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A neutron powder diffraction study of the superconductor Hg-1223 via Pb substitution

X S Wu[†], C Gou[‡], D F Chen[‡], H M Shao[†] and S S Jiang[†]

[†] National Laboratory of Solid State Microstructures and Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

[‡] China Institute of Atomic Energy, PO Box 275-30, Beijing 102413, People's Republic of China

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Abstract. The mercury-based superconductor Hg-1223 with Pb substituted for Hg has a transition temperature ($T_c^{R=0}$, the zero-resistance temperature, ~ 135 K; T_c^{dia} , the diamagnetic onset temperature, = 143 K) higher than that for pure Hg-1223 compound. The structure of this Pb-doped sample has been investigated via neutron powder diffraction. Some selected bond distances are compared to those of Pb-free Hg-1223 cuprate. The contents of Pb and oxygen have been refined. The estimated valence of copper is about 2.30, which is consistent with that for YBCO superconductor.

1. Introduction

After the discovery of high-temperature superconductivity in the mercury-based copper oxides [1, 2], three phases bearing the formula $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$, where $n = 1, 2, 3$, were isolated [1–3]. The critical temperatures were reported to be 96 K and ~ 128 K for Hg-1201 ($n = 1$) and Hg-1212 ($n = 2$), respectively. The Hg-1223 phase ($n = 3$) has a T_c of about 135 K under atmospheric pressure and it can even achieve a critical temperature of $T_c = 164$ K under high pressure [4]. The crystal structure of this mercury-based compound ($n = 3$) has the space group symmetry $P4/mmm$ [5–8], which is similar to that of the Tl-based compound $\text{Tl}(\text{Ba}, \text{Sr})_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$. The main difference in crystal structure between these two compounds is the amount of oxygen deficiency in the Hg–O plane as compared to that in the Tl–O plane. The former is less than 50%, and the latter is almost 100%. The oxygen content in the Hg–O plane may play an important role as regards the hole concentration in the Cu–O conducting plane. Therefore, we may consider the possibility of doping holes or electrons in the Hg–O plane by varying the oxygen content to enhance the critical temperature in the mercury family of compounds and to form a good superconductor.

More recently Shao *et al* [9] have successfully synthesized Pb-doped Hg-1223 superconductors. For the optimally Pb-doped sample ($\text{Hg}_{0.7}\text{Pb}_{0.3}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ is the nominal composition), the transition temperature is higher than that of Pb-free Hg-1223 cuprate. The measured critical temperatures are $T_c^{R=0}$ (the zero-resistance temperature) ~ 135 K, and T_c^{dia} (the diamagnetic onset temperature) = 143 K. To refine the crystal structure for the substituted compound and to explore the mechanism for the enhancement of the critical temperature, we have performed neutron powder diffraction experiments on oxygen-annealed $\text{Hg}_{0.7}\text{Pb}_{0.3}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ at room temperature. The results of these studies are reported herein.

2. Experimental procedures

The powder sample of $\text{Hg}_{0.7}\text{Pb}_{0.3}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ used in this study was prepared as described elsewhere [9]. Briefly, HgO and PbO with high purity were mixed with the precursor $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ in the cation ratio of Hg/Pb/Ba/Ca/Cu = 0.7/0.3/2/2/3, and ground. The ground mixture was then pressed into rectangular pellets with dimensions of $2 \times 4 \times 20 \text{ mm}^3$. The pressed pellets were sealed together in a vacuum quartz tube. The rapid annealing technique was repeated four times. Then, this tube was placed in a steel container, and the whole system was put in a furnace and heated to a temperature of $850 \text{ }^\circ\text{C}$ slowly. After being maintained at this temperature for 10 hours, it was cooled to room temperature in one step. After sintering, oxygenation was carried out. Since the neutron powder diffraction experiments require about 10 g of material, this procedure was repeated several times for each batch of samples. To ensure the quality of the samples for neutron scattering study, the standard four-probe method and the mutual-inductance technique were used to determine the resistivity and susceptibility. The transition temperatures were almost the same for each run. The measured transition temperature $T_c^{R=0}$ (the zero-resistance temperature) is $\sim 135 \text{ K}$, and T_c^{dia} (the diamagnetic onset temperature) is $> 140 \text{ K}$, similarly to in the case reported by Shao *et al* [9].

