Superconducting Properties of Te-Substituted (Tl$_{2-x}$Te$_x$)Ba$_2$CaCu$_2$O$_{8-\delta}$

Syahrul Humaidi$^*$, Eddy Marlianto$^1$, S. Marhaposan$^1$, R. Abd-Shukor$^2$

$^1$Department of Physics, FMIPA, Univ. Sumatera Utara, Jln Bioteknologi 1, Medan, Indonesia
$^2$School of Applied Physics, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

*syahrul1@usu.ac.id, eddy5@usu.ac.id, mar_posan@yahoo.co.id, ras@ukm.edu.my

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Abstract. The Tl$_{2-x}$Te$_x$Ba$_2$CaCu$_2$O$_{8-\delta}$ (Tl-2212) high temperature superconductors with $x = 0.0-0.5$ have been prepared by the standard solid-state reaction method. The precursor powder were sintered at 900°C for 24 h with several grindings and heating. The powder were then pressed into pellets and heated at 910°C in oxygen flow for 4 min followed by furnace cooling. The electrical resistance versus temperature dependence measurements showed metallic normal state behavior for all samples. Substitution of Te at the Tl-site led to multi-phasic samples. The $x = 0.4$ sample showed the highest $T_c$ $\text{zero} = 98$ K and $T_c$ $\text{onset} = 111$K. The Tl-2212 phase increased from 50% for $x=0$ up to 92% in the $x=0.4$ sample.

Introduction

The Tl-based cuprate superconductors have been of interest due to the relatively high transition temperatures. The effects of various elements and compounds on Tl$_2$Ba$_2$CaCu$_2$O$_8$ (Tl-2212) and other cuprate high temperature superconductors (HTSC) have been studied in order to improve the superconducting properties. This includes the effect of magnetic and non-magnetic particles, complex oxides, nanoparticles and various compounds [1-5]. The optimal method to prepare the Tl-2212 phase has also been reported [6]. The basic structure of Tl-Ba-Ca-Cu-O superconducting phase contains the (Tl-O)$_2$ bilayers or (Tl-O) monolayer separated by BaO-CuO$_2$-Ca-CuO$_2$-BaO layers. The transition temperature for Tl-Ba-Ca-Cu-O system is in the range of 85K to 125K. The Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10-\delta}$ (Tl-2223) shows $T_c = 125$ K, Tl$_2$Ba$_2$CaCu$_2$O$_{8-\delta}$ (Tl-2212) shows $T_c = 110$ K and Tl$_2$Ba$_2$CuO$_{6-\delta}$ (Tl-2201) shows $T_c = 80$ K. The Tl$_2$Ba$_2$Ca$_2$Cu$_2$O$_{8-\delta}$ phases are relatively easy to prepare. However, the high temperature processing of the Tl superconductors is further complicated by the volatility of Tl$_2$O$_3$, leading to highly porous and of low density materials. The highest transition temperature was observed when the samples were partially melted at higher than 900°C [7]. The Tl-2212 phase showed $T_c$ $\text{zero}$ of 110K and $T_c$ $\text{onset}$ of 112K.

It was also reported that addition of Ag showed lowering of $T_c$ values to around 70K [8] in the Tl-2212 phase. Doping of YBa$_2$Cu$_3$O$_7$ with TeO$_2$ leads to increase in the sample density and reduce degradation in wet atmosphere [9]. Te was also reported to improve the transition temperature of the Tl-1212 phase [10]. Other rare-earth elements were also reported to improve the phase formation of the Tl-based superconductors [11,12]. In this brief paper we report on the effect of Te on the superconducting properties and phases formation of the Tl-2212 phase. The ionic radius of Te$^{4+}$ with coordination number six is 0.97 Å. This is smaller than the ionic radius of Tl$^{+}$ (1.50 Å) but bigger than Tl$^{3+}$ (0.885 Å) with the same coordination number [13]. Hence, the objective of this work was to determine the effect of Te on the superconducting properties of the Tl-2212 phase. The transition temperature and phase formation of the materials are reported.

