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EFFECT OF Cr_2O_3 ON THE TRANSITION TEMPERATURE AND PHASE FORMATION OF $Tl_{2-x}Cr_xBa_2CaCu_2O_{8-\delta}$ SUPERCONDUCTOR

(Kesan Cr_2O_3 Terhadap Suhu Peralihan dan Pembentukan Fasa Superkonduktor $Tl_{2-x}Cr_xBa_2CaCu_2O_{8-\delta}$)

Syahrul Humaidi[1]* and Roslan Abd-Shukor[2]

[1]*Department of Physics,*
FMIPA-Universitas Sumatera Utara, Jln Bioteknologi 1, Medan 20155, Indonesia
[2]*Department of Applied Physics,*
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

**Corresponding author: syahrul1@usu.ac.id*

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Abstract

The Tl-based high T_c superconductors, $Tl_{2-x}Cr_xBa_2CaCu_2O_{8-\delta}$ (Tl2212) have been prepared *via* the solid-state reaction method. The substitution of Cr into the Tl-site was aimed to investigate the role of Cr on the transition temperature and phase stability of the Tl2212 phase. $Ba_2CaCu_2O_y$ precursor material was synthesized using $BaCO_3$ (99.9%, Aldrich), CaO (99.99%, Alfa Aesar), and CuO (99.9%, Alfa Aesar) powder as the starting compound. The powders were mixed and sintered at 900 ^oC for 24 hours before cooled to room temperature. The precursor was mixed with Tl_2O_3 (99.9%, Alfa Aesar) and Cr_2O_3 (99.9%, Merck) powders before being pressed to obtain $Tl_{2-x}Cr_xBa_2CaCu_2O_8$ pellet. The pellets were heated at 900 ^oC with oxygen flow for 4 minutes. The transition temperature, T_c was determined using the standard four-point probe electrical resistance measurements from 50 K to 300 K with a constant current of 20 mA. The phases were determined by powder X-ray diffraction (XRD) method using CuK_α source with λ= 1.5418 Å. Based on XRD analysis, the x = 0, 0.2, and 0.6 showed unit cell belonging to the 14/mmm space group. In the x = 0.4, the space group changed to P4/mmm which is the Tl1212 phase. It was found that the optimum composition was $Tl_{1.8}Cr_{0.2}Ba_2CaCu_2O_{8-\delta}$ and the maximum zero-resistance temperature, $T_{c\text{-}zero}$ was 96 K, and the onset temperature, $T_{c\text{-}onset}$ was 116 K. It was observed that the transition temperatures decreased with increasing Cr_2O_3. The volume fraction of the Tl2212 phase in this composition was 88% with the *c*-lattice parameter equals to 29.388Å. Superconductivity was destroyed in the x = 1.0 samples.

Keywords: transition temperature, structure, Tl2212 phase

Abstrak

Superkonduktor suhu tinggi berasaskan Tl iaitu, $Tl_{2-x}Cr_xBa_2CaCu_2O_{8-\delta}$ (Tl2212) telah disediakan melalui kaedah tindak balas pepejal. Penggantian Cr pada kedudukan Tl dilakukan untuk menyelidik peranan Cr terhadap suhu genting dan kestabilan fasa superkonduktor Tl2212. Bahan pelopor $Ba_2CaCu_2O_y$ disintesis dengan menggunakan serbuk $BaCO_3$(99.9%, Aldrich), CaO(99.99%, Alfa Aesar) dan CuO(99.9%, Alfa Aesar) sebagai campuran awal. Serbuk ini kemudiannya disinter pada 900 ^oC selama 24 jam dan dibiarkan sejuk sehingga suhu bilik. Bahan pelopor ini kemudianmya dicampurkan dengan serbuk Tl_2O_3 (99.9%, Alfa Aesar) dan serbuk Cr_2O_3(99.9%, Merck) untuk menghasilkan pelet $Tl_{2-x}Cr_xBa_2CaCu_2O_8$. Pelet kemudiannya disinter

