (Iyo et al., 2001). But sintering technique in the high-pressure is not a suitable practical application.
Later on (Nawazish and Mumtaz, 2007) were prepared $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_{2}\text{Ca}_x\text{Cu}_{2}\text{Zn}_y\text{O}_{11-\delta}$ by using two step of solid state reaction method with $\text{ZnO}$, $\text{Ba(NO}_3)_2$, $\text{Ca(NO}_3)_2$ and $\text{Cu(CN)}$ as starting compound. Recently, was studied effect of Mg nano-oxide addition on superconductivity of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_x\text{Cu}_y\text{O}_{11-\delta}$ by using a single step solid state reaction method (Mohammed, 2012). The samples in this study were synthesized under normal pressure with Cr substitution at the Ti site.

It is interesting to studied the effect of Cr on the superconductivity of $(\text{Tl}_{1-x}\text{Cr}_x)$ $\text{Sr}_2\text{Ca}_x\text{Cu}_y\text{O}_{11}$ phase. Also Cr was substituted to Tl-1234 due to never any amount of high purity (>99.99%) CuO nano size, SrO and CaO were mixed completely using an agate mortal to obtain a homogeneous mixture. The precursor powders were heated at 90°C for 24 h with several intermittent grindings. Appropriate amounts of $\text{Tl}_2\text{O}_3$ and $\text{Sr}_2\text{O}_3$ were then added to the precursor powders, completely mixed and then pressed into pellets form of 1.3 cm diameter and 0.2 cm thickness. These pellets were then wrapped in a silver foil to reduce possible volatilization of Tl. The wrapped materials were first heated at 870°C in the flowing oxygen for 1 hour, followed by furnace cooling to room temperature. In order to compensate thallium loss during heating, excess 10% of $\text{Tl}_2\text{O}_3$ were added.

2. MATERIALS AND METHODS

2.1. Materials

Samples with nominal starting composition of $(\text{Tl}_{1-x}\text{Cr}_x)$ $\text{Sr}_2\text{Ca}_x\text{Cu}_y\text{O}_{11}$ with $x = 0.0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 were mixed by the solid state reaction method using metal oxides powders. Appropriate amounts of high purity (>99.99%) CuO nano size, $\text{Sr}_2\text{O}_3$ and $\text{Ba}_2\text{O}_3$ were mixed completely using an agate mortal to obtain a homogeneous mixture. The precursor powders were heated at 900°C for 24 h with several intermittent grindings. Appropriate amounts of $\text{Tl}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ were then added to the precursor powders, completely mixed and then pressed into pellets form of 1.3 cm diameter and 0.2 cm thickness. These pellets were then wrapped in a silver foil to reduce possible volatilization of Tl. The wrapped materials were first heated at 870°C in the flowing oxygen for 1 hour, followed by furnace cooling to room temperature. In order to compensate thallium loss during heating, excess 10% of $\text{Tl}_2\text{O}_3$ were added.

2.2. Characterization Methods and Instrumentation

The powder X-ray diffraction method using a Bruker D8 Advance diffractometer with Cuka source was used to identify the resultant phases. The volume fraction of superconducting phases was estimated by assuming that the amount of the phases are proportional to the strongest diffraction line of each phase, i.e., the (110) reflection of the 1212 and the (200) reflection of the 1201 phase.

The electrical resistance versus temperature measurements was carried out using the four-point method with silver paste contacts in conjunction with closed cycle refrigerator from CTI Cryogenic (Model 22) and a temperature controlled from Lake Shore (Model 330). A constant current source between 1 and 100mA was used throughout the measurements. The Tc onset is defined as the temperature where there is a sudden drop in the resistance.

