Effect of Li_2O on the Microstructure, Magnetic and Transport properties of Tl-2223 Superconductor

R. Shipra,^{1,2} A.S. Sefat²

¹*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA*

²*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

Abstract

The present study gives an account of the effect of addition of Li_2O on the ease of phase formation and superconducting properties of $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (Tl-2223) material. Li_2O slightly decreases the superconducting transition temperature, while an optimal concentration of 20% Li_2O improves the critical current density (J_c) by $\sim$ two fold. We also found substantial effects on the synthesis temperature, microstructure and normal state transport properties of Tl-2223 with Li_2O addition. Short-time annealing under flowing Ar+4% H_2 (1 hr.) further improves the superconducting volume fractions, as well as J_c .

Introduction

Among all Tl-based cuprate superconductors, Tl-2223 has the highest transition temperature ($T_c \sim 128$ K) and a better phase stability during synthesis at ambient pressure, for example compared to $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9.8}$ (Tl-1223) with a similarly high T_c (~ 123 K).^{1,2} High volatility of Tl_2O_3 makes synthesis of Tl-2223 complex and a slight variation in the synthesis condition can give rise to other Tl-based cuprate phases.³ Some reports even emphasize the role of excess Ca and Cu in stabilizing the Tl-2223 phase based on cations intermixing among themselves.^{4,5} Another difficulty in synthesis of Tl-2223 is accounting for the toxicity of Tl. In this work, we study the effect of Li substitution for Tl. Our basic hypothesis is that lithium can sit in place of toxic thallium to the extent that 2223 structure remains stable.

In Tl-2223, Tl exists in both +3 and +1 oxidation states that can vary with oxidation and reduction thermal anneals. It is reported that some of the Tl^{+3} substitutes Ca^{+2} while some Cu^{+} can sit at Tl^{+3} in the Tl-O plane.⁴ The ionic sizes of Tl^{+3} , Ca^{+2} and Cu^{+2} are close to that of Li^{+} .⁶ Although we have nominally accounted for Li on Tl atomic site, the small Li^{+} can potentially substitute at any combination of cationic sites, influencing charge balance. There is no literature report of such chemical substitution in Tl-2223; however, there are a few reports on Tl-2212 with Tl-site substitution^{7,8} by Rb^{+} and K^{+} which have similar sizes to Tl^{+} . Li substitution may be more favored at Cu^{+2} and Ca^{+2} sites; for example, it was found that Li at Ca site drastically decreased T_c , but when substituted for Cu, the T_c decrease was slow for the same amounts of substitution in Bi-2212.⁹ Other reports suggested an optimum amount of Li concentration ($\sim 20\%$ per formula unit) to improve the T_c and J_c of Bi-2212, Hg-1223, (Tl,Pb)-1223.^{10,11,12,13} Reports on less

(structurally, chemically) complex cuprates like $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) provided additional insight on the effect of Li substitution at the Cu-site.^{14,15,16} For example, the non-magnetic Li^+ impurity was found to suppress T_c more rapidly as compared to magnetic impurities like Ni^{+2} .^{17,14} In melt-textured YBCO, Li^+ acted as effective pinning centers at optimal concentrations.¹⁸ Structurally, in Bi-2212 and LSCO, Li substitution at Cu increased the c axis length.^{11,16} It was also observed that the Li addition promoted the phase formation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) and decreased the synthesis temperature to lower values, compared to Li free Bi-2212.^{19,11} In this work, we provide a simple route to obtain polycrystalline Tl-2223 superconductors with high reproducibility and present a way to improve its superconducting properties with the addition of Li_2O and thermal annealing. In the past, long time thermal annealing in an evacuated sealed quartz tube played an important role in increasing $T_c \approx 128$ K.^{19,5,20} However at such high annealing temperatures, no discussion on the effect of Tl loss and inter-site cation substitution on T_c was discussed.²⁰ In this study, we did short time (1 hour) thermal annealing at a low temperature (250 °C) under flowing $\text{Ar}+4\%\text{H}_2$, as longer duration (~ 5 hours) resulted in the formation of Tl-free impurity phases. The annealing condition was carefully chosen and based on the results obtained by Maignan *et al* for Tl-2201.^{1,21} The focus on this study is to add knowledge regarding the effect of Li on the crystal structure, microstructure, normal and superconducting properties of Tl-2223.

