

The Role of Molybdenum on Superconductivity in Tl-Based Cuprates

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Abstract- Bulk thallium based superconductors with nominal starting composition of $(\text{Tl}_{2-x}\text{Mb}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x)$ were prepared through a solid-solid reaction technique. A Ba-Ca-Cu-O precursor was made for this purpose by mixing and grinding the stoichiometric amounts of BaCO_3 , CaCO_3 and CuO followed by sintering at 850°C . Finally, appropriate amounts of MoO_2 and Tl_2O_3 were added to the precursor and the whole mixture was calcined at 950°C under oxygen flow. Different phases including the high- Tl-2223 , Tl-2212 , Tl-1223 , Tl-1212 phases were formed in the resulting compound. Some other phases were also found when the Tl to Mo ratio was changed from 1.6 : 0.4 to 1 : 1 in $\text{Tl}_{1.6}\text{Mo}_{0.4}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ superconductor. From the resistivity measurements, the critical temperature $T_{c(0)}$ for the compound was found to around 89 K. The 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.

Index Terms- calcined, cuprate, oxycarbonates

I. INTRODUCTION

Tl-based cuprates thin films are the more promising candidate for high critical current density, High frequency and high performance application and microwave passive devices operating at temperature above 77K. 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) [2]. Tl-1223 and Tl-2223 phases were important due to relatively high critical temperature shown by them. Tl-based copper oxides are thermally unstable phases, and rapid loss of thallium takes place above 875°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 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] 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 $2\text{-}5\mu\text{m}$ [6]. The doping of Molybdenum showed greater ability of transition element to generate or to stabilize new superconductors by occupying the Thallium sites. The Transition element such as Mo, V, Cr collapsed the intergrowths of $(110)\text{-}[1201]_1$ $[\text{S}_2\text{CC}]$ structure of the thallium oxycarbonates was not known. It was most probable that the atomic positions differ from those expected for the true rock salt layer. [7]. Stabilization of new superconducting thallium cuprates by Molybdenum with “1212” structure exhibited a T_c ranging from 40K, when as-synthesized, to 86K after annealing in a reduced atmosphere [8]. The doping of Mo and W in $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ can stabilize the Tl-1212 phase. The Mo substituted 1212 phase showed superconductivity around 70 K. Some Mo-doped Tl-1222 samples also exhibited weak 100 K superconductivity [7]. 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

The Mo doped Tl-based superconducting oxide powders were synthesized by the conventional with a two-step solid-state reaction method [9]. For precursors, stoichiometric amounts of BaCO_3 , CaCO_3 and CuO were mixed and finely grinded in an agate mortar. The mixture was calcined in an open platinum crucible at 850°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 superconductor, a mixture of Tl_2O_3 and MoO_2 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. The ratio of Tl_2O_3 and MoO_2 was varied to 1:1 for other compound. This mixture 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].

The resulting powders were pelletized for resistivity measurements at a pressure of $0.0280\text{tonne}/\text{mm}^2$ using polymer press (PF-M15). The pellets were annealed at 600°C for 6 hours under oxygen flow. Finally pellets were characterized by resistivity vs. temperature (R-T) measurement 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 with $\text{Cu K}\alpha_1/\text{K}\alpha_2$ 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. Some peaks are common for both compounds at $2\theta = 26.54, 26.76, 28.84, 32.08, 35.18, 38.74, 42.92, 48.28, 52.68$ and 53.54 . As the Molybdenum content was increased further, extraneous phases appeared in the synthesized compound. The peak (003), (004) and (101) (at $2\theta = 20.78^\circ, 21.87^\circ$ and 25.04°) were appeared for $TlMoBa_2Ca_2Cu_3O_x$ Cuprates. But, it vanished completely for $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ compounds. Again, Two peaks (0012) and (104) of the Tl-2223 and Tl-1223 phases (at $2\theta=30.02^\circ$ and 30.45°) were prominent in $TlMoBa_2Ca_2Cu_3O_x$ compound whereas, it is much diminished in the $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ cuprate.

