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Influence of Complexing Agent in Tl-Containing Sol-Gel Derived Precursor on Critical Temperature Enhancement of $Tl_{0.5}Pb_{0.5}Sr_{1.8}Yb_{0.2}CaCu_2O_7$ Superconductor

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Abstract: Superconducting oxide ceramics of composition $Tl_{0.5}Pb_{0.5}Sr_{1.8}Yb_{0.2}CaCu_2O_7$ was prepared by using a single-step sol-gel process using two different complexing agents (tartaric acid and citric acid). The effect of the complexing agents (0.0-11.0% (w/w %)) on superconductivity of the samples were studied. It was found that the values of critical temperature, $T_{c, zero}$ was enhanced from 88 K (for the sample without any complexing agents) to 95 K (for sample with 11 w/w % tartaric acid) and 97 K (for sample with 11 w/w% citric acid). SEM analysis showed formation of ultra-fine grains with 1-2 μm average grains size for the sample without complexing agents. Addition of the complexing agents induced growth of elongated grains of 5-10 μm in average length. The T_c enhancement was discussed in terms of changes in hole concentration and sample microstructure as a result of use of the complexing agents.

Key words: Single-step, sol-gel, complexing agents, Tl-1212, superconductor, microstructure

INTRODUCTION

Thallium-based (Tl-based) high temperature superconductor (HTS) with its high transition temperature is an interesting family of high-temperature ceramic superconductors. The discovery of the thallium-based superconductor in 1988 (Sheng and Hermann, 1988) has resulted in the findings of other superconducting phases of the system such as Tl-2223, Tl-2234, Tl-1223 and Tl-1212 (Goretta *et al.*, 1992; Mair *et al.*, 1995). Among them, more attention was given to the single Tl-layered Tl-1223 which produces high critical temperature (T_c) and critical current density (J_c) and has shown good performance in magnetic fields (Lao *et al.*, 2000). However, Tl-1212, which has similar structure to YBCO, has been suggested to show better performance in magnetic fields as the shorter insulating distance between the superconducting CuO_2 layers could lead to reduced anisotropy through interlayer coupling and less severe thermally activated flux motion (Lao *et al.*, 2000).

Synthesis of single-phased Tl-based compounds using powder oxides is difficult due to the constrain imposed by Tl_2O_3 that melts and evaporates at 717°C at atmospheric pressure whereas formation of the high- T_c phase typically takes place above 900°C (Salleh *et al.*, 2005). In order to reduce loss of thallium, a modified

conventional solid state synthesis which employed a two-step method was usually used. Using this method, in the first stage non-Tl-containing precursor was prepared before proceeding to the second stage where Tl_2O_3 was added to the precursor before final sintering for a short duration, usually between 3-10 min. The short sintering period is to minimize Tl_2O_3 loss but it usually results in incomplete diffusion of thallium.

On the other hand, the sol gel method offers unique advantages over the conventional solid state method as better composition control and chemical homogeneity is achievable as in the procedure, the precursors were manipulated at molecular level thus achieving homogeneity on a micro- or nano-meter scale (Van Bael *et al.*, 1998). Sol-gel synthesis of bulk superconducting powder can be used to shorten the duration taken for the preparation process as sol-gel procedure was suggested to reduce the diffusion path in the solid state reaction (Van Bael *et al.*, 1998). Use of sol-gel route preparation of Bi-based and Y-based superconducting materials has been widely reported (Fransaer *et al.*, 1989; Xu *et al.*, 1990; Mao *et al.*, 1997) but reported research on sol-gel route for Tl-based superconductors is very few. Wagner and Gritzner (1994) reported on the fabrication of bulk Tl-1234 prepared from tartaric acid gels and Yoo *et al.* (1997) reported on

fabrication of thick film of Tl-2223 via sol-gel technique combined with a two-step method. Recently, Sudra and Gritzner (2006) reported on Gd-doped (Tl,Pb)-1212 prepared using two-step approach in which the Tl-free precursor were prepared via malic gel technique. However, interestingly, single-step synthesis of Tl-based superconductors using Tl-containing sol-gel derived precursors has not been reported.

