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Synthesis and neutron powder diffraction study of the superconductor $HgBa_2Ca_2Cu_3O_{8+\delta}$ by Tl substitution

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Abstract

Substitution of Tl for Hg was performed in the Hg based 1223 phase $HgBa_2Ca_2Cu_3O_{8+\delta}$ ($T_c = 135$ K), resulting in an increase of the superconducting transition temperature to 138 K for samples with a nominal composition of $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$. The crystal structure of this solid solution has been investigated by neutron powder diffraction techniques at room temperature and at 10 K. The compound has the same crystal structure as Hg-1223 with the space group symmetry P4/mmm and lattice parameters $a = 3.8489(1)$, $c = 15.816(1)$ Å. Rietveld analysis results indicate that Hg is partially replaced by Tl, and the oxygen content, δ, is 0.33. The lattice-parameter changes resulting from the Tl substitution are too small to account for the T_c change by mimicking the effect of pressure. No phase transition occurs down to 10 K.

1. Introduction

Shortly after the discovery of superconductivity in the Hg–Ba–Cu–O system [1], three phases bearing a formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$, where $n = 1$, 2, and 3, were isolated [2,3]. With $n = 3$, the 1223 phase $HgBa_2Ca_2Cu_3O_{8+\delta}$ has a T_c of 133–135 K under atmospheric pressure depending on synthesis procedures [2,4–10]. The crystal structure of this Hg compound has space group symmetry P4/mmm, similar to that of the single layer Tl compound $Tl(Sr, Ba)_2Ca_2Cu_3O_{9-\delta}$. The main difference in the crystal structures between these two compounds is the amount of oxygen deficiency in the Hg–O plane as compared to that in the Tl–O plane. In the Hg-1223 structure, the oxygen atom is nearly absent in the Hg–O plane in a stoichiometric ($\delta = 0$) composition which eliminates the hole-doping mechanism crucial for cuprates. Thus the stoichiometric $HgBa_2Ca_2Cu_3O_8$ usually exhibits poor superconductivity. However, after annealing in an oxygen atmosphere, δ increases to less than 50% and Hg-1223 becomes a good superconductor with a T_c above 130 K. Contrarily, in the Tl-1223 structure, the oxygen position in the Tl–O plane is almost fully occupied. This complete occupation of the oxygen position makes the Tl compound over-doped with holes. An over-doped Tl-1223 material is metallic, but also has poor superconducting properties. The difference in oxygen content between the Hg-1223 and Tl-1223 in the Hg–O and Tl–O planes can be understood as due to the difference in valency of the Tl^{+3} and Hg^{+2} cations within the preferred coordinate geometries. Therefore, substitution of Hg by Tl in the Hg family of compounds, if possible, may lead to fractional oxygen occupancy necessary to form a good superconductor. Recently, there have been several

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attempts to synthesize new Tl and Hg based compounds by substitution. For example, Isawa et al. [11] have studied the effect of Pb doping in Hg-1223 and found it decreases T_c. Hur et al. [12] found that Hg based $Hg_{0.5}Tl_{0.5}Ba_2(Ca_{1-x}Sr_x)_2Cu_3O_{8+\delta}$ ($x=0.14$) has a T_c of 132 K, less than that of the pure Hg-1224 compound. Hg substitution of Tl in $Tl_2Ba_2CaCu_2O_{8+\delta}$ [13] also reduces the superconducting transition temperature.

Another approach to increase T_c in a cuprate superconductor is by applying pressure to it. In fact, T_c's greater than 150 K have been achieved for the Hg-1223 phase at pressures above 10 GPa [14] and the detailed relation between pressure-induced structural changes and T_c's have been established for the Hg family of compounds by neutron powder diffraction [6]. It is interesting to ask whether the structure of Hg family of compounds at high pressure can be achieved at ambient pressure by chemical substitution.

