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Synthesis and Formation of T11223 and T1223 High-T*c* Superconductors

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ABSTRAK

Kaedah penyediaan superkonduktor $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl1223) dan $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$ (Tl2223) menggunakan komposisi permulaan dan suhu sinter yang pelbagai dibincangkan. Tl2223 berfasa tunggal dengan $T_{c\ sifar}$ antara 106 dan 109 K telah disediakan menggunakan komposisi permulaan $Tl_2Ba_2Ca_2Cu_3O_{10}$ dan $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10}$ dalam sistem tidak tertutup dengan pemanasan sekitar 20 minit pada 910 °C dalam aliran O_2. Sampel berfasa utama Tl1223 (~ 70%) telah disediakan dengan komposisi $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$ dengan memasukkan sampel dalam kerajang emas dan disinter dalam aliran oksigen pada 940°C selama 3 jam.

ABSTRACT

The preparation methods of $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl1223) and $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$ (Tl2223) superconductors using a variety of starting compositions and sintering temperatures are discussed. Single-phased Tl2223 with T_c between 106 to 109 K can be prepared using $Tl_2Ba_2Ca_2Cu_3O_{10}$ and $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10}$ as starting compositions in a non-closed system by heating around 20 min at 910°C in flowing O_2. Samples with Tl1223 major phase (~ 70%) can be prepared from $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$ composition with the sample wrapped in gold foil and sintered in flowing oxygen at 940 °C for 3 hours.

Keywords : High-temperature superconductor, synthesis of: $Tl_2Ba_2Ca_2Cu_3O_{10}$ and $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$, electrical resistance, X-ray diffraction

INTRODUCTION

The Tl-based high-temperature superconductors are an interesting family of compounds that can form phases with different numbers of CuO or TlO layers and critical temperatures (T_c). Single TlO layered $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ series and double TlO layered $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ series have been established with a maximum critical current T_c of 114 K (n=3) and 125 K (n=3) respectively. Preparation of Tl-based materials is more difficult compared to the well known

RE123 (RE-rare earth) materials due to the high volatility of Tl during heating and the growth of competing secondary phases (Abd-Shukor 1993). The Tl_2O_3 used in the preparation process is volatile at 717°C at atmospheric pressure and as such it is very volatile above that temperature. To minimize Tl_2O_3 loss, several groups used the precursor method where component oxide is mixed and calcined separately before Tl_2O_3 is added (Chen *et al.* 1994; Parkin *et al.* 1988; Sheng and Hermann 1988). Several methods also employ heating of samples in a closed system by using metallic foils (usually gold) to wrap the samples or sealed gold tubes (Luo *et al.* 1996; Subramanian *et al.* 1988). There are conflicting reports on preparation of Tl2223 using $Tl_2Ba_2Ca_2Cu_3O_{10}$ starting composition; some groups reported mixed Tl2223 and Tl2212 phases (Hazen *et al.* 1988; Parkin *et al.* 1988) while others reported dominant Tl2223 phase (Abd-Shukor and Hashim 1994; Xin *et al.* 1991). Bulk Tl1223 was repeatedly synthesized by partial substitution of Pb for Tl and using calcium- and copper-rich starting compositions (Liu *et al.* 1992; Paranthaman *et al.* 1994). Several groups have also reported the preparation of single phased Tl-based compounds using non-stoichiometric starting compositions (Liu *et al.* 1991; Nanjundaswamy *et al.* 1993; Parkin *et al.* 1988). Replacement of the exact amount of Tl_2O_3 that has evaporated during initial heating was also suggested (Abd-Shukor and Hashim 1994).

It is interesting to explore other synthesis methods of the Tl1223 and Tl2223 materials with the aim of producing better quality samples and shorter time for synthesis of the materials. Also, the use of gold foils/gold tubes which are expensive can be avoided if the Tl-based materials could be rapidly synthesized in a non-closed system. In this paper we report the synthesis of Tl2223 and Tl1223 in a non-closed system using different starting compositions. The effect of synthesizing Tl1223 in a closed system is also discussed. Powder X-ray diffraction and d. c. electrical resistance-temperature measurements are used to characterize their normal and superconducting properties.

EXPERIMENTAL DETAILS

The samples were prepared using the solid state synthesis method. Tl2223 was prepared from two different compositions: $Tl_2Ba_2Ca_2Cu_3O_{10}$ and $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10}$. Tl1223 was prepared from $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$ and $Tl_{0.5}Pb_{0.5}Sr_2Ca_2Cu_3O_9$ compositions. Appropriate amounts of high purity (≥ 99.99 %) powders of Pb_2O_3, $SrCO_3$, BaO, CaO and CuO were mixed according to the relevant nominal composition and ground in an agate mortar. The powders were then calcined in air at around 900°C for 48 h with several intermittent grindings. Appropriate amounts of Tl_2O_3 were then added to the resultant powders according to the relevant nominal starting composition used. The powders were then mixed and pressed into pellets of 12.5 mm diameter and 3 mm thickness under a load of 5 tons using a hydraulic press. Some of the samples were wrapped in gold foil to minimize the loss of Tl during heating. The pellets were then placed in an alumina boat and sintered in a tube

furnace at different temperatures between 895°C and 920°C for Tl2223 and between 940°C and 955°C for Tl1223 in flowing oxygen for different durations followed by oven cooling to room temperature. The oxygen was kept flowing until the temperature reached below 300°C.