In sol-gel processing, usage of complexing agent such as tartaric acid, citric acid and oxalic acid, is an advantage as the complexing agent slows down the pace of hydrolysis and condensation in the chemical process to allow gel formation and thus helps in prevention of partial crystallization of the metal salts and phase segregation during synthesis (Kareiva *et al.*, 1996; You *et al.*, 1998). As a result, transparent solutions and homogenous gels are produced. Among the complexing agents, tartaric acid and citric acid have received the most attention. Application of both tartrate-based gel and citrate-based gels were found to be successful in the fabrication of Bi-based and Y-based superconductors (Varma *et al.*, 1990; Kareiva *et al.*, 1996; Mao *et al.*, 1997; Baranauskas *et al.*, 2001). However, to our knowledge, there is no previous report on preparation of bulk Tl-1212 via Tl-containing tartrate gel or Tl-containing citrate gel.

In this research, we report the effect of tartaric acid and citric acid on preparation of bulk Tl-1212 superconductor via single-step sol-gel process with starting composition of $Tl_{0.5}Pb_{0.5}Sr_{1.8}Yb_{0.2}CaCu_2O_7$. In the single step process, acetate salts of thallium and lead were introduced at the initial stage of the sol-gel route during preparation of superconducting samples. Results of powder X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) investigations on the bulk samples are presented and analyzed.

MATERIALS AND METHODS

Reagent-grade acetate salts of Tl, Pb, Sr, Yb, Ca and Cu with stoichiometric ratio of 0.5:0.5:1.8:0.2:1:2 were dissolved in hot acetic acid solution (25% (v/v)) producing blue coloured solution. The solution was stirred for 30 min at 80°C before the addition of reagent grade tartaric acid (or citric acid). Different amount of tartaric acid (or citric acid) were added based on the weight to weight percent (w/w (%)) of complexing agent to mixture of acetate salts. The tartaric acid-based samples were labeled as SGT-1, SGT-2 and SGT-3 with addition of 1.5, 6.0 and 11.0 weight percent (w/w (%)) of tartaric acid, respectively. The citric acid-based samples with addition of 6.0 and 11.0 weight percent (w/w (%)) of the complexing

agent were labeled as SGC-2 and SGC-3, respectively. After addition of tartaric acid (or citric acid), the stirring was continued for another 30 min at 80°C. The solution was kept at a constant pH of 3. Subsequently, all solutions were then subjected to heat treatment to evaporate the solvent which involved heating at 120°C for 5 h. During this period, the viscosities of the blue solution increased until clear, dark blue gel were formed. Further heating of the dark blue gel produced dried solid substance, brown in colour, which was then ground in agate mortar. The grinding process resulted in grayish-black powder which was then calcined at 400°C for 6 h to produced brittle black foam. The brittle black foam was then ground and pelletized and was sintered under flowing oxygen at 1000°C for 5 min. All SGT and SGC samples were prepared using the same procedure and under the same conditions mentioned earlier.

The complexing agent-free sample (SG-0) was prepared slightly differently to avoid uncontrolled hydrolysis and condensation. After dissolving of salts in hot acetic acid solution, the mixture was heated at ~90°C and stirred continuously for 7 h until the volume became one-third of the original volume and the mixture turned viscous and sticky. The continuous stirring was to ensure that the mixture was homogenous and no precipitation was formed during the process. The solution was then subjected to the same calcination and sintering stages as the rest of the samples.

All thermal treatments were performed in a Lenton model PTF 12/35/500 three-zone tube furnace. Calcinations were performed in air and while sintering of the pellets were performed in controlled oxygen flow. The resistance versus temperature relationship of the samples were determined using standard four-point-probe method with silver paint contacts in a Janis model CCS 350ST cryostat combined with a closed cycle refrigerator from CTI Cryogenics model 22. Scanning electron microscopy analysis was carried out using JEOL model JSM-6360LA scanning electron microscope. Structural characteristic of the samples were examined by an X-ray diffractometer, Philips X'pert Pro model PW3040 equipped with Cu-K $_{\alpha}$ radiation.

The 1212:1201 phase ratios was calculated from the estimation of the diffraction intensities of 1212, 1201 and other phases observed using the equations below:

$$Tl-1212(\%) = \frac{\Sigma I_{1212}}{\Sigma I_{1212} + \Sigma I_{1201} + \Sigma I_{others}} \times 100\%$$

$$Tl-1201(\%) = \frac{\Sigma I_{1201}}{\Sigma I_{1212} + \Sigma I_{1201} + \Sigma I_{others}} \times 100\%$$

where, I is the peak intensity of the present phases. Similar equations were used by Hamadneh *et al.* (2006) in the estimation of 2223:212 phase ratio in their work of Bi(Pb)-2223 superconductor prepared via co-precipitation method.