To improve the resolution and remove the background resulting from the inelastic neutron scattering, neutron powder diffraction was performed on a neutron triple-axis spectrometer equipped with an analyser at the Chinese Institute of Atomic Energy (CIAE). The sample was contained in a vanadium can with an inner diameter of 6 mm, and a wall thickness of 0.1 mm. A wavelength of 1.541 \AA was selected from the (004) planes of a pyrolytic graphite monochromator at a take-off angle of $2\theta_m = 54.76^\circ$. The analyser was pyrolytic graphite in the (002) setting. The collimation was $29'$ in the pile, $40'$ monochromator–sample, $28'$ sample–analyser and $40'$ analyser–detector.

Table 1. Intensity data for powder neutron diffraction.

FWHM parameters	U (deg^2)	3.4497
	V (deg^2)	1.5482
	W (deg^2)	0.3708
Fraction of Gauss component	γ	0.6188
Zero-point shift	Z (deg)	-0.0045
R -factor	R_{WP} (weighted pattern)	10.89
	R_P (pattern)	8.35
	R_E (expected)	3.33
Scattering amplitudes (10^{-12} cm)	$b(\text{Hg}) = 1.266$	$b(\text{Pb}) = 0.940$
	$b(\text{Ba}) = 0.525$	$b(\text{Ca}) = 0.490$
	$b(\text{Cu}) = 0.772$	$b(\text{O}) = 0.581$

The diffraction data were collected by step scanning at 0.1° intervals over the angular range from 10° to 70° . The Rietveld analysis program RIETAN [10] was used to analyse the collected data.

3. Results and discussion

The structure of Hg-1223 superconductor has been widely studied by powder x-ray and neutron diffraction techniques [5–8, 11, 12]. This compound has the symmetry of $P4/mmm$ with $a \sim 3.85 \text{ \AA}$, and $c \sim 15.85 \text{ \AA}$. We assume that the Pb-doped Hg-1223 compound

has the same symmetry as the pure Hg-1223 superconductor. The structure parameters of pure Hg-1223 obtained by Chmaissem *et al* [8] from their neutron powder diffraction study were used as the initial values for the lattice constants and atomic coordinates. According to RIETAN, the background function is assumed as

$$Y_{ib} = \sum_{j=0}^5 b_j \Psi_i^j \quad \Psi_i^j = \frac{2(\theta_i - \bar{\theta})}{\Delta\theta}$$

where $\bar{\theta} = (\theta_{max} + \theta_{min})/2$, and $\Delta\theta = \theta_{max} - \theta_{min}$. The background parameters b_n were refined periodically during the refinement. The final overall parameters for all phases are listed in table 1.

Some impurity peaks are also observed in the diffraction pattern and confirmed to arise from the small amounts of non-superconducting impurity phases CaHgO_2 and BaCuO_2 . The RIETAN program can handle a mixture of two or more phases. The structure parameters of these two impurity phases were also refined. The initial lattice constants and atomic coordinates for the CaHgO_2 and BaCuO_2 phases were taken from [11] and [12], respectively. The refined results show that CaHgO_2 has a symmetry space group of $R\bar{3}m$ with the lattice constants of $a = b = 3.5844(2)$ Å and $c = 18.7411(8)$ Å, which are consistent with those reported in [9], and BaCuO_2 has a symmetry space group of $Im\bar{3}m$ (No 211) with lattice constant of $a = 18.2543(6)$ Å, which is slightly smaller than that reported in [10] ($a = 18.2772$ Å).

Each FWHM parameter of the impurity phases was set as the same value as the corresponding parameter of the mercury-based superconductor phase (the main phase). Each phase was refined independently before they were refined together. At the initial stage for main-phase refinements, full occupation was assumed for all atoms except the partially occupied oxygen sited at the position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in the (Hg/Pb)–O plane. The contents of Pb and oxygen in the (Hg/Pb)–O plane were fixed as 0.34 [9] and 0.41 [10]. The overall isotropic thermal parameter for Pb atoms was set as the same as that for Hg atoms. The other parameters for all phases were refined successively in the following order: (a) the scale factor and background parameters; (b) parameters related to the peak profile; (c) lattice constants; and (d) atomic coordinates.

