

# Study the Effect of *Mo* on Critical Temperature and Phase Formation in *Tl* - Based Cuprates

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**Abstract** – It has long been recognized that elemental doping is an effective way of stabilizing superconducting phase and raising  $T_c$ . After extensive experiments, we synthesized and characterized a series of new superconducting cuprates by Mo-doping. Bulk thallium based superconductors with nominal starting composition of  $(Tl_{2-x}Mo_xBa_2Ca_2Cu_3O_x)$  were prepared through a solid-solid reaction technique. For this purpose a Ba-Ca-Cu-O precursor was prepared by taking the stoichiometric amounts of  $BaCO_3$ ,  $CaCO_3$  and  $CuO$  with subsequent mixing and grinding followed by sintering at  $850^\circ C$ . Finally, appropriate amounts of  $MoO_3$  and  $Tl_2O_3$  were added to the precursor and the whole mixture was calcined at  $950^\circ C$  under oxygen flow. Different phases including the high- $T_c$  Tl-2223, Tl-2212, Tl-1223, Tl-1212 phases formed in the resulting compound were identified. Some other phases were also found when the Tl to Mo ratio was changed from 1.6: 0.4 to 1.4 :0.6 and 1 : 1 in  $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$  superconductor. From the resistivity measurements, the critical temperature  $T_{c(0)}$  for the compound was found to around 89 K. The enhanced doping of Molybdenum (Mo) in Tl-cuprates induces pairing mechanisms to occur outside the  $CuO_2$  layers and thus reducing high- $T_c$  phase formation and hence the  $T_{c(0)}$  value.

**Keywords** – Calcined, Sintering, Stabilize, Synthesis, Cuprates.

## I. INTRODUCTION

Since the discovery of high critical transition temperature (high  $T_c$ ) superconductor by Bednorz and Müller (1986), a great effort has been put towards the research of high  $T_c$  materials. Tl- based cuprates thin films are the more promising candidate for various applications in both electronics and electrical power related devices. Tl-system has not only high transition temperature but also more superconducting phases than others. Hence comparative studies on structural and physical properties of this series of phases might provide us more information on the mechanism of high  $T_c$  superconductivity [1]. In 1988 Sheng and Hermann reported Tl-based superconducting cuprates with high critical temperature (120K). Tl-1223 and Tl-2223 phases were important due to relatively high critical temperature shown by them [2]. Tl- based copper oxides are thermally unstable phases, and rapid loss of thallium takes place above  $875^\circ C$ . Hence it was difficult to prepare pure single phase [3]. An excess quantity of thallium (compensating the loss of Tl by evaporation during heating) was necessary to the formation of the 1223 phase. In order to prevent Thallium loss during the reaction, samples had been wrapped in noble metal foils as Au, Ag, Pt, Ni foils and had been

used in the synthesis of Tl-based superconductors.[4] Both heating temperature and heating time were also important to the formation of the 1223 phase[5]-[6]. Recently, doped Tl-based cuprates have been extensively studied due to their stability and phase purity. Eder and Gritzner reported the formation of high quality Tl-1223 and Tl-1212 superconducting materials with well-connected grains by doping with rare earth oxides. The Tl-1212 crystallites are usually polygon shaped with dimensions in the order of 2-5 $\mu m$  [7]. It was recognized that elemental doping is an effective way of stabilizing superconducting phase and raising  $T_c$ . Mo substituted cuprates could successfully be prepared with a two-step solid-state reaction method. The doping of Molybdenum showed greater ability of transition element to generate or to stabilize new superconductors by occupying the Thallium sites. The Mo substituted 1223 phase exhibited  $T_c$  (onset) of 105 K and  $T_c$  ( $\rho = 0$ ) of 94 K, which might be improved by optimizing starting composition and preparation procedure. It was found that the substitution Mo in  $TlSr_2CaCu_2O_7$  can stabilize the 1212 phase. The Mo substituted 1212 phase showed superconductivity around 70 K. Some Mo-doped Tl-1222 samples also exhibited weak 100 K superconductivity [8]. It was found that pressing before the final annealing reduces the tape thickness and increased the  $J_c$ . Stabilization of new superconducting thallium cuprates by Molybdenum,  $Tl_{0.8}Mo_{0.2}Sr_2CaCu_2O_{7-\delta}$  with the “1212” structure whose  $T_c$  increases from 40 K, when as-synthesized, to 86 K after annealing in a reducing atmosphere whereas substitution of Ba for Sr in the oxycarbonates does not significantly influence the superconducting properties[6][9]. The motivation behind the work was to see the effect of doping of molybdenum on the phase formation and critical temperature of Tl-based cuprates.

