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FORMATION AND CHARACTERIZATION OF (Tl,M)Sr1212 (M= Bi, Pb, Cr) SUPERCONDUCTING CERAMICS

(Penyediaan dan Pencirian Superkonduktor Seramik (Tl,M)Sr1212 (M= Bi, Pb, Cr))

A. Ali Yusuf, A.K. Yahya and F. Md. Salleh*

Faculty of Applied Sciences,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor

**Corresponding author: faizah163@salam.uitm.edu.my*

Abstract

The derivatives of Tl1212 phase superconductors were prepared using precursors derived from coprecipitation reaction of appropriate stoichiometric metal acetates and oxalic acid based on nominal starting compositions; $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$, $Tl_{0.5}Pb_{0.5}Sr_{1.8}Yb_{0.2}CaCu_2O_7$ and $Tl_{0.9}Cr_{0.1}Sr_2Ca_{0.9}Pr_{0.1}Cu_2O_7$. The oxalates precursors were calcined at 600 ^oC for 24 hours following which sintering were done at 870 ^oC for 1 hour. All three superconducting oxides showed metallic normal state properties with $T_{c\ onset}$ of around 100 ^oC and $T_{c\ zero}$ of between 90 –94 ^oC. The transport critical current density (J_c) of the samples are around 3 – 6 A/cm^2 while the room temperature resistivity ($\rho_{300\ K}$) values are in the range of 7 – 10 mΩcm. Powder X-ray diffraction (XRD) patterns of all samples reveals presence of dominant 1212 phase. Scanning electron micrographs reveal fine and irregular shaped grains (<2 μm).

Keywords: Tl1212 superconductor, coprecipitation method

Abstrak

Superkonduktor berfasa Tl1212 terbitan; $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$, $Tl_{0.5}Pb_{0.5}Sr_{1.8}Yb_{0.2}CaCu_2O_7$ dan $Tl_{0.9}Cr_{0.1}Sr_2Ca_{0.9}Pr_{0.1}Cu_2O_7$ telah disediakan menggunakan bahan pelopor hasil tindakbalas kopemendakan antara logam asetat dan asid oksalik. Bahan pelopor oksalat dikalsin pada 600 ^oC selama 24 jam dan kemudian disinter pada 870 ^oC selama 1 jam. Kesemua superkonduktor oksida terhasil bersifat logam pada keadaan normal dan bertukarmenjadi superkonduktor pada suhu antara 90 –94 ^oC. Nilai ketumpatan arus (J_c) superkonduktor tersebut adalah 3 – 6 A/cm^2 dan kerintangan pada suhu bilik ($\rho_{300\ K}$) dalam lingkungan 7 – 10 mΩcm. Pembelauan sinar-X (XRD) menunjukkan kesemua superkonduktor mengandungi fasa 1212 yang dominan. Imej mikroskop imbasan electron (SEM) memperlihatkan zarah halus tanpa bentuk tertentu dengan saiz zarah <2 μm.

Kata kunci: Superkonduktor Tl1212; kaedah kopemendakan

Introduction

Single Tl-O layer superconducting compounds, for example TlSr1212 and its derivatives are potential compounds for application in magnetic field. The presence of single Tl-O insulating layer in the compounds structures leads to stronger coupling between adjacent Cu-O planes [1]. Substitution of rare earth elements in TlSr1212 stabilized the 1212 phase which then improved its superconducting behavior [4]. Superconductivity of around 100 K has been observed in the TlSr1212 derivatives such as $(TlPb)Sr_2CaCu_2O_7$ [2], $(TlBi)Sr_2CaCu_2O_7$ [3] and $(TlCr)Sr_2CaCu_2O_7$ [4] systems synthesized via the conventional solid state method.