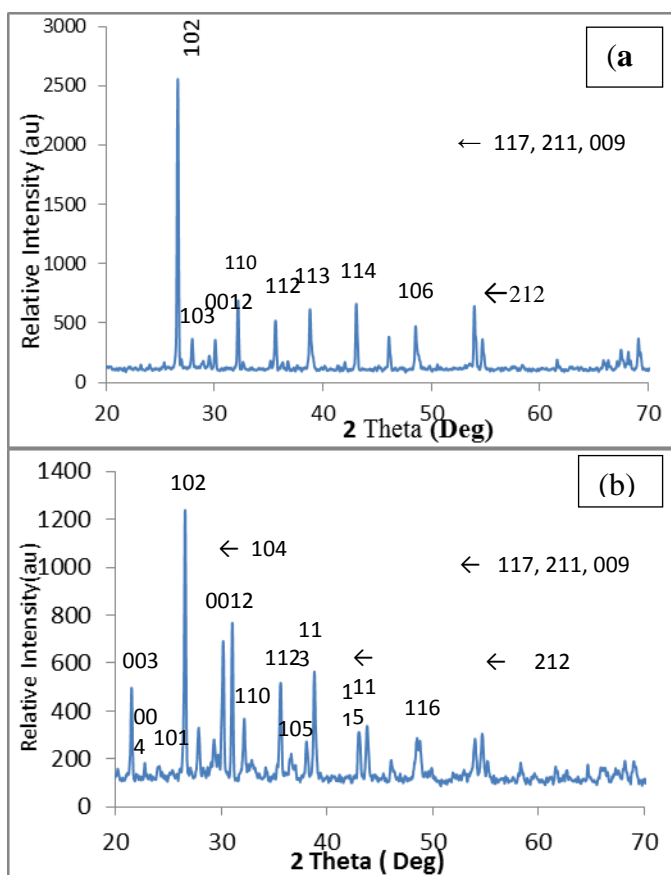
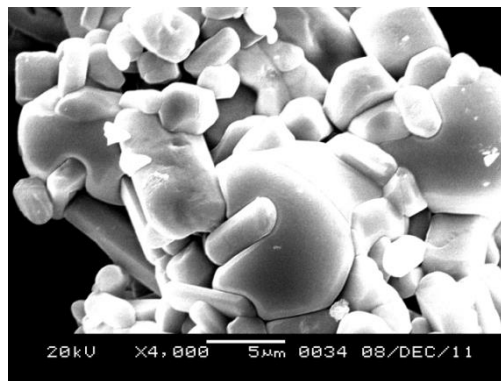


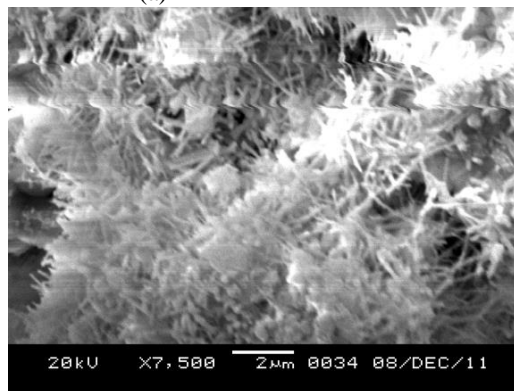
Figure 1: X-ray diffractogram of (a) $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ and (b) $TlMoBa_2Ca_2Cu_3O_x$ superconducting cuprates.

The disappearance of peaks at $29.88, 35.36^\circ$ and 45° in the diffractogram for the $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ compound is another important observation. Though it was begun with a starting nominal composition to form $(Tl_{2-x}M_b)_xBa_2Ca_2Cu_3O_x$ structure, the other phases Tl-2212, Tl-1223, Tl-1212 were also seen. X-ray powder diffraction reveals a multiphase mixture in the two samples.

From scanning electron micrographs, the surface morphology of the compound of $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ cuprate is seen partially separated and relatively large tetragonal like structures with better grain homogeneity (Fig 2a). The samples were conglomerate of randomly oriented lamellar microcrystals of 2223 phases with average dimension of $5\mu m$.



(a)



(b)

Figure 2: Scanning Electron Micrographs (SEM) (a) $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ and (b) $TlMoBa_2Ca_2Cu_3O_x$ superconducting cuprates.

As the Molybdenum content was increased, the sample crystallizes into needle like structure which was preserved over the entire concentration range covered with dimension of $2\mu m$.

The $T_{c(0)}$ value of $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ cuprate was found to be 89K and that of $TlMoBa_2Ca_2Cu_3O_x$ -cuprate was 80 K as indicated by Figs. 3a & 3b. The addition of more Mo can lead to a significant decrease in the superconducting transition temperature.

B. Discussion:

The new peaks obtained in the XRD of the $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ and $TlMoBa_2Ca_2Cu_3O_x$ 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.

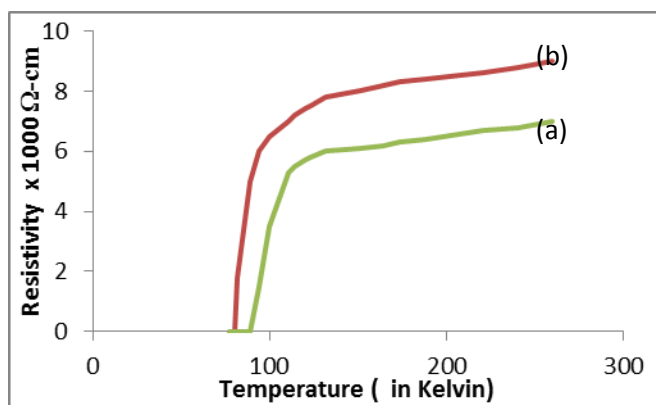


Figure 3: Temperature vs Resistivity of (a) $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ and (b) $TlMoBa_2Ca_2Cu_3O_x$ cuprates.

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 lattice, which in turn lowers the T_c of the material [7]. 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 μm to 2 μm as the content of Molybdenum increased in Tl-based Superconductor.

IV. CONCLUSIONS

In conclusion, $Tl_{1.6}Mo_{0.4}Ba_2Ca_2Cu_3O_x$ and $TlMoBa_2Ca_2Cu_3O_x$ compounds are fabricated by doping of Molybdenum in the Ba-Ca-Cu-O precursor 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 of 1201 structure or for disturbing the local oxygen distribution in the phases [7] 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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