Electrical Properties of Li Substituted (Tl0.85Cr0.15)Sr2-xLixCaCu2O7 Superconductor

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Abstract. The effects of Li substitution for Sr in (Tl0.85Cr0.15)Sr2-xLixCaCu2O7 (Tl-1212) with \( x = 0 - 0.10 \) were investigated. Tl-1212 superconductor pellets were prepared via solid-state reaction and precursor method. The samples were characterized by x-ray diffraction and four-point probe methods. The XRD patterns showed that all samples formed mixed phases of Tl-1212 and Ca0.3Sr0.7CuO2 (CSCO). The temperature-dependent resistance measurements showed metallic-behavior for all samples with onset transition temperature, \( T_{c \text{ onset}} \) between 96 K and 105 K and zero resistance temperature, \( T_{c \text{ zero}} \) between 85 K and 94 K. The transition-width, \( \Delta T_c \) of all samples was in the range of 4 K to 11 K. The \( x = 0.02 \) and 0.07 sample showed increase in \( T_{c \text{ onset}} \) to 105 K and 102 K, respectively. This work showed that Li improved the transition temperature for \( x = 0.02 \) and 0.07 samples although the dominant phase was not Tl-1212.

1. Introduction

The discovery of high-temperature superconductivity in the TlBaCaCuO system by Sheng and Hermann in 1988 [1], have induced many scientists and researchers to investigate a new high temperature record. Since then, many new superconducting phases have been synthesized. Based on a research by Nakajima et. al, Tl-based 1212 type phases such as TlBa2CaCu2O7 and TlSr2CaCu2O7 have similar structures as YBCO-123 (also rare earth-123 i.e Nd and Gd) [2]. Some work reported that TlSr2CaCu2O7 becomes superconducting at about 80 K [3]. Another reported that TlSr2RCu2O7 (R = rare earth) becomes superconducting at 90 K [4]. Following this discovery, a novel Cr-substituted TlSr2CaCu2O7 with \( T_c \) up to 110 K has been recorded [5]. In 2001, a study about the effect of transition metals substituted on (Tl0.85Cr0.15)Sr2CaCu2O7 system has recorded lower \( T_c \) reading with the substitution of Zn and Mn [6] and rare-earth elements [7] on (Tl0.85Cr0.15)Sr2CaCu2O7 had been reported. The co-precipitation method has been used to prepare ultra-fine (Tl0.85Cr0.15)Sr2CaCu2O7 powders [8].

Most of the efforts to improve \( T_c \) of the Tl-1212 phase were by addition of trivalent ions, especially the rare-earth elements [4,9]. Rare-earths elements have also been used to improve the Bi1.6Pb0.4Ba2CaCu2O10 superconductor [10]. Substitution of single and monovalent alkali metals such as lithium into Tl-based high-temperature superconductors is interesting to study. Li is a light element that may give rise to high-frequency phonons if incorporated into the crystal lattice. The effective ionic size with 6-fold coordination of Li+ (0.76 Å) is close to Cr+3 (0.62 Å), Cu+2 (0.73 Å), Tl+3 (0.885 Å) and...
Sr\(^{2+}\) (1.18 Å) [11]. Tl exists in both +3 and +1 oxidation states in the Tl-based high-temperature superconductors. Substitution of Li into Tl\(_2\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10}\) shows \(T_c\) increases up to 117 K [12]. Most rare-earth elements with trivalent ions (R\(^{3+}\)) are effective in stabilizing the Tl-1212 phase.

The objective of this study was to investigate the effect of Li substitution on Sr sites in (Tl\(_{0.85}\)Cr\(_{0.15}\))Sr\(_{2-x}\)Li\(_x\)CaCu\(_2\)O\(_7\) for \(x = 0 - 0.10\). The X-ray diffraction method was used to determine the phase and the DC electrical resistance versus temperature measurements was performed to determine \(T_c\).

This work showed that Ca\(_{0.3}\)Sr\(_{0.7}\)CuO\(_2\) was presented as a major or minor phase in all samples. The monovalent Li\(^{+1}\) improved the transition temperature in some of the samples as this alkali metal was substituted into Tl-1212.