The samples were analyzed by powder X-ray diffraction method using Siemens D 5000 diffractometer with Cu-K_α radiation. The lattice parameter of the samples was obtained from the computer fittings of observed *d* values of diffractograms for individual samples. The volume percent of the 2223 and 2212 phases were estimated from the ratio of intensity of the low angle peaks ($2\theta \sim 5°$ for 2223 and $2\theta \sim 6°$ for 2212 i.e. the (002) reflection of both phases. The volume percent of the 1223 and 1212 phases were estimated from the ratio of intensity of the (110) peaks for both phases. Electrical resistance measurements between 35 K and 300 K were carried out using the four-point probe technique with silver paint contacts in conjunction with a closed cycle refrigerator from CTI Cryogenics Model 22.

RESULTS AND DISCUSSION

Table 1 shows the starting composition, sintering temperature, sintering time, resultant phases and T_c of the samples. All the XRD peaks are indexed with tetragonal unit cells. For $Tl_2Ba_2Ca_2Cu_3O_{10}$ composition, single-phased Tl2223 (sample 3A) with T_c of 106 K can be produced without wrapping in gold foil by fast heating at 910°C for 10 min followed by furnace cooling and heating it again for 10 min at the same temperature (10+10 min). The results also show that the optimum temperature for the formation of the 2223 phase is around 910°C and the short heating duration (~20 min) is sufficient for stabilization of the phase. The low T_c (84 K) for Sample 1A which was sintered for 300 min at 895°C indicates formation of a low temperature-phase. This may be caused by the loss of Tl due to the prolonged heating or the slightly lower sintering temperature used. For Sample 2A, sintering at 900°C for 10 min produces dominant Tl2223 (67%) but did not eliminate the minor 2212 phase (33%). XRD pattern for Sample 3A (*Fig. 1*) showed dominant 2223 phase with no significant impurity peaks. The calculated lattice parameters are a = 3.849 Å and c = 35.627 Å. The temperature dependent resistance measurements for Sample 3A and Sample 8C are shown in *Fig. 2*. Single-phased Tl2223 with T_c ~109 K can also be prepared from $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10}$ by heating around 894-900°C for 240 min (Sample 4B) or around 910°C for 20 min (Sample 6B). XRD pattern for Sample 4B and Sample 6B (figure not shown) showed no noticeable secondary or parasitic peaks which are sometimes expected when using non-stoichiometric starting compositions. Sintering at a higher temperature of 920°C (Sample 5B) causes increase in Tl2212 minor phase. Our observation on sample 3A is different from Y. Xin *et al.* (1991) who reported formation of 95% pure Tl2223 after heating at 895°C for 48 h. Our results indicate that 20 min of heating at 910°C is sufficient for the chemical reaction to produce 2223 phase. The shorter heating duration can also reduce excessive loss of thallium.

TABLE 1
The starting composition, sintering temperature, sintering duration, resultant phases and T_c of the samples. * indicates that sample was wrapped in a gold foil

Starting Composition	Sample	Sintering Temp. (°C)	Sintering Time (min.)	Resultant Phase Major	Minor	$T_{c\ zero}$ (K)	$T_{c\ onset}$ (K)
$Tl_2Ba_2Ca_2Cu_3O_{10}$	1A	895	300	unknown	unknown	106	84
	2A	900	10	2223 (67 %)	2212 (33 %)	123	111
	3A	910	10+10	2223(>98%)	-	123	106
$Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10}$	4B	900	10				
		894	240	2223(>98%)	-	119	109
	5B	910	20				
		920	15	2223 (85 %)	2212 (15 %)	123	108
	6B	910	20	2223(>98%)	-	121	109
$Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$	7C	940	180				
		940	195	1212 (53 %)	1223 (47 %)	123	112
	8C*	940	180	1223 (70 %)	1212 (30 %)	122	112
	9C	940	180				
		950	180	1212 (63 %)	1223 (37 %)	125	112
	10C*	947	300	1212 (51 %)	1223 (49 %)	123	75
	11C*	940	180				
		950	180	1223 (56 %)	1212 (44 %)	125	112
	12C	940	360	1223 (52 %)	1212 (48 %)	120	112
	13C*	947	120	1212 (54 %)	1223 (46 %)	Not known	Not known
$Tl_{0.5}Pb_{0.5}Sr_2Ca_2Cu_3O_9$	14D	955	300	1212 (52%)	1223 (48%)	88	75
	15D*	940	300	1212 (55 %)	1223 (45 %)	Not known	Not known

