Stabilization of the Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ superconductor by Hg doping

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Abstract

Hg doping of the triple-CuO$_2$ layer oxide superconductor Tl$_{2-x}$Hg$_x$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ (TI-2223) is investigated. Modest substitution of Hg$^{2+}$ ions for Ti$^{3+}$ ions leads to the stabilization of the TI-2223 structure and an apparently optimized superconducting onset temperature $T_c=130$ K. The situation is reminiscent of partial Bi ions replacement by Pb ions in the lower-$T_c$ Bi based oxide superconductors. Overdoping with Hg in TI-2223 leads again to a decrease in $T_c$.

The superconducting transition temperature for pure Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ (TI-2223, the highest-$T_c$ TI based oxide superconductor) apparently varies from 113 K to 127 K even if the compound has an optimized oxygen concentration. Indeed, nearly all physical measurements on TI-2223 reported in the literature are for samples with $T_c$ in the range 113 K to 120 K [1]. It is apparent that an overall optimized, stable phase of this material is difficult to achieve, and even the maximum possible $T_c$ for TI-2223 is still an open question. Many technologically relevant superconductor parameters are enhanced when the crystal structure is stabilized, and such a stable phase is crucial for reliable and reproducible measurement of physical properties. The observation [2] that Pb doping in the Bi-O planes of the related material Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ stabilizes that structure suggests that a similar result can be achieved in TI-2223 by doping into the TI-O planes. Hg is a favorable candidate for such a substitution. We have found that partial substitution of Ti ions by Hg ions in TI-2223 produces a stable double-(Ti/Hg)O layered phase with a highly reproducible onset $T_c$ of 130 K.

We have investigated the effects of Hg doping in the TI-2223 superconductor by preparing a series of samples with final stoichiometry Tl$_{2-x}$Hg$_x$Ba$_2$Ca$_2$Cu$_3$O$_{10-y}$ with $x$ ranging from 0 to 1. With $x=0$ (pure TI-2223), the as-prepared samples display variable $T_c$'s ranging from 115 K to 123 K, depending on the preparation conditions. There is little $T_c$ improvement upon oxygen annealing. This behavior is consistent with previous studies of TI-2223 [1] and indicates typically a non-optimized structural configuration for the material even after oxygen annealing. With $x \neq 0$, however, we find the striking result that, independent of preparation conditions, the addition of small quantities of Hg in TI-2223 consistently produces superconductors with onset $T_c$'s as high as 130 K. Subsequent oxygen annealing is not necessary nor does it have a marked effect on $T_c$ or the volume fraction of superconductivity in the specimen. Hg doping into the TI-O layers of TI-2223 leads directly to a stabilized phase with an optimized oxygen stoichiometry and a maximized $T_c$.

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Bulk polycrystalline specimens in the Tl-2223 structure with final stoichiometry \( \text{Tl}_{2-x}\text{Hg}_{x}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-x} \) with \( x \) ranging from 0 to 1 were synthesized by a two-step solid-state reaction technique [3,4]. A precursor of \( \text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7 \) was prepared by dissolving appropriate amounts of the high-purity metal nitrates \( \text{Ba(NO}_3\text{)}_2 \), \( \text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} \), and \( \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} \) into de-ionized water. The solution was heated and mixed at \( \sim 200^\circ\text{C} \) until it dried into a blue powder. This powder was calcined in air at 620\(^\circ\text{C} \) for 1 h and then slowly heated to 900\(^\circ\text{C} \) over 1 h. The resulting powder was ground, pressed into pellets, and annealed at 920\(^\circ\text{C} \) for 48 h in a pure oxygen flow. Appropriate amounts of \( \text{HgO} \) and \( \text{Tl}_2\text{O}_3 \) were then completely mixed and intimately ground with the precursor in a glove box. The resulting powder was again pressed into pellets which were vacuum sealed into quartz tube ampules. The quartz ampules were heated slowly to a temperature between 860\(^\circ\text{C} \) and 870\(^\circ\text{C} \) maintained at that temperature for 5 to 6 h, and then cooled to room temperature within 3 h.