Besides the conventional solid state method, other methods such as coprecipitation and sol-gel have been employed for the synthesis of superconducting oxides. These alternatives are mainly seeking to improve the bulk material quality and reducing particle size for further applications of the material. Coprecipitation is a solution-based procedure where simultaneous precipitation of soluble components with a precipitating agent produces fine and highly homogenized powder. Solid state synthesis using chemicals derived from coprecipitation has been reported to produce high quality superconducting oxides [5,6,9]. Various reports on synthesis of superconducting BiPbSrCaCuO and YBaCuO systems via coprecipitation method can be found [5-6] but reports on the preparation of Tl-based superconducting systems via coprecipitation are sparse in literature and are limited to the preparations of non-thallium precursor materials [7]. Coprecipitated Tl-containing precursor materials are not adopted due to the high volatility of thallium oxide during heating at high temperatures. However, Bernhard [9] had successfully synthesized Tl2223 superconductors from coprecipitated Tl-containing precursors by special heating techniques. Recently, we have studied the optimum heating condition to synthesize (TlBi)Sr1212 from coprecipitated Tl-containing powders [8].

The aim of this paper is to determine the possibility of using the same heating conditions in producing other TlSr1212 derivatives, i.e. (TlPb)Sr1212 and (TlCr)Sr1212. The transport critical current density (J_c), room temperature resistivity ($\rho_{300\ K}$), powder X-ray Diffraction (XRD) and microstructure investigations using scanning electron microscope (SEM) of the samples are given and discussed.

Experimental

The coprecipitation process used was in general similar to that described earlier in Ref. [9]. Reagent-grade acetates of respective elements that make up $Tl_{0.8}Bi_{0.2}Sr_2Ca_{0.8}Y_{0.2}Cu_2O_7$ (S1) composition were dissolved in glacial acetic acid and were reacted with excess amount of oxalic acid at 50 ^oC under continuous stirring, yielding precipitation of mixed oxalate. The same reaction procedure was also applied in cases of $Tl_{0.5}Pb_{0.5}Sr_{1.8}Yb_{0.2}CaCu_2O_7$ (S2) and $Tl_{0.9}Cr_{0.1}Sr_2Ca_{0.9}Pr_{0.1}Cu_2O_7$ (S3) compositions. In each case, the oxalate precipitate was filtered, washed and dried overnight at 80 ^oC and ground to powdery state. The calcination for all samples were done at 600 ^oC for 20 hours in air at heating and cooling rates of 1 ^oC/minute. The samples were reground and pressed into pellets before they were sintered at 870 ^oC in flowing O_2 using a tube furnace for 60 minutes followed by furnace cooling to room temperature.

Electrical resistance (dc) measurements for all samples were carried out using the standard four-point-probe method with silver paint contacts in a Janis model CCS 350ST cryostat in conjunction with a closed cycle refrigerator from CTI cryogenics model 22. Room temperature resistivity ($\rho_{300\ K}$) was investigated using the Van der Pauw technique. The phase characterization was done by powder X-ray diffraction (XRD) using a Siemens D5000 diffractometer with Cu-K_α source. Volume fraction of any particular phase in the samples was determined from the ratio of the highest XRD intensity peak for the phase to the total intensity peaks (highest peak only) of all phases under consideration. Transport critical current densities (J_c) were measured in zero magnetic field using electric field criterion of 1 μVcm^{-1}. Scanning electron micrographs were recorded using Leica S440 scanning electron microscope.

Results and Discussion

Powder X-ray diffraction patterns (Figure 1) for all samples showed presence of dominant 1212 phase and minor 1201 phase. The 1212 peaks were indexed as tetragonal unit cell with space group P4/mmm. In addition, presence of $SrCO_3$ impurity was also found in all the samples. The volume ratio of 1212 phase to 1201 phase and $SrCO_3$ impurity of all samples are tabulated in Table 1. The highest percentage of Tl1212 phase was observed for S1 (83 vol %) while that for S2 and S3 were 80 vol % and 70 vol %, respectively. The lowest percentage of $SrCO_3$ impurity was observed for S2. The normalized resistance versus temperature curves of all samples is shown in Fig. 2. All samples showed metallic normal state behavior and were observed to superconduct with $T_{c\ onset}$ between 100 - 103 ^oC and $T_{c\ zero}$ between 90 – 94 ^oC. $T_{c\ onset}$, $T_{c\ zero}$, resistivity (at 300K), transport critical current density (J_c) and 1212 phase :1201 phase : $SrCO_3$ impurity ratio for all samples are listed in Table 1.