To answer these questions, we carried out Tl substitution experiments in the Hg-1223 compound. Our results [15] clearly demonstrated that the superconducting-transition temperature of the substituted material was enhanced. An as-sintered $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ sample already has a T_c ($R=0$) of 133 K which is above that of an as-sintered non-doped sample. After annealing in oxygen, this sample exhibited a higher $T_c(R=0)$ of 138 K. To refine the crystal structure for the substituted compound and to determine the reason for the T_c enhancement, we have performed neutron powder diffraction experiments on oxygen-annealed $HgBa_2Ca_2Cu_3O_{8+\delta}$ and $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ samples at room temperature and at 10 K. The results of these studies are reported herein.

2. Experimental methods

The powder samples of $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$ were synthesized as described elsewhere [15]. Briefly, a nominal $Ba_2Ca_2Cu_3O_7$ precursor was prepared first. HgO (99.9%) and Tl_2O_3 (99.99%) were mixed with the precursor and ground in a plastic bag filled with N_2 gas. The cation ratio of $(Hg_{1-x}Tl_x)$/Ba/Ca/Cu was 1223, where $x=0$, 0.2. The ground powder was then pressed into rods of 6 mm in diameter and 15 mm in length. The pressed rods were put inside a quartz tube, evacuated and sealed. The sealed quartz tube was placed in a high-temperature oxygen-proof steel cylindrical container. A tube furnace was preheated to 860°C. The container with the contents was then introduced into the furnace and kept at 860°C for 400 min. At that time the furnace power was turned off and the content was allowed to cool to room temperature. After the sintering, the sample was annealed in O_2 at 500°C for 10 h. Since the neutron powder diffraction experiments require ~2 g of material, this procedure was repeated several times for each sample. To ensure the quality of the sample for neutron-scattering study, we have measured the resistivity and susceptibility for each run and found differences in T_c values less than 1 K.

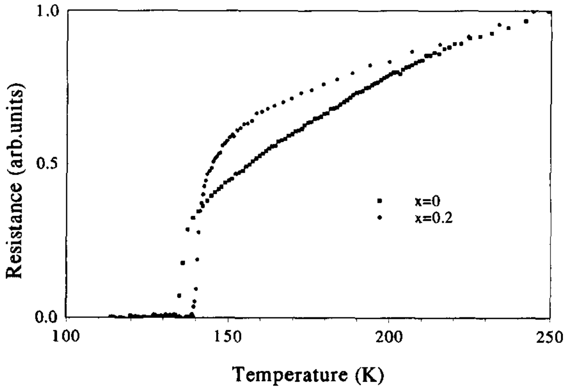

Fig. 1. Temperature dependence of resistivity for oxygen-annealed (a) $HgBa_2Ca_2Cu_3O_{8+\delta}$ and (b) $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$.

Resistances of samples were measured by the standard four-probe technique with an AC frequency of 27 Hz. AC susceptibility measurements were also carried out using the mutual-inductance technique with an AC signal of 400 Hz. The zero-resistance temperatures of the as-sintered samples with $x=0$, 0.2 are 124 K and 133 K, respectively. The higher T_c value of the Tl substituted sample suggests that favorable hole concentrations already exist for this sample. After annealing in an oxygen atmosphere, the T_c of the undoped sample is increased to 135 K, consistent with other reported results [4–10]. The annealed $x=0.2$ sample has a high onset temperature of 145 K and a $R=0$ T_c of 138 K. Fig. 1 shows the resistance versus temperature curves for the samples with $x=0$, 0.2 in the starting composition, respectively. Fig. 2 shows the results of AC susceptibility measurements for the annealed samples with $x=0$, 0.2. The diamagnetic signal confirms that the superconducting-transition temperatures for pure and doped Hg-1223 are 135 K and 138 K, respectively.