RESULTS AND DISCUSSION

Powder X-ray diffraction patterns revealed that all samples consist of dominant 1212 major phase (95-98 vol.%) accompanied with a small amount of 1201 phase (2-5 vol.%). The XRD diffractograms also showed existence of low intensity unidentified peaks which may be due to the presence of small amount of unknown impurities. Figure 1 shows XRD patterns for (a) SGT-0, (b) SGT-1, (c) SGT-2 and (d) SGC-2 samples.

Table 1 shows the weight percent (w/w%) of complexing agent used, values of $T_{c\text{ zero}}$, $T_{c\text{ onset}}$ and volume ratio of 1212:1201 phases for all samples. The high 1212 phase ratio of between 97-98 vol.% for all samples showed that the single step sol gel preparation procedure using Tl-containing precursor is effective in producing high quality samples. The SG-0 sample prepared without any complexing agents showed 95 vol.% 1212 phase. For SGT-1 sample with 1.5% w/w tartaric acid, 1212 vol.% was maintained at 95%. However, there is a slight reduction of up to 3 vol.% (SGT-3 sample) in 1212 phase with increasing tartaric acid. For the SGC-2 and SGC-3 samples, the 1212 vol.% also showed a slight reduction from 94 to 93 vol.% with increasing citric acid of 6 and 11% w/w, respectively. In general, these results showed that the 1212 phase formation did not deteriorate but was rather

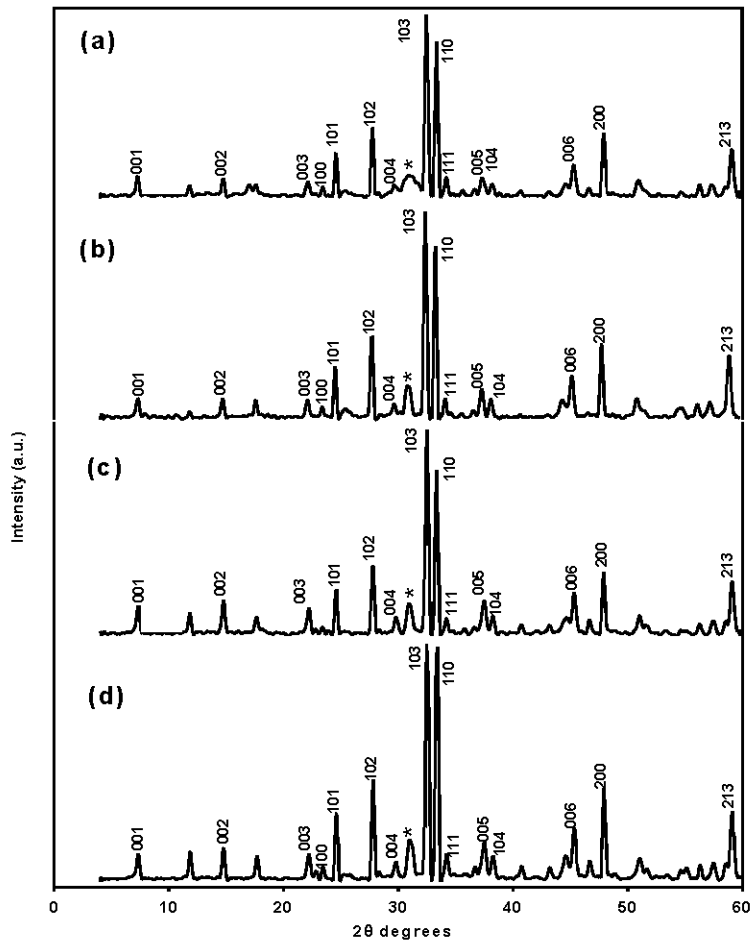


Fig. 1: XRD patterns for (a) SGT-0, (b) SGT-1, (c) SGT-2 and (d) SGC-2. The peak associated with 1201 phase is labeled with an asterisk