Based on the XRD data and $T_{c\ onset}$ of the samples, it is clear that the 1212 phase is responsible for its observed superconductivity. The presence of 1201 phase of around 17 vol % in both TlCr1212 and TlPb1212 and 8 vol % in TlBi1212 does not affect its superconductivity as the observed $T_{c\ onset}$ of Tl1201 was reported to be below 50 K [10]. The transport critical current density values of all samples were determined to be around 1.6 – 4.3 A/cm^2 with the highest J_c observed for TlPb1212.

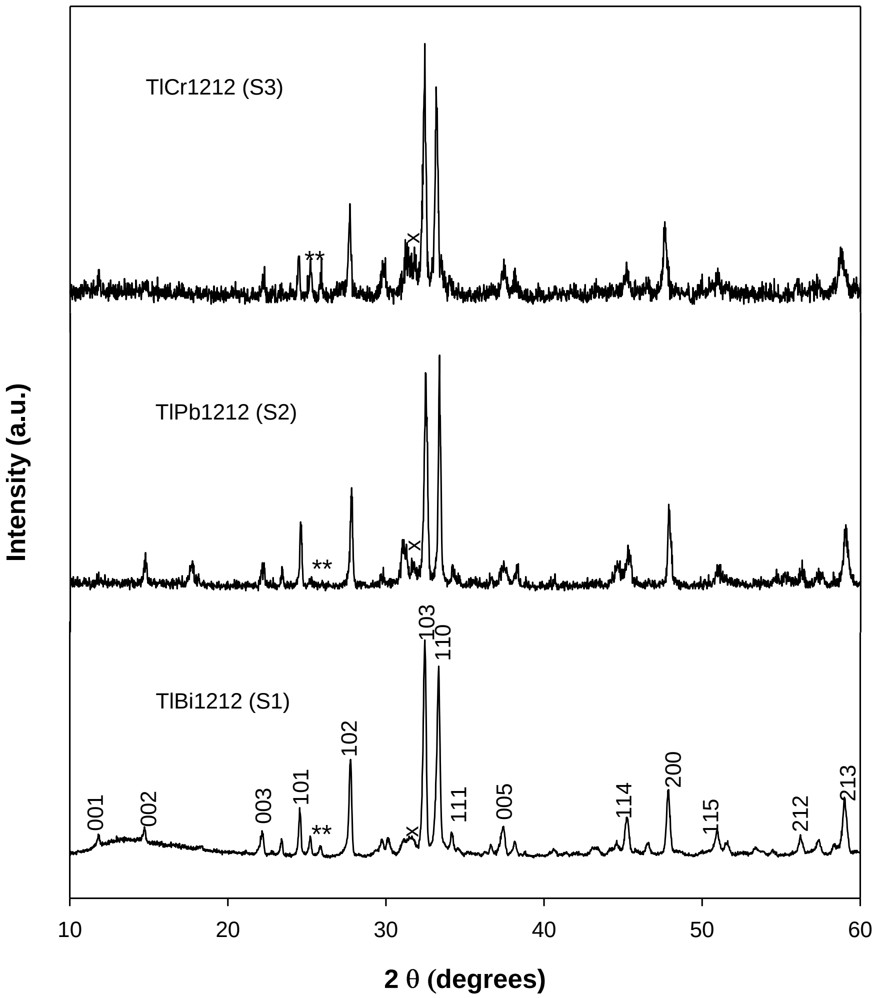

Figure 1 : Powder X-ray diffraction patterns for (Tl,M)Sr1212 (M=Cr, Pb, Bi) samples. Peaks identified as 1201 phase and $SrCO_3$ impurity are marked with x and *, respectively.