Experimental Method

Samples with the nominal starting composition (Tl$_{2-x}$Te$_x$)Ba$_2$CaCu$_2$O$_8$ with $x = 0.0$, 0.1, 0.2, 0.3, 0.4 and 0.5 were prepared by the solid-state reaction method. Appropriate amounts of high purity
BaCO₃, 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 two intermittent grindings. Appropriate amounts of Tl₂O₃ and TeO₂ were then added into the precursor and completely mixed before being pressed into pellets of 1.3 cm in diameter and 0.2 cm thickness. The pellets were heated at 900°C in flowing oxygen for 4 min, followed by furnace cooling to room temperature. In order to compensate for thallium loss during heating, excess of 10% Tl₂O₃ was added.

The dc electrical resistance measurements in a range of 50 – 300K 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. A constant current source between 1 and 100mA was used throughout the measurements. The powder X-ray diffraction (XRD) pattern was recorded using a Bruker model D8 Advance diffractometer with CuKα radiation. The volume fraction of the phase was determined using $Tl_{2212} (%) = \frac{I(2212)}{I_{total}}$ where $I(2212)$ is the sum of intensities of peaks belonging to the Tl-2212 phase and $I_{total}$ is the total intensity of all the peaks in the XRD pattern.

Results and Discussion

The XRD patterns of the $x = 0, 0.1$ and 0.4 samples are presented in Fig. 1. Fig. 1(a) shows three highest peaks: (105), (107) and (110) between $25^\circ$< $2\theta$< $35^\circ$. These peaks indicated that the samples are showing a major phase of Tl-2212. Some peaks: (004), (002), (006), (103), (105), (107), (1110), (0012), (200) and (1112) are common in all the samples. Based on the calculation, the volume fraction of the Tl-2212 phase in for $x = 0$ was around 50%. The other 50% belongs to the Tl-2201 phase. When Te was introduced, extra peaks were observed namely, (0010) at $2\theta$=29.97°, (217) at $2\theta$=57.77° for the $x = 0.1$ and 0.3 samples. However, the (0010) peak was completely vanished for $x = 0.4$ samples.

Some peaks for example, (101) at $2\theta$=24.24° of the Tl-1212 phase, (0014) at $2\theta$=29.97°, (1011) at $2\theta$=36.84° of Tl-2223 phases as well as (109) peak at $2\theta$=49.73° of Tl-1234 phase were observed in $Tl_{1.9}Te_{0.1}Ba_2CaCu_2O_{8-\delta}$. From the calculation, the Tl-2212 phase in $Tl_{1.9}Te_{0.1}Ba_2CaCu_2O_{8-\delta}$ (Fig. 1b) compound was around 76% and Tl-2201 makes the remaining phase. Our calculation of Tl-2212 phase showed that a value of 92% for $Tl_{1.6}Te_{0.4}Ba_2CaCu_2O_{8-\delta}$ (Fig. 1c) and $Tl_{1.7}Te_{0.3}Ba_2CaCu_2O_{8-\delta}$ have been obtained. The volume fraction of Tl-2212 phase increased as Te content was increased.

The electrical resistance versus temperature curves are shown in Fig. 2. The onset transition temperature, $T_{c \text{ onset}}$ is defined as the temperature where there is a sudden drop in resistance and can be obtained from the crossing point of the linear fit of the highest slope and the metallic high temperature part of the $\rho(T)$ curve for each sample. The zero-resistance temperature, $T_{c \text{ zero}}$ is the temperature where the resistance drops to zero and can be estimated from the extrapolation of the linear part of the resistivity to the temperature axis.

