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Physica C 234 (1994) 24–28

PHYSICA C

Stabilization of the $Tl_2Ba_2Ca_2Cu_3O_{10}$ superconductor by Hg doping

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Received 3 June 1994; revised manuscript received 26 September 1994

Abstract

Hg doping of the triple-CuO_2 layer oxide superconductor $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10}$ (Tl-2223) is investigated. Modest substitution of Hg^{2+} ions for Tl^{3+} ions leads to the stabilization of the Tl-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 Tl-2223 leads again to a decrease in T_c.

The superconducting transition temperature for pure $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223, the highest-T_c Tl 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 Tl-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 Tl-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 $Bi_2Sr_2Ca_2Cu_3O_{10}$ stabilizes that structure suggests that a similar result can be achieved in Tl-2223 by doping into the Tl–O planes. Hg is a favorable candidate for such a substitution. We have found that partial substitution of Tl ions by Hg ions in Tl-2223 produces a stable double-(Tl/Hg)O layered phase with a highly reproducible onset T_c of 130 K.

We have investigated the effects of Hg doping in the Tl-2223 superconductor by preparing a series of samples with final stoichiometry $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10-\delta}$, with x ranging from 0 to 1. With $x=0$ (pure Tl-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 Tl-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 Tl-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 Tl–O layers of Tl-2223 leads directly to a stabilized phase with an optimized oxygen stoichiometry and a maximized T_c.

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SSDI 0921-4534(94)01331-4

Bulk polycrystalline specimens in the Tl-2223 structure with final stoichiometry $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10-\delta}$ with x ranging from 0 to 1 were synthesized by a two-step solid-state reaction technique [3,4]. A precursor of $Ba_2Ca_2Cu_3O_7$ was prepared by dissolving appropriate amounts of the high-purity metal nitrates $Ba(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$ into de-ionized water. The solution was heated and mixed at ~200°C until it dried into a blue powder. This powder was calcined in air at 620°C for 1 h and then slowly heated to 900°C over 1 h. The resulting powder was ground, pressed into pellets, and annealed at 920°C for 48 h in a pure oxygen flow. Appropriate amounts of HgO and Tl_2O_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°C and 870°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 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 ± 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 steric effect. The minor impurity phases detected include $BaCuO_2$ and Ca_2CuO_3. 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 Hg ions substitute for 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 enchanced stability of the Hg doped Tl-2223.

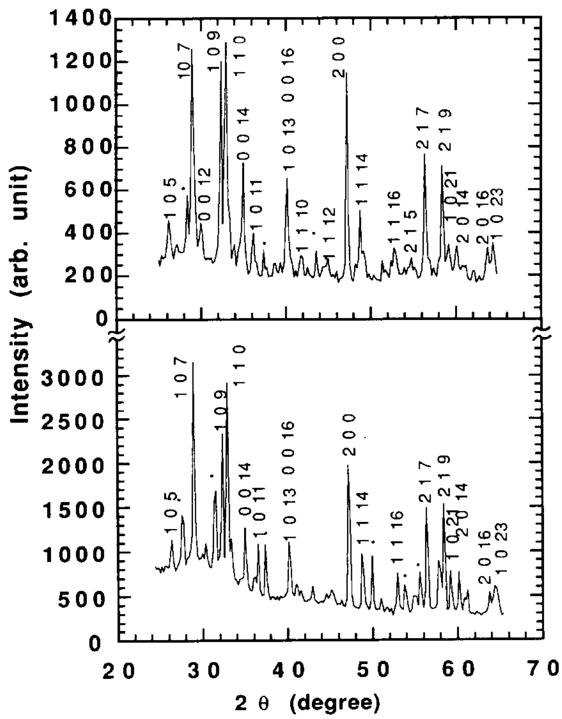

Fig. 1. X-ray diffraction patterns of Hg-doped Tl-2223 samples with (a) $x=0.3$ and (b) $x=0.6$. The reflections (h k l) are indexed as shown. Peaks marked with (*) are due to impurity phases.