pada 900 °C dengan aliran gas oksigen selama 4 minit. Suhu peralihan, T_c ditentukan dengan pengukuran rintangan elektrik menggunakan kaedah piawai empat titik dalam suhu 50 K hingga 300K dengan bekalan arus malar 20 mA. Pecahan fasa diperolehi daripada kaedah pembelauan serbuk sinar-X (XRD) menggunakan sinar CuKα dengan panjang gelombang λ= 1.5418Å. Berdasarkan analisis XRD, sampel x = 0, 0,2, dan 0.6 adalah pada kumpulan ruang 14/mmm. Untuk sampel x = 0.4 kumpulan ruang berubah menjadi P4/mmm iaitu fasa yang berlainan (Tl1212). Didapati bahawa suhu peralihan sifar maksimum, $T_{c\ sifar}$ adalah 96 K dan suhu perlalihan mula, $T_{c\ mula}$ adalah 116 K bagi komposisi $Tl_{1.8}Cr_{0.2}Ba_2CaCu_2O_{8-\delta}$. Pecahan isipadu daripada fasa Tl2212 dalam sampel ini adalah 88% dengan parameter kekisi c bersamaan 29.388 Å. Sifat superkonduktor hilang pada komposisi x = 1.0.

Kata kunci: suhu peralihan, struktur, fasa Tl2212

Introduction

High temperature superconductor (HTSC) based on copper oxides have critical temperature greater than 77 K (above liquid nitrogen temperature). Some of the common types of HTSCs include YBaCuO (YBCO), BiSrCaCuO (BSSCO), TlBaCaCuO (TBCCO), HgBaCaCuO, and HgTlBaCaCuO. Many efforts are being made to enhance the transition temperature of HTSCs. Some researchers modified the fabrication techniques of the materials [1-4]. Most of the research works [5-9] deal with doping and atomic substitution. The thallium-based copper oxide superconductor consists of several phases with a different number of copper oxide layers. Previous works on thallium-based high temperature superconductor concentrated on several phases of Tl-based HTSCs. T_c of $TlBa_2CaCu_2O_{7-\delta}$ (Tl1201) was around 70 K [10], whereas $Tl_2Ba_2CaCu_2O_{8-\delta}$ (Tl1212) had T_c of 110 K [11]. The $TlBa_2Ca_3Cu_4O_{11-\delta}$ (Tl1234) was reported with T_c of around 114 K [12].

The role of Cr at the Tl-sites in Tl-based superconductor has been widely studied. Chromium is an effective element for substitution in Tl-Sr-Ca-Cu-O systems [13]. There have been several reports on the effect of Cr on the superconductivity of Tl-1212 phase. The substitution of Cr for Tl or Ca site improves the superconducting behavior [11, 14, 15]. Cr substitution improves the critical temperature up to 110 K [16]. The $Tl_2Ba_2CaCu_2O_{8-\delta}$ samples with high purity were reported to have T_c of 106 K [17, 18]. The samples were prepared from metal oxides with a starting composition Tl2212 and heated at 900 °C for 24 hours followed by adding appropriate amounts of Tl_2O_3 and heated again at 915-920 °C for 4-5 minutes. In a previous report, it has been observed that the volume fraction of Tl2212 phase increased as Te content was increased [19]. It is interesting to investigate the effects of Cr in other phases of the Tl-based superconductor. In this paper, we report the effects of Cr on the superconducting properties and phase formation of the Tl-2212 phase.