Experimental

For synthesizing polycrystalline samples equivalent to $\text{Li}_x\text{Tl}_{2(1-x)}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($\text{Li}_x\text{Tl-2223}$), first a precursor was prepared having a composition equivalent to $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ and then appropriate molar amounts of Tl_2O_3 and Li_2O were added to complete the formation of the desired compound, with $x = 0, 0.1, 0.2, 0.3$, or 0.4 . First of all, BaCO_3 , CaCO_3 and CuO were ground in the cationic ratio of 2:2:3, and calcined subsequently three times at 880 °C, 890 °C, and 900 °C, respectively in air, with homogenizing grinding steps in between. Each calcination was done for 12 hrs. The final mixture was pelletized at a pressure of 6000 tonnes/ m^2 and sintered at 910 °C in air for 48 hrs. The X-ray diffraction (XRD) pattern showed the mixture (precursor) consisting of BaCuO_2 , Ca_2CuO_3 and CuO , to which Tl_2O_3 and Li_2O were then added. The best optimized ratio of Tl_2O_3 :precursor for preparing the single phase Tl-2223 was found to be 1.1:1.

For synthesizing $\text{Li}_{0.1}\text{Tl-2223}$ and $\text{Li}_{0.2}\text{Tl-2223}$, the ratio of $\text{Li}_2\text{O}:\text{Tl}_2\text{O}_3$:precursor were mixed in the molar ratio of 0.05:1.05:1 and 0.1:1:1, respectively. The mixed powders were ground well, and pressed by applying a pressure of 1500 tonnes/ m^2 into ¼ inch single pellets each weighing between 0.5-0.75 grams. Each pellet was wrapped in a gold foil, sealed in a quartz tube individually under 0.9 atm. of oxygen, and then heated at 910 °C for 3 hrs. For synthesizing $\text{Li}_{0.3}\text{Tl-2223}$ and $\text{Li}_{0.4}\text{Tl-2223}$, $\text{Li}_2\text{O}:\text{Tl}_2\text{O}_3$:precursor were mixed in the ratio of 0.15:0.95:1 and 0.2:0.9:1. The pellets were sintered at 900 °C, also in sealed quartz tube with 1 atm. of oxygen. We must note that neither phase formed at 910 °C with XRD patterns showing numerous impurities, hence large sensitivity of phase formation to small temperature differences. The ‘as-prepared’ pellets were broken to retrieve pieces for ‘annealing’ studies ($\text{Ar}+4\%\text{H}_2$ for 1 hr). The data of 10, 20, 30 and 40% nominal Li_2O addition are shown below.

XRD patterns were obtained using X’pert PRO MPD powder diffractometer in the 5-90° 2 θ range. The refined cell parameters were determined from Le Bail refinements/matching of the

experimental data (reference code: 01-081-0044) in the X'pert HighScore Plus software. Zero shift, unit-cell dimensions and profile values are the only parameters that were refined. The T_c and J_c were determined from magnetic measurements performed on SQUID magnetometer. The zero-field-cooled (ZFC) data were collected while increasing the temperature from 5 K to 150 K while the field-cooled (FC) data were obtained while cooling from 150 K in field. For a few samples we determined the resistive transition by transport measurements with Physical Property Measurement System (PPMS) by Quantum Design (USA). For estimating J_c , field-dependent isothermal magnetization hysteresis curves were obtained at 5 K.

Results and discussion

Figure 1 shows the XRD pattern of the as prepared $\text{Li}_x\text{Tl-2223}$ samples. Tl-2223 sample contained BaCO_3 (shown as #) as the only impurity while addition of Li_2O promoted Tl-2212 and BaCuO_2 (both marked as *) impurity phases. Well-resolved XRD peaks indicate good crystallinity and can be indexed accordingly. The lattice parameters obtained for as prepared Tl-2223 and Li added Tl-2223 are shown in Table 1. With increasing Li content, c lattice parameter decreases while a lattice parameter remains almost constant or slightly changes. For LSCO, a -lattice parameter along with total volume decrease, while the c/a increases when Li presumably substitutes Cu.²² Therefore, there may be a possibility that Li is not substituting Cu here. After annealing, the decreasing trend in c lattice parameter is more systematic as seen in Table 1. It is to be noted that no extra impurity peak appeared in the XRD patterns after annealing. However the impurity peaks became more intense and sharp.

Figure 1: X-ray diffraction patterns of the as-prepared samples with nominal formula of $\text{Li}_x\text{Tl}_{2(1-x)}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($\text{Li}_x\text{Tl-2223}$), where $x = 0, 0.1, 0.2$ and 0.4 . Bragg peaks contributing to phases of BaCO_3 and Tl-2212 are denoted as # and *, respectively. All peaks are normalized to the (110) peak position.