The powder X-ray diffraction patterns of these samples are consistent with a \( \text{2223-type structure} \) [5]. Fig. 1 shows the X-ray patterns of Hg doped Tl-2223 samples with (a) \( x=0.3 \) and (b) \( x=0.6 \). All the major peaks correspond to the (Tl/Hg)-2223 phase. The lattice parameters of Hg doped Tl-2223 are reported in Table 1, which shows that as the Hg doping level increases, the \( a \) lattice parameter changes little (within our experimental error of \( \pm 0.01 \)), but the \( c \) lattice parameter slightly increases with increasing Hg concentration. Since the ionic radius of Hg is larger than that of Tl, the increase of the \( c \) lattice parameter is more likely due to a aferic effect. The minor impurity phases detected include \( \text{BaCuO}_2 \) and \( \text{Ca}_2\text{Cu}_3\text{O}_5 \). For the \( x=1 \) sample, a secondary superconducting phase, Tl-1223, was also detected in addition to the above-mentioned impurity phases. Energy dispersive X-ray spectroscopy (EDX) also demonstrates that the incorporated \( \text{Hg} \) ions substitute for \( \text{Tl} \) ions. Modest amounts of Hg doping result in the formation of a stable Hg doped Tl-2223 phase, independent of the stoichiometry of the starting materials. For example, a non-ideal starting stoichiometry of the form (Tl/Hg)-1223 results in a phase-separated sample with the superconducting portion in the 2223 structure. This demonstrates an enhanced stability of the Hg doped Tl-2223.

![Fig. 1. X-ray diffraction patterns of Hg-doped Tl-2223 samples with (a) \( x=0.3 \) and (b) \( x=0.6 \). The reflections (hk\( l \)) are indexed as shown. Peaks marked with (*) are due to impurity phases.](image)

<table>
<thead>
<tr>
<th>Hg concentration ( (x) )</th>
<th>( a ) (( \text{\AA} ))</th>
<th>( b ) (( \text{\AA} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x=0.0 )</td>
<td>3.849</td>
<td>35.662</td>
</tr>
<tr>
<td>( x=0.3 )</td>
<td>3.846</td>
<td>35.740</td>
</tr>
<tr>
<td>( x=0.4 )</td>
<td>3.843</td>
<td>35.754</td>
</tr>
<tr>
<td>( x=0.6 )</td>
<td>3.841</td>
<td>35.816</td>
</tr>
</tbody>
</table>

The superconducting properties of the samples were characterized by electrical measurements and DC magnetization measurements using a SQUID magnetometer. Fig. 2 shows the temperature dependence of the magnetic susceptibility for a \( \text{Tl}_{2-x}\text{Hg}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-x} \) sample with \( x \approx 0.4 \). For these measurements, the bulk sample was finely powdered in order to avoid problems due to intergrain coupling. As Fig. 2 shows, the magnetically determined onset \( T_c \) is \( \sim 127 \text{ K} \) from both the shielding
Fig. 2. Temperature dependence of the magnetic susceptibility for a Hg doped Tl-2223 sample with $x=0.4$ measured at $H_0=10$ Oe.

(zero-field cooled) and the Meissner (field-cooled) measurements. The shielding volume fraction of the sample reaches 89% and the Meissner volume fraction reaches 37% at low temperatures.

Fig. 3(a) shows the temperature dependence of the electrical resistivity for samples of Tl$_{2-x}$Hg$_x$Ba$_2$Ca$_2$Cu$_3$O$_{10-y}$ with $x=0$, 0.4, and 0.6. For all the samples, the resistivity exhibits a linear temperature dependence in the range 300 to $\sim$ 140 K. At room temperature the Hg doped samples have a higher resistivity than the undoped specimen (we note that pure Hg-1223, not shown in the figure, has a significantly higher resistivity of $\rho=27$ m$\Omega$ cm at 300 K [6]). The sample with $x=0$ shows a behavior typical of an undoped Tl-2223: a superconducting onset at 122 K and zero resistance at 116 K. The sample with $x=0.4$ shows onset of superconductivity at 130 K and zero resistivity at 126 K, while the sample with $x=0.6$ displays a superconducting onset at 125 K and zero resistance at 122 K.