## II. MATERIAL AND METHODS

Tl-based superconducting samples with different Mo content x were prepared at ambient atmosphere using the conventional two-step solid-state synthesis Technique[10]-[11]. The nominal starting compositions were  $Tl_{2-x}Mo_xBa_2Ca_2Cu_3O_y$  with x=0.4, 0.6, and 1.0. For precursors, stoichiometric amount of  $BaCO_3$ ,  $CaCO_3$  and  $CuO$  were mixed and ground thoroughly in an agate mortar. The mixture was calcined in an open platinum crucible at  $850^\circ C$  under oxygen flow for a total period of 16 h. The mixture was subjected to intermittent grindings after every 4 hours to avoid agglomeration formation. For the preparation of Mo doped Tl- based cuprate, mixture of

Tl<sub>2</sub>O<sub>3</sub> and Mo<sub>2</sub>O<sub>7</sub> at ratio of 1.6 : 0.4 was synthesized by sintering with one of the precursor samples in a platinum crucible with a lid at 950°C for 8 hours. Intermittent grindings were carried out after every 2 hours. This mixture with different ratios of Tl and Mo were added to another prepared precursors and sintered under the same experimental procedures and conditions. In order to prevent severe thallium loss and maintaining the stoichiometry of the products to ensure the formation of the desired phase during the reaction, samples were wrapped by Ag foil [4]. Due to the volatile and toxic nature of Thallium the furnace was kept inside a fume hood.

The resulting powders were pelletized for resistivity measurements at a pressure of 0.0280tonne/mm<sup>2</sup> using polymer press (PF-M15). The pellets were annealed at 600°C for 6 hours under oxygen flow. Finally pellets were characterized by resistivity measurement as a function of temperature using a standard dc four probe measuring technique. The phase compositions of the final powdered sample were analyzed by X-ray diffraction by using a Philips PW1710 model diffractometer in the 2θ range 20° - 70° using Cu Kα<sub>1</sub>/Kα<sub>2</sub> radiation. Scanning electron microscopies (SEM) were performed using Hitachi field emission S-3600N.

### III. RESULTS AND DISCUSSION

#### A. Results

The x-ray diffractograms of the compounds are shown in Fig. 1a, 1b and 1c. Some peaks [102], [103], [0012], [110], [112], [113], [114], [116], [117, 211, 009] and [212] are common for all the three compounds at 2θ = 26.54, 26.76, 28.84, 32.08, 35.18, 38.74, 42.92, 48.28, 52.68 (approx.) and 53.54. As the Molybdenum content was increased further, extraneous phases appeared in the synthesized compound. The peaks [003], [004], and [115] (at 2θ = 20.78°, 21.87° and 46.04°) were appeared for TlMoBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> Cuprates. But, it vanished completely for Tl<sub>1.6</sub>Mo<sub>0.4</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> and Tl<sub>1.4</sub>Mo<sub>0.6</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> compounds. Again, The peak [104] of the Tl-1223 phases (at 2θ = 30.45°) were prominent in TlMoBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> compound whereas, it is much diminished in the Tl<sub>1.4</sub>Mo<sub>0.6</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> and totally absent in Tl<sub>1.6</sub>Mo<sub>0.4</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> cuprate. The disappearance of peaks at 29.88, 35.36° and 45° in the diffractogram for the Tl<sub>1.6</sub>Mo<sub>0.4</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> compound is another important observation. Though it was begun with a starting nominal composition to form (Tl<sub>2-x</sub>Mb<sub>x</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub>) structure, the other phases Tl-2212, Tl-1223, Tl-1212 were also seen. X-ray powder diffraction reveals a multiphase mixture in all the three samples. From scanning electron micrographs, the surface morphology of the compound of Tl<sub>1.6</sub>Mo<sub>0.4</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> cuprate was seen partially separated and relatively large tetragonal like structures with better grain homogeneity (Fig 2a). Randomly oriented and poorly interconnected spear shaped microcrystals of 2223 phases are seen in case of Tl<sub>1.4</sub>Mo<sub>0.6</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> micrograph with average

dimension of 2μm with noticeable grain boundaries. It showed distinguished self aligned prismatic and rod like morphology. The grain size decreased as the Molybdenum content was increased. The third sample formed into conglomerate structure which was preserved over the entire concentration range covered with dimension of 2μm.