Table 1
The lattice parameters (Å) of Hg doped Tl-2223

Hg concentration (x)	a (Å)	b (Å)
$x=0.0$	3.849	35.662
$x=0.3$	3.846	35.740
$x=0.4$	3.843	35.754
$x=0.6$	3.841	35.816

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 $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10-\delta}$ 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 ~127 K from both the shielding

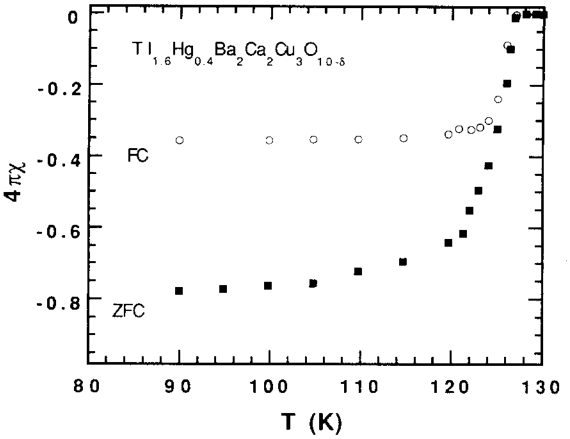

Fig. 2. Temperature dependence of the magnetic susceptibility for a Hg doped Tl-2223 sample with $x=0.4$ measured at $H_a=10$ Oe.

(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 $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10-\delta}$ with $x=0$, 0.4, and 0.6. For all the samples, the resistivity exhibits a linear temperature dependence in the range 300 to ~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 $\rho=27$ mΩ cm at 300 K [6]). The sample with $x=0$ shows a behavior typical of 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

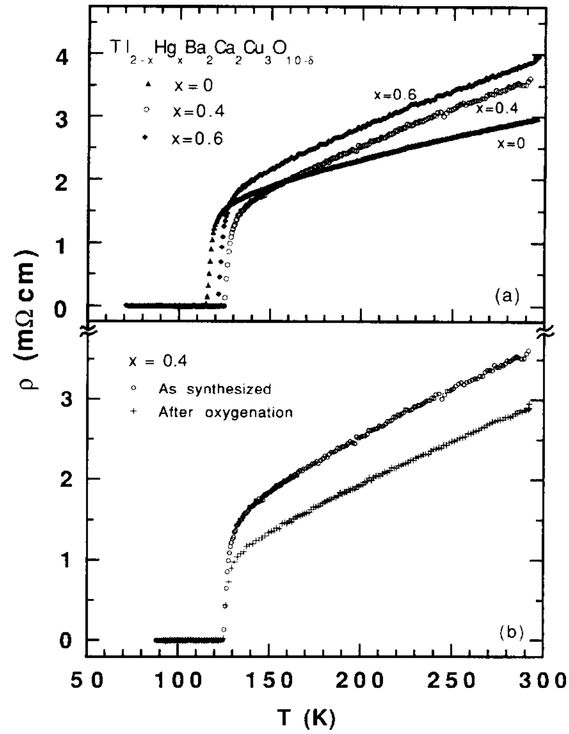

Fig. 3. Temperature dependence of the electrical resistivity for Hg doped Tl-2223 samples with (a) $x=0$, $x=0.4$, and $x=0.6$; (b) $x=0.4$ before and after oxygen treatment.

resistance of Hg doped Tl-2223 with $x \approx 0.4$ 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 mΩ cm for the as-synthesized sample and 2.9 mΩ 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 $x \approx 0.4$–0.5. For $x \geq 0.6$, 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 Tl^{3+} with Ca^{2+}, vacancies at cation sites, and the internal redox reaction $Tl^{3+} + Cu^{2+} = Tl^{(3-\delta)+} + Cu^{(2+\delta)+}$. 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 Tl^{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 Tl 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.

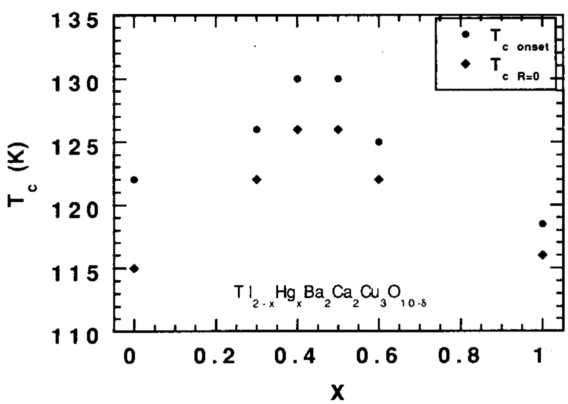

Fig. 4. Hg concentration dependence of the onset and zero-resistance T_c's for Hg doped Tl-2223.

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.

Acknowledgements

This research was supported by National Science Foundation Grant DMR90-17254 and by the Office of Energy Research, Office of Basic Energy Science Division of U.S. Department of Energy under contract DE-AC03-76SF0098. YXJ acknowledges the support of a postdoctoral fellowship from the Miller Institute for Basic Research at the University of California at Berkeley.

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