A typical temperature dependence of electrical resistance for the samples is as shown in Fig. 2. It can be seen that the normal state of all samples showed a metallic behavior until the transition temperature was reached. The resistance drops abruptly at 105 K and reach zero resistance at 93 K. Thus, the non-added sample showed $T_{c \text{ onset}} = 105$ K and $T_{c \text{ zero}} = 93$ K (Fig. 2a). The resistance versus temperature graph for $x = 0.1$ sample is shown in Fig. 2b. From the graph, it can be seen that the addition of Te gave significant effect on the critical temperature with $T_{c \text{ zero}} = 64$ K and $T_{c \text{ onset}} = 107$ K, respectively.
The resistance graph for the $x = 0.3$ and $0.4$ samples are presented in Fig. 2(c) and 2(d), respectively. It can be seen that all samples show metallic-like characteristic above $T_c$. $T_c_{\text{zero}} = 93\, \text{K}$ and $T_c_{\text{onset}} = 105\, \text{K}$ for $x = 0.3$. When $x$ was increased to 0.4, a higher $T_c_{\text{onset}} (111\, \text{K})$ as well as $T_c_{\text{zero}} (98\, \text{K})$ was observed. In term of critical temperature, this composition ($x = 0.4$) showed the highest value. The $x = 0.5$ sample showed $T_c_{\text{zero}} = 94\, \text{K}$ and $T_c_{\text{onset}} = 102\, \text{K}$. As such, the optimum level for Te substitution at the Tl-sites in Tl-2212 system is $x = 0.4$. This is in a good agreement with the previous finding on Ag addition [8]. Multiphase samples were also observed in Tl$_{2-x}$Mo$_x$Ba$_2$CaCu$_2$O$_8$-$\delta$ [14].

The plot of $d\rho/dT$ is also shown in Fig. 2. The linear fit indicates the background normal state resistivity. The superconducting properties can be greatly influenced by the superconducting fluctuations behavior (SFB). The fluctuation includes the deviation of the electrical resistivity from the linear metallic normal state behavior curve at temperatures well above the zero-resistance-temperature, $T_c_{\text{zero}}$. SFB which is a result of the formation of Cooper pairs at the very initial stage is suggested to dominate the excess conductivity region. Fig. 2 shows that the temperature where the resistance deviates from the linear resistive behavior decrease as Te content was increased. This shows that superconducting fluctuations were decreased to lower temperature as a result of Te...
substitution. The peak temperature \( T_p \) of \( dR/dT \) however, increased with Te content indicating the increase in the transition temperature. Samples with \( x = 0.3 \) and 0.4 showed two or more \( dR/dT, T_p \) peaks indicating multiphasic behavior.

![Fig. 2. Normalized electrical resistance and the temperature derivatives, \( dR/dT \) of \( \text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8-\delta} \): (a) \( x = 0 \), (b) \( x = 0.1 \), (c) \( x = 0.3 \), (d) \( x = 0.4 \) and (e) \( x = 0.5 \). The linear fit was for the resistance above \( T_c \). \( T_p \) is the peak of \( dR/dT \).]
The results of critical temperature measurement can be tabulated in Table 1 below:

<table>
<thead>
<tr>
<th>Te content (%)</th>
<th>x=0.0</th>
<th>x=0.1</th>
<th>x=0.2</th>
<th>x=0.3</th>
<th>x=0.4</th>
<th>x=0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tl-2212 phase (%)</strong></td>
<td>50</td>
<td>76</td>
<td>84</td>
<td>90</td>
<td>92</td>
<td>78</td>
</tr>
<tr>
<td><strong>Tc onset (+1K)</strong></td>
<td>105</td>
<td>107</td>
<td>98</td>
<td>105</td>
<td>111</td>
<td>102</td>
</tr>
<tr>
<td><strong>Tc zero (+K)</strong></td>
<td>93</td>
<td>64</td>
<td>54</td>
<td>93</td>
<td>98</td>
<td>94</td>
</tr>
<tr>
<td><strong>Tp (dR/dT)/K</strong></td>
<td>96</td>
<td>97</td>
<td>92</td>
<td>100</td>
<td>100</td>
<td>92</td>
</tr>
</tbody>
</table>

In conclusion, the optimum composition to optimize $T_c$ onset as well as $T_c$ zero was found in the Tl$_{1.6}$Te$_{0.4}$Ba$_2$CaCu$_2$O$_{8-δ}$ sample. XRD pattern showed the occurrence of secondary phase for all samples. The preparation of the sample began with starting composition Tl$_{2-x}$Te$_x$Ba$_2$CaCu$_2$O$_{8-δ}$. However, some other phases were also observed. This implied that the samples produced were mixed phase with Tl-2212 as the major phase. Our work indicated that $x = 0.4$ showed the highest transition temperature and highest Tl-2212 volume fraction.

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