2. Experimental details

Samples with nominal compositions (Tl\(_{0.85}\)Cr\(_{0.15}\))Sr\(_{2-x}\)Li\(_x\)CaCu\(_2\)O\(_7\) \((x = 0, 0.02, 0.05, 0.07\) and \(0.10\)) were prepared by using the solid-state reaction method. Appropriate amounts of high purity (99.9+% \(\%\)) powders of Tl\(_2\)O\(_3\), Cr\(_2\)O\(_3\), SrCO\(_3\) (or SrO), CaO (or CaCO\(_3\)), CuO and Li\(_2\)CO\(_3\) from Sigma Aldrich were mixed and ground in an agate mortar. The precursor powders were then calcined in air at about 800\(^\circ\)C for 48 h with several intermittent grindings to obtain homogenous powders. Appropriate amounts of Tl\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) were then added to the precursor and completely mixed. The powders were then pressed into pellets with 13 mm diameter and 2 mm thickness under a load of 7 tons using a hydraulic press. The pellets were then placed in a ceramic boat and heated in a tube furnace at 1000\(^\circ\)C in flowing oxygen for 4 min followed by furnace cooling to room temperature.

The powder X-ray diffraction method was used to determine the resultant phases. A Bruker model D8 Advance diffractometer with CuK\(\alpha\) source was used. The volume fraction of the phases were estimated by assuming that the amounts of Tl-1212 and the Ca\(_{0.3}\)Sr\(_{0.7}\)CuO\(_2\) (CSCO) phases are proportional to the strongest diffraction line of each phase, i.e. the (103) reflection of the Tl-1212 phase and the (041) reflection of the CSCO phase [13,14]. The lattice parameters were calculated by employing at least 10 diffraction peaks. The percentage of the volume fraction for Tl-1212 and CSCO phase has been calculated by using the formula:

\[
\text{Tl-1212 \%} = \frac{\sum l_{Tl-1212}}{\sum l_{CSCO} + \sum l_{Tl-1212}} \times 100\%
\]

\[
\text{CSCO \%} = \frac{\sum l_{CSCO}}{\sum l_{CSCO} + \sum l_{Tl-1212}} \times 100\%
\]

The DC electrical resistance versus temperature measurements was carried out using the four-point probe method with silver paste contacts in conjunction with a closed cycle refrigerator from CTI Cryogenics Model 22 and temperature controller from Lake Shore Model 330. A constant current source between 1 and 100 mA was used throughout the measurements.

3. Results and discussion

The XRD patterns (Figure 1) shows the \(x = 0\) and 0.07 substituted samples exhibited the Tl-1212 (space group P4/\(\overline{mm}\)) as the major phase while CSCO (space group Cmcm (63)) exhibited as the major phase in the \(x = 0.02, 0.05\) and 0.10 substituted samples (Table 1). CSCO phase was reported to be a minor phase in some high-temperature superconductors [14]. Our results were due to the calcination temperature (800\(^\circ\)C) of the precursor as the melting point of Li\(_2\)CO\(_3\) was 723\(^\circ\)C. A study reported that 900\(^\circ\)C calcination temperature of (Tl\(_{0.85}\)Cr\(_{0.15}\))Sr\(_2\)CaCu\(_3\)O\(_7\) superconductor resulted in a mixed Tl-1212 and Tl-1201 phase [6]. This indicated that Li did not enhance the formation of the Tl-1212 phase. It can be seen from the data in Table 1 that the lattice parameters of all samples did not vary systematically from the non-substituted sample. For example, the \(x = 0\) sample showed \(a = 3.8202\) Å and \(c = 12.0187\) Å and \(x = 0.07\) sample showed \(a = 3.8173\) Å and \(c = 12.0187\) Å for Tl-1212 phase.
Figure 1. XRD patterns of (Tl\(_{0.85}\)Cr\(_{0.15}\))\(\text{Sr}_2\)\(\text{Li}_x\text{CaCu}_2\text{O}_7\) for \(x = 0-0.10\). * indicate CSCO and # indicate Li\(_2\)CO\(_3\).