Preparation of Tl1223 using $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$ composition by sintering at 940°C for 3 h in O_2 with the sample wrapped in gold foil (Sample 8C) produces 1223 major phase with T_c of 112 K. The X-ray diffraction for Sample 8C (*Fig. 1*) showed 1223 major peaks (70%) with minor 1212 phase (30%). The calculated lattice parameters for the 1223 major phase are a = 3.820 Å and c = 15.18 Å. We also observed that sintering the $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$ composition at 940°C in a non-closed system (without gold foil) (Sample 7C) or increasing the sintering temperature (Samples 9C,11C,13C) caused significant increase in Tl1212 phase. Preparation of Tl1223 using $Tl_{0.6}Pb_{0.5}Sr_2Ca_2Cu_3O_9$ composition by sintering in O_2 at 940 - 955°C for 6 h (Sample 14D and 15D) produced dominant Tl1212 phase together with minor Tl1223 phase. Comparing the resultant phases formed for Sample 8C and Sample 15D, it is clear that the formation of 1223 phase is promoted when the non-stoichiometric starting composition $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$ is used. Our results also indicate that preparation of single phased Tl1223 may require heating in a closed system for longer than 3 h.

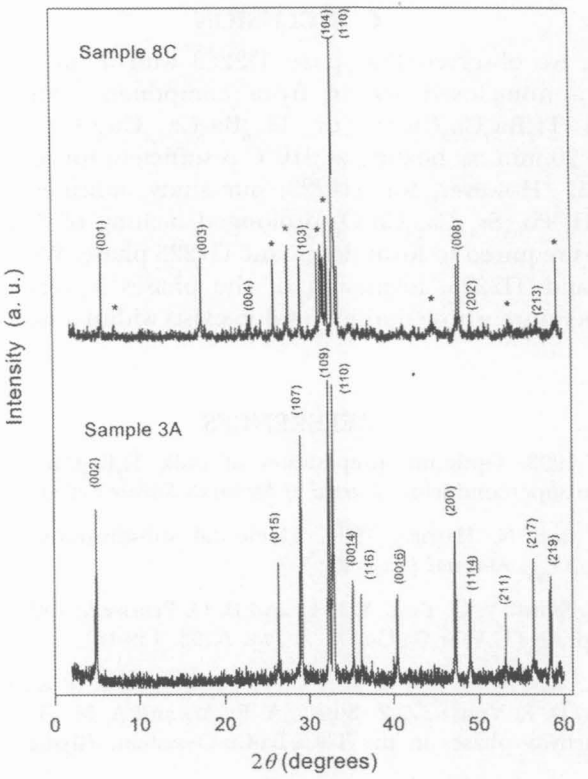

*Fig. 1: X-ray diffraction patterns for dominant Tl2223 (sample 3A) and Tl1223 (sample 8C). * indicates minor Tl1212 phase*

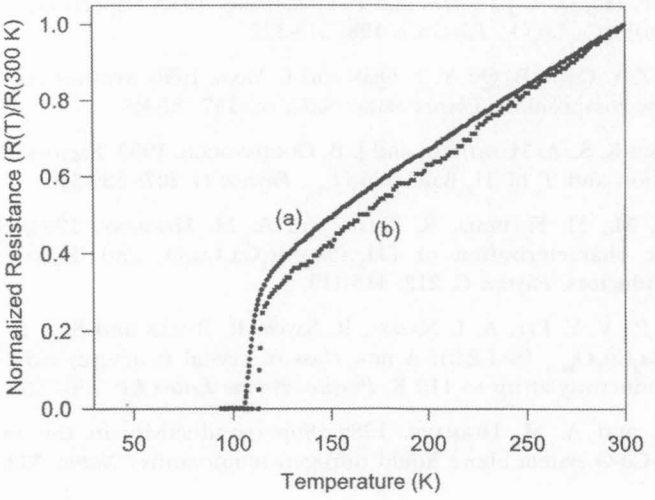

Fig. 2: Normalized resistance versus temperature curve for (a) Tl2223 (sample 3A) and (b) dominant Tl1223 (sample 8C)

CONCLUSION

In conclusion, we observed that pure Tl2223 with T_c of 106-109 K can be prepared in a non-closed system from component oxides with starting compositions $Tl_2Ba_2Ca_2Cu_3O_{10}$ or $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10}$. We found that approximately 20 min of heating at 910°C is sufficient for formation of single-phased Tl2223. However, for Tl1223, our study indicates that for starting composition $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ca_{2.4}Cu_3O_9$ prolonged heating of 3 h or longer in a closed system is required to form dominant Tl1223 phase. We observed that for both Tl1223 and Tl2223, formation of the phases is very sensitive to the sintering temperature whose optimum value exists within a narrow temperature range.

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