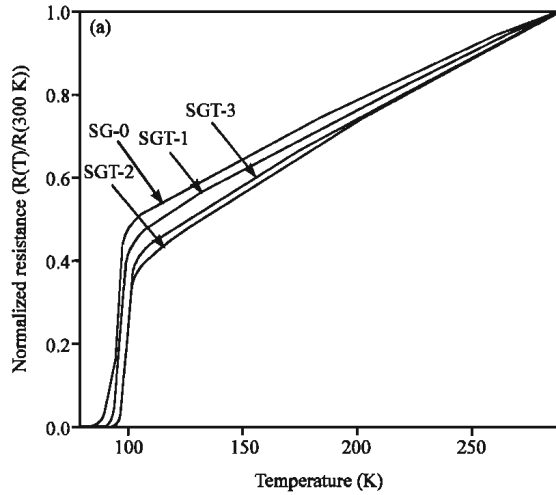


Fig. 2(a): Normalized resistance versus temperature for SG-0 and SGT samples

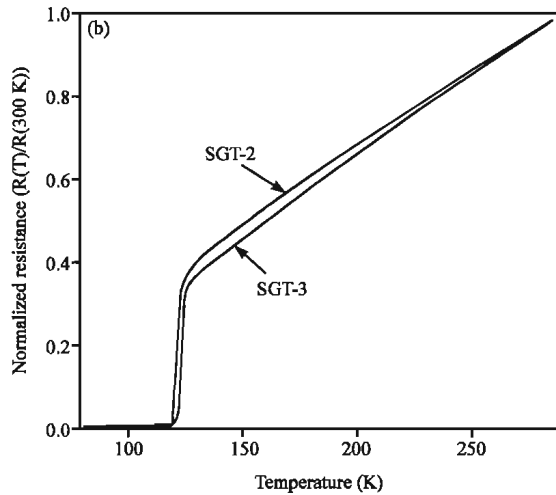


Fig. 2(b): Normalized resistance versus temperature for SGC samples

Table 1: Summary of w/w % of tartaric acid used, $T_{c \text{ zero}}$, $T_{c \text{ onset}}$ and volume ratio of 1212:1201 phases for all samples

Sample	Percentage of citric/tartaric acid (w/w)	$T_{c \text{ zero}}$ (K)	$T_{c \text{ onset}}$ (K)	1212:1201 ratio (vol. %)
SG-0	0.0	88	100	95:2
SGT-1	1.5	92	102	95:3
SGT-2	6.0	94	103	93:3
SGT-3	11.0	95	104	92:5
SGC-2	6.0	95	103	94:2
SGC-3	11.0	97	104	93:3

well maintained with addition of citric or tartaric acid as complexing agents.

Figure 2a shows the resistance versus temperature graph for SG-0 and SGT samples. SG-0 which was prepared with no complexing agent showed metallic normal state behaviour with $T_{c \text{ zero}}$ of 100 K. The SGT

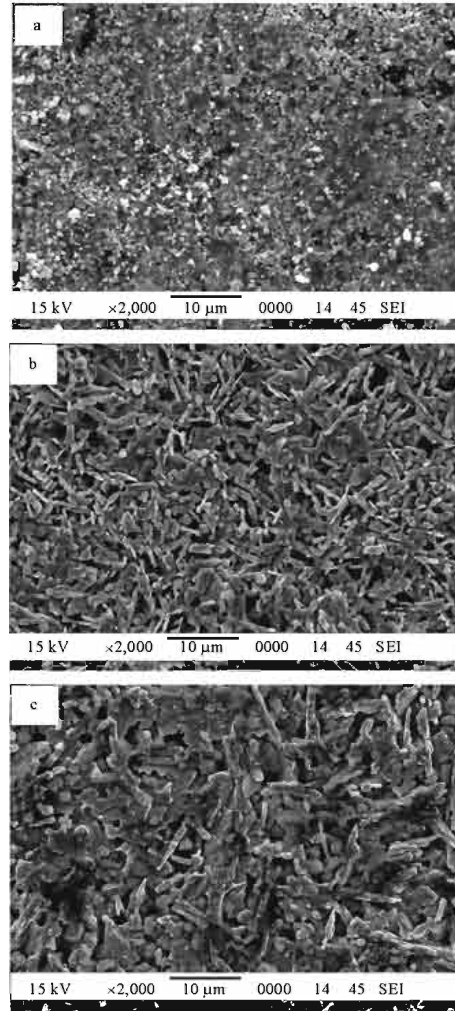


Fig. 3: SEM micrographs for samples: (a) SG-0, (b) SGT-2 and (c) SGT-3

samples showed increase in $T_{c \text{ onset}}$ and $T_{c \text{ zero}}$ with tartaric acid (Table 1). SGT samples showed enhanced $T_{c \text{ zero}}$ values of 92 K (SGT-1 sample) to 95 K (SGT-3 sample) compared the SG-0 sample which has a $T_{c \text{ zero}}$ of 88 K. The normal state of all the SGT samples showed slightly more metallic behavior with increasing tartaric acid. Figure 2b shows the resistance versus temperature measurement graph for SGC samples. SGC samples also showed enhanced $T_{c \text{ zero}}$ values of 95 K (SGC-1 sample) and 97 K (SGC-2 sample) compared to 88 K for the SG-0 sample. The normal state of all the SGC samples showed metallic behaviors.