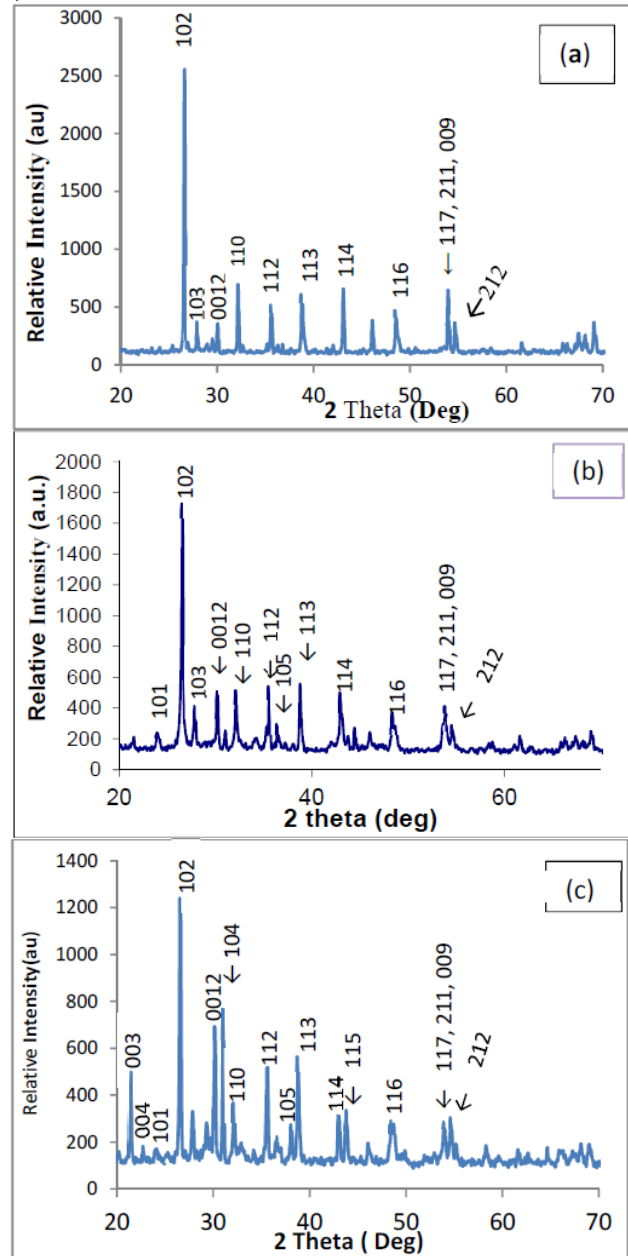
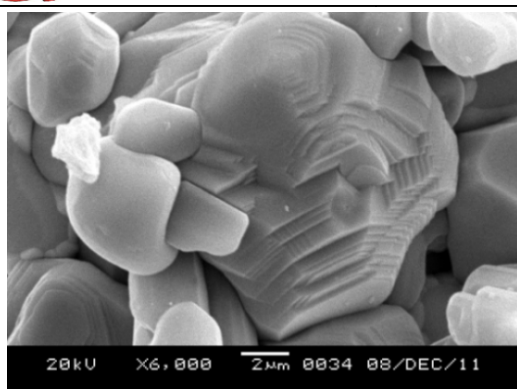
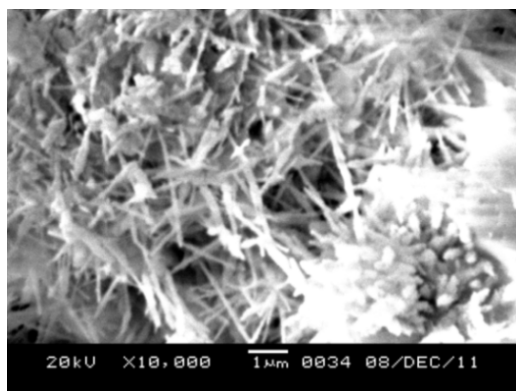


Fig.1. X-ray diffractogram of (a) Tl<sub>1.6</sub>Mo<sub>0.4</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> (b) Tl<sub>1.4</sub>Mo<sub>0.6</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> and (c) TlMoBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> superconducting cuprates.

