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Superconductivity and Transport Properties of $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10-\delta}$

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Superconducting samples of $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10-\delta}$ were prepared by solid state reaction of appropriate quantities of HgO, Tl_2O_3 and the precursor $Ba_2Ca_2Cu_3O_7$. Our best Hg-doped samples have the superconducting onsets at 130 K. Similar to the substitution of Bi ions by Pb ions stabilizing the Bi-based superconducting oxides [1], partial substition of Tl^{3+} with Hg^{2+} in Tl-2223 produces a stable Tl-2223 phase with highest possible T_c.

T_c of $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223) apparently varies from 113 K to 127 K even if the compound has an optimized oxygen concentration [2]. Studies were carried out to stabilize the higher transition phase (127 K). Our investigation indicated that Hg doping stabilizes the highest T_c phase of Tl-2223.

Bulk polycrystalline samples of $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10-\delta}$ were prepared by solid state reaction method. Appropriate amounts of HgO, Tl_2O_3, and $Ba_2Ca_2Cu_3O_7$ precursor were mixed, ground, and pressed into pellets. All the chemical handling was done in a dry box. The pellets were vacuum sealed into quartz tubes. The quartz ampoules were sintered at 830 °C to 870 °C, and finally slow cooled to room temperature.

The structures of the specimens were determined by powder x-ray diffraction. Figure 1 shows the x-ray diffraction pattern with indices of a typical $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10-\delta}$ sample with x = 0.4. A prominent low-angle reflection at $2\theta = 5°$ was detected. All the major peaks in the diffraction pattern correspond to the $Tl_{2-x}Hg_xBa_2Ca_2Cu_3O_{10-\delta}$ phase [3]. Peaks marked with * are due to impurity phases, such as $BaCuO_2$ and Ca_2CuO_3. The energy dispersive x-ray spectroscopy (EDX) analysis also suggested that incorporated Hg ions substitute for Tl ions in Tl-2223.

The superconducting properties of the samples were characterized by d.c. magnetic susceptibility and transport measurements. The magnetically determined onsets T_c for as-grown $Tl_{1.6}Hg_{0.4}Ba_2Ca_2Cu_3O_{10-\delta}$ specimens are ~ 128 K from both the shielding (zero-field-cooled) and the Meissner (field-cooled) measurements.

Figure 2 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 ρ = 27 mΩ cm at 300K [4]). The sample with x = 0 shows 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

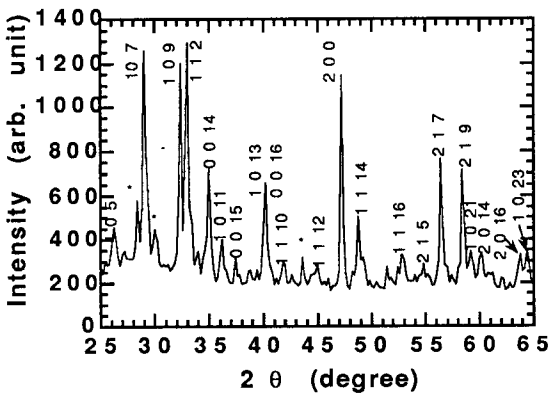

Figure 1. X-ray diffraction pattern of $Tl_{1.6}Hg_{0.4}Ba_2Ca_2Cu_3O_{10-\delta}$. The reflection (h k l) are indexed as shown. Peaks marked with * are due to impurity phases.

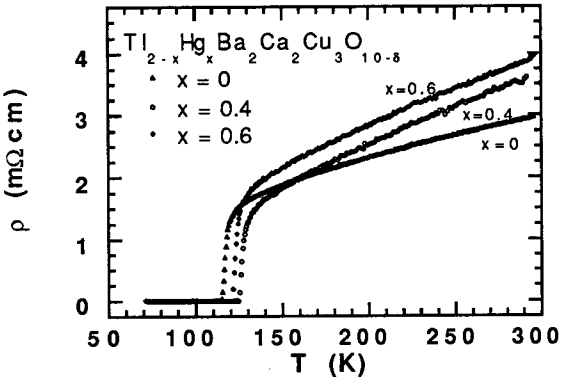

Figure 2. Temperature dependence of the electrical resistivity for Hg-doped Tl-2223 samples with x = 0, x = 0.4, and x = 0.6.

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. 2 demonstrates, modest Hg doping increases the superconducting onset temperature of Tl-2223 compounds. For x > 0.6, T_c again decreases [5]. It is most likely that partial substitution of Tl^{3+} with Hg^{2+} increases the effective Cu valence and brings the system from an overdoped 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 under-doped regime, resulting in the observed decrease of T_c.

We have successfully prepared the Hg-doped $Tl_2Ba_2Ca_2Cu_3O_{10}$ superconductors. EDX analysis indicated that Hg ions partially replaced Tl ions in the system. Our best Hg-doped sample has the onset superconducting transition temperature at 130 K. Partial substition of Tl^{3+} with Hg^{2+} in $Tl_2Ba_2Ca_2Cu_3O_{10}$ produces a stable Tl2223 phase with highest possible T_c.

Note added: After completion of this work, we become aware of a related study of Hg-doping in Tl-2223, whose finding agree with ours with x=0.4 [6].

References

1. R.J. Cava et al., Physica C 153-155 (1988) 560.
2. Thallium-Based High-Temperature Superconductors. ed. A. M. Hermann and J.V. Yakhmi (Marcel Dekker, Inc./New York; Basel; Hong Kong).
3. K. Yvon and M. Francois, Z. Phys. B 76 (1989) 413.
4. C.W. Chu et al., Nature 365 (1993) 323.
5. Y.X. Jia, C.S. Lee and A. Zettl (to be published).
6. F. Goutenoire, A. Maignan, G. Van Tendeloo, C Martin, C. Michel, M. Hervieu and B. Raveau, Solid State Commun. 90 (1994) 40.