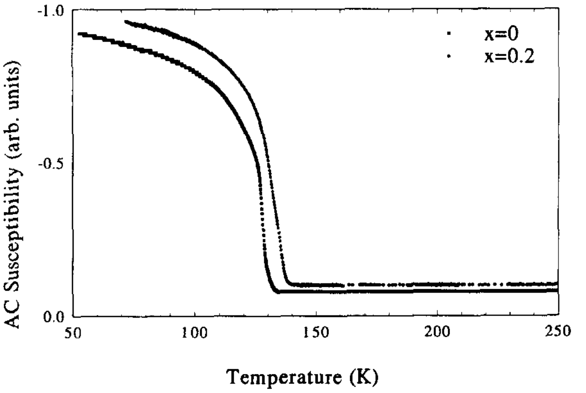

Fig. 2. AC susceptibility χ' (arbitrary units) for oxygen-annealed (a) $HgBa_2Ca_2Cu_3O_{8+\delta}$ and (b) $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$.

Neutron powder diffraction data for $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$, where x equals 0.0 and 0.2, were collected at room temperature and at 10 K using the HB4 high-resolution powder diffractometer at the High-Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. The HB4 instrument has a Ge(115) monochromator which, when $2\theta = 80°$, selects an incident neutron beam wavelength of 1.4177 Å determined on the basis of unit-cell refinements for a Si powder standard. Soller slit collimators of 12′ and 20′ are positioned before and after the monochromator crystal, respectively. An array of 32 equally spaced (2.7°) ^3He detectors, each with a 6′ mylar foil collimator, can be step scanned over a range of up to 40° for scattering angles between 11° and 135°. The powdered sample (2 g) was placed in a cylindrical Al can (4 mm in diameter and 5 cm long) and the detector scanned over a 2θ range of 11° to 135° in steps of 0.05°. For these data collections, the detector array was scanned over two regions which had the effect of overlapping up to 8 detectors for steps in the middle of the pattern. Overlapping detectors for a given step serves to average the counting efficiency and the 2θ zero-point shift for each detector. Using the known absorption cross-section [16] and the number of Hg atoms per cm^3 in the sample can, we have estimated that $\mu R = \sim 0.15$ for our samples, where μ is the linear absorption coefficient (in units of cm^{-1}) and R is the radius (in units of cm) of the cylindrical Al sample can. Therefore, the intensity absorption correction [17] for these samples should be negligible, and was not applied.

3. Results and discussion

Refinements of the structure parameters were made using the GSAS program [18] with an initial model used for Hg-1223 in earlier neutron powder diffraction experiments [19]. The regions of intensities affected by the peaks of Al container were excluded from the refinement. Similar to previous work on the pure Hg end-member [5,6,19,20], full occupation was assumed for all atoms except the partially occupied oxygen sites at the positions $(\frac{1}{2}, \frac{1}{2}, 0)$ of the $(Hg_{1-x}Tl_x)$–O layers. Attempts were made to allow the Hg occupancy to vary and to partially replace Hg by Cu, but that did not yield improvement in the agreement factor. Recently, on the basis of single-crystal X-ray refinements Finger et al. [21] suggested that the excess oxygen in Hg-1212 and Hg-1223 sites at $(\frac{1}{2}, 0, 0)$ and $(\frac{1}{2}, 0.4, 0)$, but not at $(\frac{1}{2}, \frac{1}{2}, 0)$ as reported in earlier neutron-scattering work. To test these ideas, we refined undoped Hg-1223 using their model and found that changing the positions of excess oxygen had little effect on the agreement factor. However, a similar refinement on $HgBa_2CaCu_2O_{6+\delta}$ [19] indicates that the weighted R factor (R_{wp}) increases with the proposed new oxygen positions. Therefore, we conclude that our neutron-diffraction data do not support the model proposed by Finger et al. [21].