The signature peak for Li\(_2\)CO\(_3\) is at \(2\theta = 31.8^\circ\) (which does not overlap with the Tl-1212 and CSCO peaks). From Table 1, Li substituted sample with \(x = 0.02\) showed the highest amount of Ca\(_{0.3}\)Sr\(_{0.7}\)CuO\(_2\) phase. The lattice parameter for CSCO phase (\(x = 0.02\)) Li substituted sample was \(a = 3.5193\) Å, \(b = 16.2180\) Å and \(c = 3.8944\) Å. Li\(^+1\) was not substituted into the Tl-1212 crystal lattice. In the YBa\(_2\)Cu\(_3\)O\(_7\) system, Li was substituted into the Cu site [15].
The resistance versus temperature curves shows that the transition temperature was slightly increased as Li was substituted (Figure 2). The normal state resistance versus temperature curves showed metallic behavior for all samples. The onset transition temperature ($T_{\text{c onset}}$) of the samples was between 96 K and 105 K. The zero resistance temperature ($T_{\text{c zero}}$) was between 85 K and 94 K. Sample with $x = 0.05$ showed the lowest temperature reading for both $T_{\text{c onset}}$ and $T_{\text{c zero}}$ (96 K and 85 K). The transition-width ($\Delta T_{\text{c}}$) of all samples is in the range of 4 K to 11 K (Table 1). Sample with $x = 0.02$ showed the highest increase in $T_{\text{c onset}}$ and $T_{\text{c zero}}$ although the major phase was CSCO. This indicated that the optimum Li composition for the (Tl$_{0.85}$Cr$_{0.15}$)Sr$_2$Li$_x$CaCu$_2$O$_7$ superconductor was at $x = 0.02$ even though the Tl-1212 type phase was not the dominant phase in the sample. Anomalies in the electrical resistance and diamagnetic signals were reported at various temperatures in CSCO [16] but not observed in our measurements.

Table 1 shows $T_{\text{c zero}}$, $T_{\text{c onset}}$, $\Delta T_{\text{c}}$, the percentage of the volume fraction $V_{\text{Tl-1212}}$ and the lattice parameter for Tl-1212 phase, and $V_{\text{CSCO}}$ of the samples.
Table 1. $T_c$, $T_c^\text{onset}$, $\Delta T_c$, the percentage of the volume fraction $V_{Tl-1212}$ and the lattice parameter for Tl-1212 phase, and $V_{CSCO}$ for (Tl$_{0.85}$Cr$_{0.15}$)Sr$_{2-x}$Li$_x$CaCu$_2$O$_7$ ($x = 0 – 0.10$) samples

| $x$ | 0   | 0.02 | 0.05 | 0.07 | 0.10 |
|-----|-----|------|------|------|------|
| $T_c^\text{zero}$ [K] | 93  | 94   | 85   | 91   | 92   |
| $T_c^\text{onset}$ [K] | 94  | 105  | 96   | 102  | 99   |
| $\Delta T_c$ [K] | 4   | 11   | 11   | 11   | 7    |
| $V_{Tl-1212}$ / % | 51  | 23   | 30   | 73   | 30   |
| $a$ (Å) | 3.8202 | 3.8173 | 3.8187 | 3.8173 | 3.8173 |
| $c$ (Å) | 12.0187 | 11.9975 | 12.0116 | 12.0187 | 11.9928 |
| $V_{CSCO}$ / % | 49  | 77   | 70   | 27   | 70   |
| $a$ (Å) | 3.5241 | 3.5193 | 3.5241 | 3.5186 | 3.5172 |
| $b$ (Å) | 16.2339 | 16.2180 | 16.2339 | 16.2149 | 16.2180 |
| $c$ (Å) | 3.8906 | 3.8944 | 3.8867 | 3.8852 | 3.8852 |

4. Conclusion
The effect of Li substitution on (Tl$_{0.85}$Cr$_{0.15}$)Sr$_{2-x}$Li$_x$CaCu$_2$O$_7$ system was investigated. These results showed that Li was not able to stabilize the Tl-1212 phase. X-ray diffraction patterns showed that all samples formed mixed phases of Tl-1212 and Ca$_0.3$Sr$_0.7$CuO$_2$. Substitution of Li in (Tl$_{0.85}$Cr$_{0.15}$)Sr$_{2-x}$Li$_x$CaCu$_2$O$_7$ superconductor enhanced the transition temperature in $x = 0.02$ and $x = 0.07$ sample.

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