Table 1: For Tl-2223, samples, syntheses, and resulting lattice parameters and superconducting transition temperatures.

Sample name	Reactants, sintering and annealing conditions	a (Å)	c (Å)	T_c (K) (magnetic)
Tl-2223-as prepared	$1.1\text{Tl}_2\text{O}_3 + \text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_v$ sintered at 910 °C	3.8502(1)	35.6381(8)	123
$\text{Li}_{0.1}\text{Tl}$ -2223-as prepared	$0.05\text{Li}_2\text{O} + 1.05\text{Tl}_2\text{O}_3 + \text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_v$ sintered at 910 °C	3.8518(1)	35.6358(15)	122
$\text{Li}_{0.2}\text{Tl}$ -2223-as prepared	$0.1\text{Li}_2\text{O} + 1.0\text{Tl}_2\text{O}_3 + \text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_v$ sintered at 910 °C	3.8507(1)	35.6102(7)	122
$\text{Li}_{0.4}\text{Tl}$ -2223-as prepared	$0.2\text{Li}_2\text{O} + 0.9\text{Tl}_2\text{O}_3 + \text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_v$ sintered at 900 °C	3.8522(2)	35.6145(1)	121
Tl-2223-annealed	Tl-2223-as prepared + annealing at 250°C for 1 hour under flowing Ar+4% H_2	3.8496(1)	35.6509(10)	123
$\text{Li}_{0.1}\text{Tl}$ -2223-annealed	$\text{Li}_{0.1}\text{Tl}$ -2223-as prepared + annealing at 250°C for 1 hour under flowing Ar+4% H_2	3.8509(1)	35.6406(7)	122
$\text{Li}_{0.2}\text{Tl}$ -2223-annealed	$\text{Li}_{0.2}\text{Tl}$ -2223-as prepared + annealing at 250°C for 1 hour under flowing Ar+4% H_2	3.8504(1)	35.6214(7)	122
$\text{Li}_{0.4}\text{Tl}$ -2223-annealed	$\text{Li}_{0.4}\text{Tl}$ -2223-as prepared + annealing at 250°C for 1 hour under flowing Ar+4% H_2	3.8509(1)	35.603(1)	121

Figure 2 shows the scanning electron micrographs (SEM) of the as prepared Li_xTl -2223 samples. The grain size for lithium-free Tl-2223 ($x=0$) is less than 20 μm , which seems to increase in Li incorporated samples of $x=0.1, 0.2, 0.4$. This trend is similar to that observed in Li doped (Tl,Pb)-1223 and Bi-2212 superconductors.^{12,11} For $\text{Li}_{0.1}\text{Tl}$ -2223, clear evidence of spiral growth (indicated by red arrow in Fig. 2b and 2d) due to the presence of screw dislocations, similar to that observed in YBCO, leading to slab like grains.²³ Such morphologies may

Figure 2: Scanning electron micrographs of pure and Li_xTl -2223. Li addition seems to improve microstructure by

lead to specific grain orientations causing a degree of alignment. Li incorporated pellets were much shinier in appearance compared to Li free Tl-2223.

Figure 3 is the temperature-dependent magnetic susceptibility, showing ZFC (open symbols)-FC (closed symbols) curves of $\text{Li}_x\text{Tl-2223}$ samples. It is evident that T_c only slightly decreases with the addition of lithium, similar to that reported for (Tl,Pb)-1223.¹² Such a small change in T_c indicate that Li is definitely not substituting Cu in the Cu-O plane for which the T_c decrease is quite high at even smaller concentrations.^{16,18} Not much change in the T_c from magnetization was observed after annealing in Ar+4% H_2 as shown in Table 1. For as-prepared Tl-2223 (Fig. 3a), ZFC curve shows an upturn (reproducible feature) below 75 K. With Li doping, the upturn gets suppressed and the screening as well as Meissner fractions improve, showing best results for $\text{Li}_{0.2}\text{Tl-2223}$. Annealed Tl-2223 sample improves with sharper diamagnetic transition (Fig. 3b), while there is not much change or trend within $\text{Li}_x\text{Tl-2223}$. Longer anneal-time (~5 hrs) at 250 °C decreased the T_c as well as the superconducting volume fraction of Tl-2223, and therefore the data are not presented here.