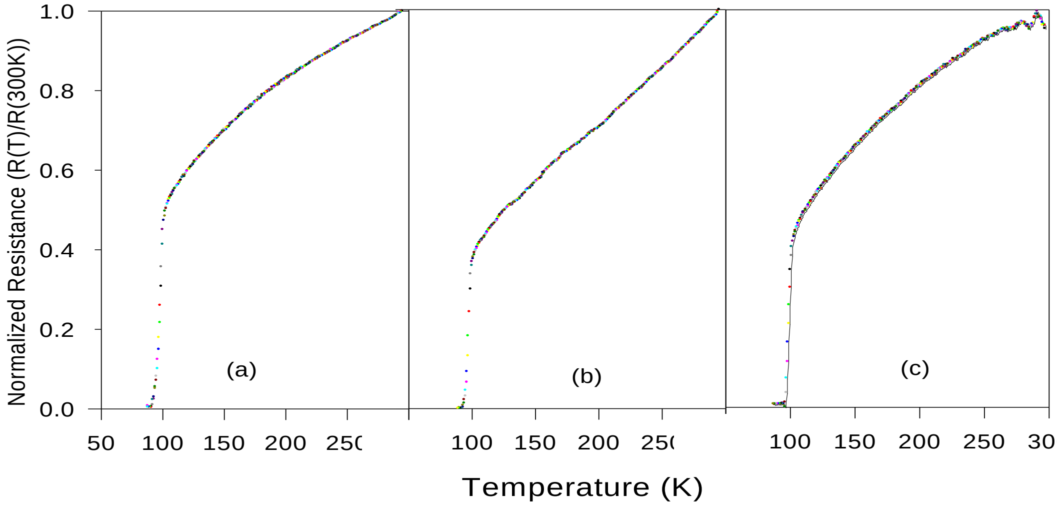

Figure 2 : Normalized resistance versus temperature curve for (Tl,M)Sr1212 (M=Cr, Pb, Bi) samples (a) (TlCr)Sr1212, (b) (TlPb)Sr1212 and (c) (TlBi)Sr1212. The vertical axes for all graphs are the same.

Table 1 : $T_{c\ onset}$, $T_{c\ zero}$, resistivity (at 300K), transport critical current density (J_c) and 1212:1201:$SrCO_3$ impurity ratio for all samples

Sample	$T_{c\ onset}$ (K)	$T_{c\ zero}$ (K)	Resistivity at 300 K (mΩ.cm)	J_c at 60 K (A/cm^2)	1212 :1201: $SrCO_3$ impurity ratio (vol %)
TlBi1212	103	94	10	3.2	83:8:9
TlPb1212	100	91	7.7	4.3	80:17:3
TlCr1212	101	90	10	1.6	70:17:13