As Fig. 3(a) demonstrates, Hg doping can increase the superconducting onset temperature of as-grown Tl-2223 compounds. It is well known that $T_c$ for some superconducting oxides is a sensitive function of the oxygen stoichiometry, and the $T_c$ of Hg-1223 can be enhanced significantly by oxygen annealing [6,7]. To explore this possibility in Hg doped Tl-2223, we performed oxygen annealing on previously characterized samples.

Fig. 3(b) shows the temperature dependence of the resistance of Hg doped Tl-2223 with $x=0.4$ both before and after oxygen annealing. After the initial measurement on the as-synthesized sample was performed, the same sample with Au leads attached was annealed in a pure oxygen flow at 300°C for 10 h. As Fig. 3(b) shows, the sample has the same onset temperature (130 K) and zero-resistivity temperature (126 K) both before and after oxygen annealing. The value of the resistivity at room temperature is 3.7 m$\Omega$ cm for the as-synthesized sample and 2.9 m$\Omega$ cm after oxygen treatment. Oxygen annealing changes the value of the normal-state resistivity but not the superconducting-transition temperature. This result suggests that as-synthesized specimens of Hg doped Tl-2223 are already in an optimized oxygen configuration state, and no further increase of $T_c$ is possible through oxygen annealing. On the other hand, elevated temperature annealing reduces the disorder of the system and therefore lowers the normal-state resistivity.
We have investigated the maximum possible $T_c$ for Hg-doped Tl-2223 over a broad range of Hg concentration. Fig. 4 shows the resistively determined onset and zero-resistance $T_c$'s for Hg doped Tl-2223 versus Hg concentration $x$. The data indicate a maximum $T_c$ near $x \approx 0.4 \text{--} 0.5$. For $x \gtrapprox 0.6$, $T_c$ again decreases. We have not successfully synthesized a pure Hg compound in the Tl-2223 structure (i.e. with $x=2$).

We now briefly discuss the stabilization of the Tl-2223 by moderate Hg doping. Pure Tl-2223 with ideal stoichiometry would have all the copper atoms in the 2+ state, making it an insulator. A higher Cu valence state, which is necessary for a cuprate to be superconducting, is created via the substitution of Ti$^{3+}$ with Ca$^{2+}$, vacancies at cation sites, and the internal redox reaction Ti$^{3+} + Cu^{2+} = Ti^{(3-x)+} + Cu^{(2+x)+}$. These complex internal mechanisms are difficult to control during synthesis and consequently there results for “pure” Tl-2223 a range of superconducting transition temperatures between 113 K and 127 K even for those samples with optimal oxygen concentrations. Partial substitution of Ti$^{3+}$ with Hg$^{2+}$ increases the effective Cu valence and brings the system from an under-doped regime to an optimally doped regime and thus promotes the formation of the 2223 phase. As the Hg concentration increases further (beyond $x=0.6$), the system goes from the optimally doped regime to an overdoped regime, resulting in the observed decrease of $T_c$. Further oxygen annealing is unable to enhance $T_c$ for these specimens.

The ability to use Hg doping to easily and reproducibly achieve a stabilized 130 K high-$T_c$ structure has important implications. First, the measurement of intrinsic materials properties is greatly facilitated with the availability of high-quality, reproducible samples. Second, our findings may have technological implications. The ability to prepare stable, high-$T_c$ structures which do not require post-synthesis anneals or other treatments is often crucial in thin-film and device applications. The high reproducible 130 K onset superconducting temperature, which is the highest reported for a Ti based oxide superconductor, also suggests a stabilization of other important parameters, such as the critical current, critical field, elastic moduli, and resistance to structural degradation.

Note added

Recently Goutenoire et al. [8] have published results of Hg doping in Tl-2223. Their findings for $x=0.4$ are in agreement with the $x=0.4$ results presented here.

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References