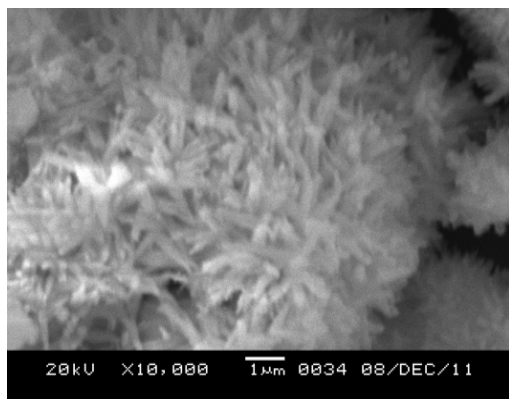
The T<sub>c(0)</sub> value of Tl<sub>1.6</sub>Mo<sub>0.4</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> and Tl<sub>1.4</sub>Mo<sub>0.6</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> cuprates were found to be 89K and 86K and that of TlMoBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> -cuprates was 80 K as indicated by Figs. 3a, 3b and 3c. The addition of more Mo can stabilize the superconducting phases but lead to a significant decrease in the superconducting transition temperature.



(a)



(b)



(c)

Fig.2. Scanning Electron Micrographs (SEM)  
(a)  $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_y$ , (b)  $Tl_{1.4}Mo_{0.6}Ba_2Ca_2Cu_3O_y$  and  
(c)  $TlMoBa_2Ca_2Cu_3O_y$  superconducting cuprates.

#### B. Discussion:

The new peaks obtained in the XRD of the  $Tl_{1.4}Mo_{0.6}Ba_2Ca_2Cu_3O_y$  and  $TlMoBa_2Ca_2Cu_3O_y$  cuprate samples can be explained from the fact that some additional possible unconventional pairing interactions may occur outside the  $CuO_2$  layers in high- $T_c$  superconductors. The Mo doping promoted the growth of Tl-2223 and Tl-1223 superconducting phases and suppressed other phases. On the other hand Mo dopant may disturb the local oxygen distribution in both in the 2212 and 1212 lattices, which in turn lowers the  $T_c$  of the material [8].

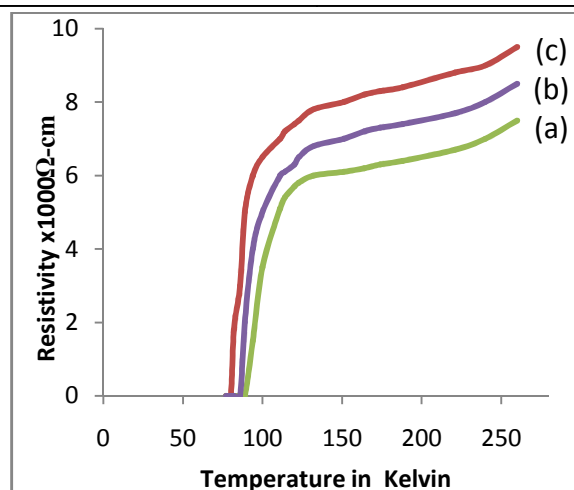


Fig.3. Temperature vs Resistivity of  
(a)  $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_y$ , (b)  $Tl_{1.4}Mo_{0.6}Ba_2Ca_2Cu_3O_y$   
and (c)  $TlMoBa_2Ca_2Cu_3O_y$  cuprates.

The separation of tetragonal shaped like grains was much more complete in case of  $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$  (figure 2(a)). More completed separation reduces lump formation and leads to much better grain homogeneity. It is seen that the size of the crystals decreased from 5  $\mu m$  to 2  $\mu m$  as the content of Molybdenum increased in Tl-based Superconductor.

#### IV. CONCLUSION

In conclusion,  $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_y$ ,  $Tl_{1.4}Mo_{0.6}Ba_2Ca_2Cu_3O_y$  and  $TlMoBa_2Ca_2Cu_3O_y$  compounds are fabricated by doping of Molybdenum in the Tl-site of Tl-Ba-Ca-Cu-O cuprates at nominal starting compositions. It is found that the lowering of  $T_c$  value in Mo doped Tl-cuprates may be due to intergrowth of oxycarbonates or for disturbing the local oxygen distribution in the phases [8] or it induces the additional pairing mechanisms formed at the outside the  $CuO_2$  layers. The results show that great ability of transition element is to generate or to stabilize new superconductors by occupying the Thallium sites.

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