Materials and Methods

Samples with the nominal starting composition $(Tl_{2-x}Cr_x)Ba_2CaCu_2O_8$ with x = 0.0, 0.2, 0.4, 0.6, and 0.8 were prepared by the solid state reaction method. Appropriate amounts of high purity (>99.99%) $BaCO_3$, CaO, and CuO were mixed completely using an agate mortar to obtain a homogeneous mixture. The precursor powders were heated at 900 °C for 24 hours with several intermittent grinding. Appropriate amounts of Tl_2O_3 and Cr_2O_3 with appropriate mole% were then added to the precursor and completely mixed before being pressed into pellets with 1.3 cm diameter and 0.2 cm thickness under 7 ton/cm^2 of pressure. The pellets were heated at 900 °C in flowing oxygen for 4 minutes. This was followed by furnace cooling to room temperature. An excess of 10% Tl_2O_3 was added to compensate for the thallium lost during heating.

The dc electrical resistance measurements were performed between 50 K and 300 K. The four-point method with silver paste contact was used for the measurement. A closed cycle refrigerator from CTI Cryogenic Model 22 cryostat and a temperature controller from Lake Shore Temperature Controller Model 340 was employed. A constant current source between 1 mA and 100 mA was used throughout the measurements. The powder X-ray diffraction (XRD) method was used to identify the phases. A Bruker model

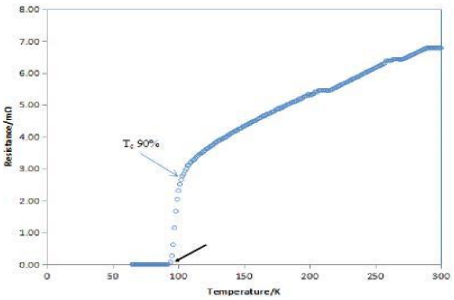
D8 Advance diffractometer with CuKα radiation source with λ=1.5418Å was used. A software from Eva program was used to analyze the XRD patterns.

Results and Discussion

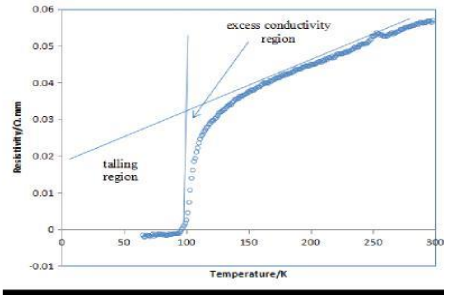
The curves of electrical resistance as a temperature function are shown in Figures 1(a) to 1(d). Samples with x = 0.0- 0.6 showed metal-like behaviour above the transition temperature. For x = 0 the resistance dropped abruptly at 105 K, where it is defined as $T_{c\ onset}$. The zero resistance occurs at 93 K and is denoted as $T_{c\text{-}zero}$. A narrow transition width ΔT_c of 12 K was observed. For samples with x = 0.2, $T_{c\text{-}onset}$ was observed to increase to 116 K and $T_{c\text{-}zero}$ was 96 K. However, ΔT_c increased to 20 K. When the content of Cr was increased to x = 0.4, $T_{c\text{-}onset}$ decreased to 105 K. A drastic decrease of $T_{c\text{-}onset}$ occurred for x = 0.6 with $T_{c\text{-}onset}$ of 84 K and a narrower ΔT_c of 13 K. Samples with x = 0.8 showed a high $T_{c\text{-}onset}$, but $T_{c\text{-}zero}$ decreased to 60 K. This is due to the high resistivity in the normal state (Table 1). It is interesting to note that superconductivity was not observed in the x = 1.0 sample. The transition temperatures and room temperature resistivity of $Tl_{2-x}Cr_xBa_2CaCu_2O_{8-\delta}$ is presented in Table 1.

A previous finding on the Tl-1212 phase using Cr_2S_3 as a source of Cr [18] reported that $T_{c\text{-}onset}$ is between 90 K and 105 K. This is due to the high resistivity in the normal state. In this work the highest $T_{c\text{-}onset}$ as well as $T_{c\text{-}zero}$ was observed in the x = 0.2 samples indicating an optimal doping level was achieved. This also coincided with the lowest normal state resistivity at 297 K, which indicates the optimization of hole concentration as a result of Cr substitution [20]. Using XRD patterns and analysis by EVA programme, the lattice parameters were calculated and presented in Table 2.