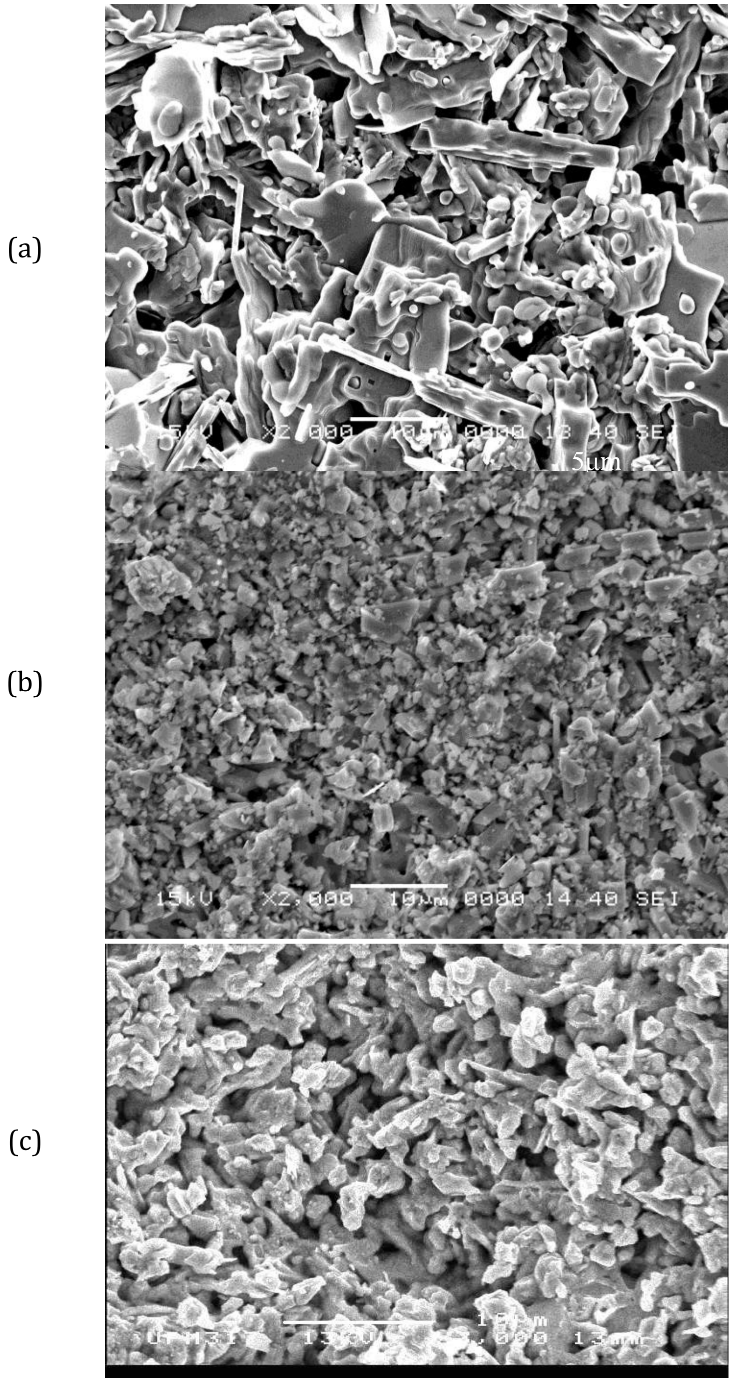

Figure 3: Scanning electron micrographs for (Tl,M)Sr1212 (M=Bi,Pb,Cr) samples
(a) (TlBi)Sr1212, (b) (TlPb)Sr1212 and (c) (TlCr)Sr1212.

Microstructures of the fractured sections of all samples are shown by SEM micrographs in Fig. 3. The micrographs of all samples showed porous microstructure and irregularly-shaped grains. Among the samples, microstructure with the finest grain (~2-4 μm) was observed for TlPb1212 while the microstructure for TlBi1212 showed the largest grain (3-10 μm). The micrograph of TlCr1212 sample showed grains of ~3 μm in sizes. Previous work on $Tl_{0.5}Pb_{0.5}Sr_{1.8}Yb_{0.2}CaCu_2O_7$ [11] and $Tl_{0.9}Cr_{0.1}Sr_2Ca_{0.9}Pr_{0.1}Cu_2O_7$ [12] synthesized by solid state method also showed porous microstructures.

This study shows that Tl1212 superconducting ceramics can be synthesized from coprepcipitation derived precursors. However a closer look at the amount of 1212 phase composition in TlCr1212 shows a value of 70 vol %, which is lower than the amount of 1212 phase in TlBi1212 (83 vol %) and TlPb1212 (80 vol %). In the sintering process, the 1212 phase is suggested to form at sintering conditions of 870 ^oC for 60 minutes. As such, the lower 1212 phase vol% in TlCr1212 indicates that the optimum sintering temperature and/or duration for TlCr1212 may be slightly different and must be further investigated. The SEM micrographs which showed different grain sizes for TlBi1212, TlPb1212 and TlCr1212 indicate the effect of chemical composition on sample microstructure. The fact that TlPb1212 sample which has the finest grain size showed the highest J_c among all samples indicates the influence of microstructure on J_c [15]. However, although TlPb1212 and TlCr1212 are less porous and possess smaller grain sizes, its transport J_c values are lower than the transport J_c values of the solid state synthesized samples [11,12]. This indicates besides microstructure, the J_c may also be influenced by other factors such as secondary phase and impurities [13]. The presence of approximately 17 vol % of Tl1201 phase in addition to $SrCO_3$ impurity in both TlPb1212 and TlCr1212 may act as obstacles which prevent the continuity of supercurrent path and thus, resulted in low J_c [14].

Conclusion

In conclusion, (Tl,M)Sr1212 where (M=Bi,Pb,Cr) were successfully synthesized using coprepcipitated precursor powder by sintering at 870 ^oC for 60 minutes. The samples showed metallic normal state behavior and superconduct with $T_{c\ onset}$ of between 100 - 103 ^oC and $T_{c\ zero}$ of between 90 – 94 ^oC. The different chemical compositions were observed to affect microstructure and 1212 phase volume fraction in the samples.

Acknowledgement

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