SEM investigation on internal section of the SG-0 sample (Fig. 3a) shows ultra fine grains measuring between 1-2 μm . Addition of tartaric acid in SGT samples caused formation of elongated grains which increase in average size with tartaric acid. SGT-2 (Fig. 3b) showed

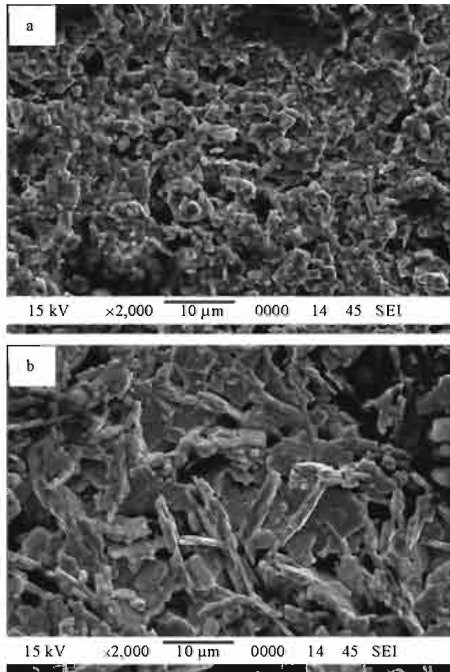


Fig. 4: SEM micrographs for samples: (a) SGC-2 and (b) SGC-3

porous microstructure with elongated grains with average size of 6-8 μm . SGT-3 (Fig. 3c) also showed elongated grains with larger average size of between 8 to 10 μm . Introduction of citric acid in SGC-2 caused the microstructure to form irregular shaped grains with average grains size between 5-10 μm (Fig. 4a). Further increase in citric acid in SGC-3 sample produced slightly elongated grains with average grain size of 10 μm (Fig. 4b). Evidence of slight partial melting can be observed for the SGT-3 and SGC-3 samples. However, no grains alignment was observed in any of the samples discussed earlier.

Present results show that addition of complexing agents in the form of tartaric or citric acid caused increase in T_c of the samples with increasing volume of complexing agent (Table 1). Because the T_c enhancements were not accompanied by a similar increase of the 1212 vol.% it is suggested that differences in 1212 phase volume may not be the reason for the observed T_c increase. It is possible that microstructural changes involving formation of elongated grains observed by SEM for both SGT and SGC samples (Fig. 3, 4) can lead to improved connectivity between grains and caused T_c to increase. However, the increase in T_c may also be due to increase in the hole concentration in the CuO_2 sheets due to several reasons such as slight differences in oxygen content between the samples or due to complex chemical reactions during the

sol-gel process. During gelation process using the complexing agents, mixed-metal species which are based on citric and tartrate ligands, were formed and these ligands may give rise to the possibility of reassembling two or more different metals which may ultimately affect the doping state of 1212 phase formed (Peleckis *et al.*, 2002).

Present results also show that for the same volume of complexing agent, the effects of tartaric (SGT samples) and citric acid (SGC samples) on T_c are not very different. It is known that tartaric acid is a polyprotic acid that has two carboxyl groups and two hydroxyl groups which are able to coordinate with metal ions to form ligands, whereas citric acid, which is also a polyprotic acid, has three carboxyl groups and only one hydroxyl group (You *et al.*, 1998). As such, our study also indicates that although T_c increases with volume of the complexing agents, it is not affected by the number of carboxyl (or hydroxyl) group in the acids.

CONCLUSION

A simple sol-gel process based on the complexation of metal ions with the help of chelating tartarate and citrate ligands has been successfully employed for the preparation of Tl-containing pre-ceramic precursors for synthesis of bulk TIPb-1212 superconductor samples. XRD confirmed formation of dominant 1212 phase together with a small amount (<5 vol.%) of 1201 phase. The salient feature of this study is the enhancement of $T_{c, \text{zero}}$ of up to 9 K and $T_{c, \text{onset}}$ of up to 4 K as a result of the use of the complexing agents. Elongated grains were observed for samples SGT-3 and SGC-3 which were prepared using 11 w/w % complexing agent. The increase in T_c may be due to changes in hole concentration or changes in sample microstructure as a result of the use of the complexing agents.

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