The $(Hg_{1-x}Tl_x)$-1223 samples were not phase pure, but include some amount of $Ca_{0.85}CuO_2$ and $CaHgO_2$. Therefore, neutron data were refined using these three phases. To reduce the number of parameters needed for the refinement, we have fixed the atomic arrangement of $CaHgO_2$ and $Ca_{0.85}CuO_2$ to the values given in Refs. [19,24,25], and only vary the isotropic thermal factors. The refinement results are consistent with our previous results [19] for the undoped Hg-1223 compound. The lattice parameters are $a = 3.8513(2)$, $c = 15.826(2)$ Å at room temperature, respectively. The partial oxygen composition in Hg–O plane was determined to be $\delta = 0.143$. The values for the lattice parameters differ slightly from previous reported results [5,6], but are well within the range reported by different groups [4–10]. Differences in lattice parameters could be due to differences in the synthesis procedures. Since most of the structure parameters are identical to other published results, we will not list them here.

For the doped Hg-1223 compound, the occupancy of Tl was strongly correlated with the thermal param-

Table 1
Positional and isotropic displacement parameters (× 100 Å^2) of three phases mixture. The agreement factors are: $R_p = 7.42$, $R_{wp} = 9.15$, $\chi^2 = 2.33$

		$(Hg_{1-x}Tl_x)Ba_2Ca_2Cu_3O_{8+\delta}$	$CaHgO_2$	$Ca_{0.85}CuO_2$
Space group		P4/mmm	R$\bar{3}$m	Fmmm
a (Å)		3.8489(1)	3.5911(2)	6.3222(8)
b (Å)		3.8489(1)	3.5911(2)	2.8051(5)
c (Å)		15.816(1)	18.673(2)	10.579(1)
Phase fraction (wt.%)		56(4)	18(2)	26(3)
(Hg, Tl) atom	Position (x, y, z)	0, 0, 0	0, 0, 0	
	U_{iso}	2.2(4)	2.7(4)	
	Hg Occupancy	0.6(1)	1	
	Tl Occupancy	0.4(1)		
Ba	Position (x, y, z)	0, 0, 0.1754(8)		
	U_{iso}	0.3(2)		
Ca	Position (x, y, z)	0.5, 0.5, 0.399(1)	0, 0, 0.5	0.25, 0.5, 0.25
	U_{iso}	0.5(1)	3.5(1)	5(1)
Cu(1)	Position (x, y, z)	0, 0, 0.5		0, 0, 0
	U_{iso}	0.8(2)		4.4(6)
Cu(2)	Position (x, y, z)	0, 0, 0.3003(7)		
	U_{iso}	0.8(2)		4.4(6)
O(1)	Position (x, y, z)	0, 0.5, 0.5	0, 0, 0.107	0, 0, 0.6263
	U_{iso}	1.3(2)	0.03(2)	3.1(4)
O(2)	Position (x, y, z)	0, 0.5, 0.3021(6)		
	U_{iso}	0.1(1)		
O(3)	Position (x, y, z)	0, 0, 0.1199(9)		
	U_{iso}	1.3(2)		
O(4)	Position (x, y, z)	0.5, 0.5, 0		
	U_{iso}	1.3(2)		
	O Occupancy	0.33(8)		

eters of the oxygen atoms. To determine the actual Tl content, the thermal parameters of these atoms were fixed at the values determined for the pure Hg-1223 compound. All other thermal parameters and atomic positions were allowed to vary, and showed no abnormal behavior. Similarly to the pure Hg-1223, we have assumed full occupancy for (Hg_{1-x}, Tl_x) and allowed x and the partial oxygen content at the (Hg, Tl)–O plane, δ, to vary. Table 1 lists the structure parameters at room temperature and Fig. 3 shows the neutron powder pattern with calculated profile. Data taken at 10 K have essentially the same profile with lattice parameters $a = 3.8472(2)$, $c = 15.801(2)$ Å. Hence no structural phase transition occurs above 10 K.