3. RESULTS AND DISCUSSION

The room temperature Powder X-Ray Diffraction (PXRD) patterns for $(\text{Tl}_{1-x}\text{Cr}_x)$ $\text{Sr}_2\text{Ca}_x\text{Cu}_y\text{O}_{11}$ superconducting samples ($x = 0.0-0.7$) are shown in Fig. 1 and 2. The diffraction lines of the patterns are well indexed by a tetragonal unit cell of Tl-1212 with space group $\text{P}4_{1}\text{mmm}$. It is interesting to note that although for all samples were used from base materials to prepare Tl-1234 but formation of PXRD patterns shows the Tl-1212 as a major phase and Tl-1201 as a minor phase. It is due to $\text{Sr}_2\text{O}_3$ in the precursor powder. For improving the formation of Tl-1234 in the $(\text{Tl}_{1-x}\text{Cr}_x)$ $\text{Sr}_2\text{Ca}_x\text{Cu}_y\text{O}_{11}$ samples should substituted $\text{Sr}_2\text{O}_3$ by other elements such as $\text{Ba}_2\text{O}_3$ (Mohammed et al., 2010).

The amounts of Tl-1212 phase are assumed to be proportional to the intensity of their strongest diffraction lines the (103), (110) and (111) reflection of the 1212 phase and the (200) reflection of the 1201 phase) contained in the samples.

The comparison between the PDXD patterns determined that intensity of samples was decreased with increasing of x. In addition the strongest diffraction lines of Tl-1212 phase in the PXRD were appeared sharply for $x = 0.2-0.3$.

The electrical resistance versus temperature curves of $(\text{Tl}_{1-x}\text{Cr}_x)$ $\text{Sr}_2\text{Ca}_x\text{Cu}_y\text{O}_{11}$ samples for $x = 0.0-0.3$ are shown in Fig. 3 and for $x = 0.4-0.7$ are shown in Fig. 4. The highest Tc (onset and zero resistance) are determine for $x = 0.2-0.3$ at (112 K and 93 K) respectively and then Tc onset are decreased to 103 K for $x = 0.7$.

As shown in Fig. 3 the $x = 0.0$ sample shown an insulator behavior and samples for $x = 0.1-0.6$ are shown a metallic normal state behavior. Also samples with $x = 0.2$ and $x = 0.3$ are shown the highest Tc onset (112 K). Meanwhile, sample with $x = 0.7$ shown the lowest Tc onset (103 K) and shown a semiconductor behavior Fig. 4.
Figure 1 shows the variation of Tc onset with Cr content(x) for all samples. As shown in (Fig. 5) the Tc onset was increased from 103K to 112 K for x = 0.7 to x = 0.2-0.3 respectively.
Table 1. $T_c$ (onset and zero) of (Tl$_{1-x}$Cr$_x$) Sr$_2$CaCu$_2$O$_7$ for samples $x = 0.0-0.7$

| $x$ | $T_c$ onset (K) | $T_c$ zero (K) |
|-----|----------------|----------------|
| 0.0 | 104            | 47             |
| 0.1 | 112            | 92             |
| 0.2 | 112            | 93             |
| 0.3 | 106            | 92             |
| 0.4 | 105            | 93             |
| 0.5 | 104            | 93             |
| 0.6 | 103            | 78             |

The $T_c$ (onset and zero resistance) of (Tl$_{1-x}$Cr$_x$) Sr$_2$CaCu$_2$O$_7$ samples are shown in Table 1.

4. CONCLUSION

In this present study, we have synthesized (Tl$_{1-x}$Cr$_x$) Sr$_2$CaCu$_2$O$_7$ phase from the starting oxide elements by a solid state reaction technique at normal pressure and studied the effect of Cr substitution on it. Also it was successfully to find out a high $T_c$ for all samples. The superconducting transition temperature enhanced as $x$ increased from 0.1-0.3 and then decreased when $x$ increased from 0.4-0.7. The PXRD patterns indicated a Tl-1212 as a major phase and Tl-1201 as a minor phase. To improve the formation of (Tl$_{1-x}$Cr$_x$) Sr$_2$CaCu$_2$O$_7$ phase have to substitute Sr$_2$O$_3$ by other elements such as BaO$_2$ to obtain a (Tl$_{1-x}$Cr$_x$) Sr$_2$Ca$_3$Cu$_4$O$_{11}$ phase.

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