For estimating the J_c in these materials, magnetic hysteresis curves were obtained at 5 K. Shown

Figure 3: Temperature-dependent magnetic susceptibility results measured under 20 Oe assuming perfect diamagnetism. The ZFC curves are closed symbols, while FC curves are open symbols.

Figure 4 is the J_c of $\text{Li}_x\text{Tl-2223}$ extracted from the magnetic hysteresis curves for the lithium added samples using the Bean's critical state formula for rectangular sample: $J_c = 20\Delta M/[b(1-b/(3a))]$, where a and b are dimensions of the cross-section of $a > b$.²⁴ Here ΔM is the hysteresis width given as, $\Delta M = M - M^+$, where M is the magnetization in field decreasing part and M^+ is the magnetization in the field increasing part of the hysteresis loop. Lithium added samples show higher J_c as compared to pure Tl-2223, with $\text{Tl}_{0.2}\text{Tl-2223}$ showing the highest J_c in both the as-prepared and annealed samples. These results match well with previous reports where J_c increases with increasing Li content and reaches a maximum for the nominal optimal value of 20%.¹² It should be noted that increasing Li content decreases the melting temperature of Tl-2223 compounds which has influenced their grain morphology as well as the J_c .

Figure 4: Field-dependence of current densities of the (a) as-prepared and (b) annealed $\text{Li}_x\text{Tl-2223}$ at $T = 5$ K, calculated using the Bean's model.

Figure 5 shows the resistivity versus temperature plots of as-prepared and annealed Tl-2223, $\text{Li}_{0.1}$, $\text{Li}_{0.2}$, and $\text{Li}_{0.4}\text{Tl-2223}$ samples. The T_c (onset) is ~ 122 K for as-prepared Tl-2223, while the resistive transition for as-prepared $\text{Li}_{0.2}\text{Tl-2223}$ is ~ 125 K. The normal-state resistivity in $\text{Li}_{0.2}$ is high compared to $\text{Li}_{0.4}\text{Tl-2223}$ and both decreases after annealing. There is no such change observed in Tl-2223 except that the transition becomes slightly broad after annealing. Figure 5(b) shows the temperature-dependent resistivity plots for $\text{Li}_{0.1}\text{Tl-2223}$ sample. The as-prepared sample shows zero resistivity at 86 K which increases to 113 K after annealing. The normal-state resistivity of the as prepared sample is high as compared to that of the annealed sample, however it follows the same temperature dependent slope as can be observed in the

Figure inset. This sample is particularly interesting as the normal state resistivity is very high with a dome like curve. Such curvatures have also been observed in Hg-1223 sample where possible loss of Hg was held responsible for such a behavior.¹⁸ The curvature and the normal state resistivity is independent of any applied magnetic field (data not presented here).

Figure 5: Temperature-dependent resistivity of as-prepared and annealed (a) Tl-2223, $\text{Li}_{0.2}\text{Tl-2223}$ and $\text{Li}_{0.4}\text{Tl-2223}$, and (b) $\text{Li}_{0.1}\text{Tl-2223}$. Inset in 5(b) is normalized data.

As discussed earlier Li is not sitting at Cu in Cu-O plane, since the T_c decrease is not strong enough plus the c - lattice parameter decreases with increasing Li. Therefore we speculate that it may sit in the Ca and/or Tl-O plane replacing Ca^{2+} and/or Tl^{+3} . Substitution at Ca^{2+} site seems more plausible since the size of Li^+ is smaller than Ca^{2+} which can very well explain the decrease in the c - lattice parameter. At the same time multi-site substitution cannot be denied and how inter-site substitutions compensate each other in complex superconductors like Tl-2223, is a big issue. The susceptibility data, J_c and normal state resistivity data also cannot be explained on the basis of such assumptions since they depend on the grain morphology and connectivity.

Conclusions

We have chemically substituted lithium in the structurally complex $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}$ cuprate superconductor, and shown that addition of Li_2O reactant lowers the synthesis temperature by 10 K and accelerates the phase formation of Tl-2223. Change in the structure and morphology indicates that Li gets into the lattice. Lithium substitution also improves the superconducting volume fraction of Tl-2223. We found that up to 10% Li_2O can be added without any increase in the amount of impurity phases. The exact location of Li can be found from diffraction neutron diffraction, and atomic substitution can be visualized from atomic resolution microscopy. $\text{Li}_{0.2}\text{Tl-2223}$, though showed the best J_c , has impure phases like Tl-2212 and BaCuO_2 . Increase in the J_c holds promise for further studies in the systematic studies of Li added Tl-based superconductors.

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