Comparing ($Hg_{1-x}Tl_x$)-1223 to the pure Hg end-member, we note that Hg is partially replaced by Tl, and the O(4) partial occupancy has increased from 0.143 for the pure to 0.33 for the doped sample. These findings are consistent with the notion that Tl substitution of Hg in the 1223 compound stabilizes the necessary fractional oxygen content, thereby increasing T_c. The partial Tl concentration obtained by the refinement is about twice the amount from the starting stoichiometry. Currently, we do not have a definite explanation for this discrepancy. We note, however, that a large Tl concentration in (Hg, Tl)-1223 is consistent with having a large amount of Hg containing impurity in the system, thereby reducing the amount Hg required to form (Hg, Tl)-1223. The lattice parameters of the ($Hg_{0.8}Tl_{0.2}$)-1223 were slightly less than that of the pure Hg-1223 sample, having $dc/dT_c = -3.03 \times 10^{-3}$ Å/K and $da/dT_c = -8.0 \times 10^{-4}$ Å/K. To compare these values quantitatively to the pressure induced lattice parameter change, we note the rate of increase of T_c with pressure for pure Hg-1223 is about 1.7 K/GPa, and the compressibilities for a- and c-axis are $\kappa_a = 2.28 \times 10^{-3}$/GPa and $\kappa_c = 4.7 \times 10^{-3}$/GPa, respectively [6]. From these data, we estimate that the pressure-induced T_c change would exhibit lattice parameter changes of $dc/dT_c = -4.4 \times 10^{-2}$ Å/K, and $da/dT_c = -5.09 \times 10^{-3}$ Å/K. These values are an order of magnitude larger than that observed in Tl sub-

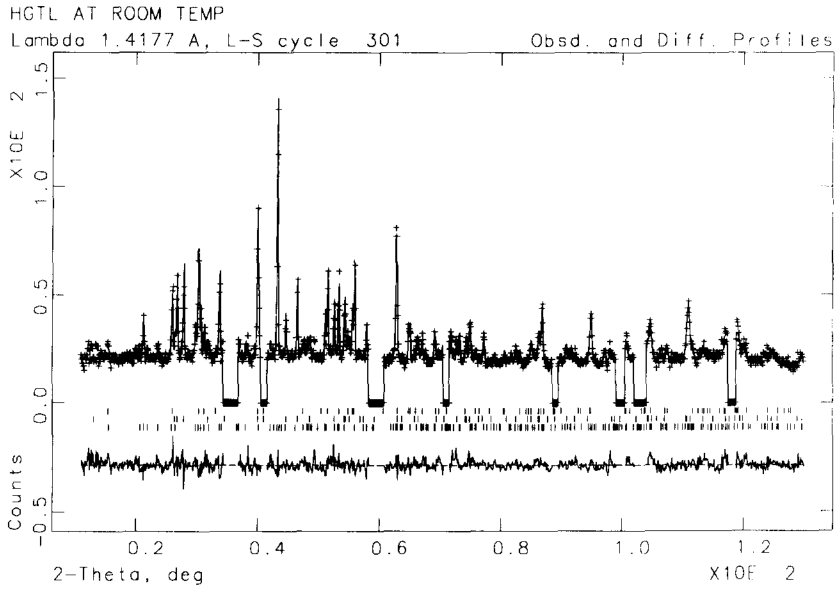

Fig. 3. Rietveld refinement patterns for (Hg, Tl)-1223 with T_c of 138. Plus marks are observed neutron-diffraction intensities, and solid lines are calculated intensities. Vertical marks below the profile indicate the positions of three different phases. The first set is for $Ca_{0.85}CuO_2$, the second set is for $CaHgO_2$, and the third is for (Hg, Tl)-1223. The curve at the bottom is the difference between the observed and calculated intensities. Peaks from the Al sample can have been excluded.

stituted samples. Therefore, the lattice parameters contraction due to partial Tl substitution of Hg is not sufficient to account for the observed T_c change.

In summary, Hg in the Hg-1223 superconductor can be partially substituted by Tl, resulting in a change in oxygen content, thereby increasing T_c. Moreover, the changes in lattice parameters by such a chemical substitution are too small to account for the T_c change by mimicking the effects of pressure.

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