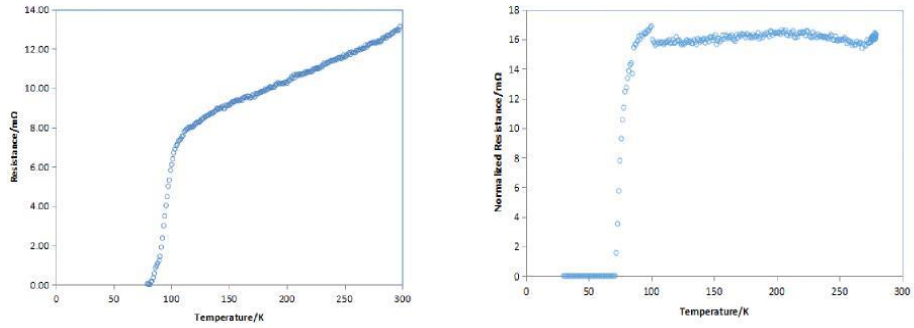
Table 2 shows the phases in the samples which consist of the Tl1212, Tl2223, Tl1223, Tl2234, and Tl1234 phases. It is noted that the Tl2212 phase was present with a volume fraction between 50% and 88%. The occurrence of multi phases in the x = 0.8 sample resulted in the reduction of $T_{c\text{-}zero}$ to 60 K. The samples were in 14/mmm and P4/mmm space group for x = 0.0 and x = 0.6. In the x = 1.0 samples, superconductivity was completely suppressed and the sample became insulating. This was due to the presence of unknown phases.



(a)



(b)



(c) (d)

Figure 1. Electrical resistance as a function of temperature for $Tl_{2-x}Cr_xBa_2CaCu_2O_{8-\delta}$ with (a) $x = 0$, (b) $x = 0.2$, (c) x 0.4 and (d) $x = 0.6$

Table 1. Transition temperatures and electrical resistivity at 297 K of $Tl_{2-x}Cr_xBa_2CaCu_2O_{8-\delta}$

x	$T_{c\text{-zero}}$ (± 1 K)	$T_{c\text{-onset}}$ (±1 K)	ΔT_c (± 1 K)	$\rho_{297\ K}$(Ωcm)
0	93	105	12	0.1562
0.2	96	116	20	0.1249
0.4	84	105	21	0.5966
0.6	71	84	13	0.5220
0.8	60	104	64	0.6072
1.0	-	-	-	-

Table 2. Phases occurrence, volume fraction, and space group of the samples

Sample	Tl-2212 Phase (%)	Tl-1212 Phase (%)	Tl-1223 Phase (%)	Tl-2223 Phase (%)	Tl-2201 Phase (%)	Tl-2234 Phase (%)	Other Phase (%)	Space group
$x = 0.0$	50	8	0	0	27	0	0	14/mmm (139)
$x = 0.2$	83	6	0	6	0	6	0	14/mmm (139)
$x = 0.4$	88	6	0	0		6	0	P4/mmm
$x = 0.6$	68	4	4	12	0	4	Tl-1234 (4)	14/mmm (139)
$x = 0.8$	46	4	4	4	0	15	Tl-1234 (15)	Pnma (60)
$x = 1.0$	40	0	0	20	6	8	Tl-1234 (2) Unknown/ 22	-

Conclusion

We have prepared Tl2212 superconductor *via* the solid-state reaction method. The addition of Cr into ($Tl_{2-x}Cr_x$)$Ba_2CaCu_2O_8$) has significantly affected the transition temperature. The volume fraction of the Tl2212 phase should be considered in the enhancement of transition temperature. Based on our experiments, it was found that the $Tl_{1.8}Cr_{0.2}Ba_2CaCu_2O_{8-\delta}$ sample can be used as a starting composition for further investigation.

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