The refined parameters were used as initial values. Ignoring the atomic anisotropic thermal parameters, an atomic isotropic thermal parameter B_j was assigned to each atom (including Pb and Hg). It was assumed that the $(0, 0, \frac{1}{2})$ position is fully occupied by Hg and Pb, so linear constraints were used. All parameters were refined again and variable parameters were updated after the refinement. A satisfactory result is obtained. Figure 1 shows the final observed and calculated diffraction profiles. The final refined structure parameters are listed in table 2. For comparison, table 2 also lists the refined structure parameters of Pb-free Hg-1223 superconductors [5, 8]. The slight difference between the structure parameters obtained by Hunter *et al* [5] and those obtained by refinement by Chmaissem *et al* [8] may be due to the different synthesis procedures.

The contents of Pb and oxygen were determined. The content of Pb was 0.382(6), which is 27% larger than that of the nominal composition, 0.30. This may be due to the existence of an Hg-enriched impurity phase of CaHgO_2 . The content of oxygen in (Hg/Pb)–O layers was 0.450(2), larger than that for Pb-free Hg-1223 (the optimum value is 0.35 [3]). This is consistent with the notion that Pb substitution for Hg in the 1223 compound stabilizes the necessary fractional oxygen content, thereby increasing T_c . The in-plane Cu(1)–O(1) bond distance (1.9228 Å) and the apical Cu(2)–O(3) bond distance (2.076 Å) are not consistent with those for Pb-free Hg-1223 compound [8], in which the in-plane Cu(1)–O(1) bond

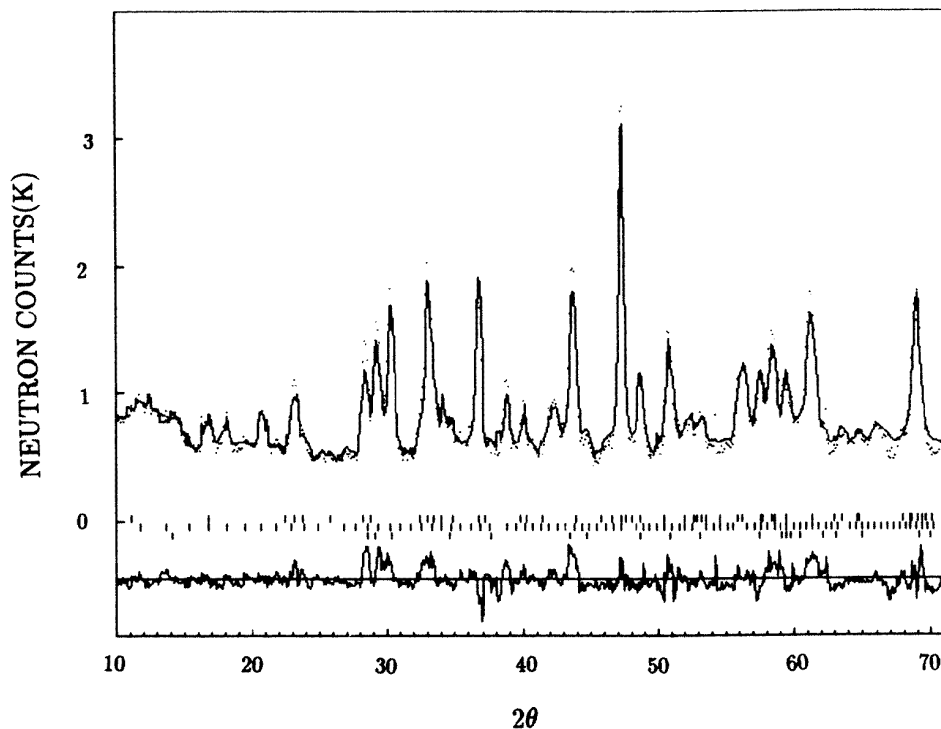


Figure 1. Measured and calculated intensities (dots and continuous line, respectively) for the sample of $\text{Hg}_{1-x}\text{Pb}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.45}$ at room temperature. The difference curve (observed – calculated values) is shown at the bottom of the figure also.

distance is $1.92508(7)$ Å and the apical $\text{Cu}(2)\text{--O}(3)$ bond distance 2.751 Å. Also, the angle between the $\text{Cu}(2)\text{--O}(2)$ bond ($\{\text{Cu}(2)\text{--O}(2)\text{--Cu}(2)\}$) in the $\text{Cu}\text{--O}$ layer is 173.41° for our sample. This value is less than those obtained in [8] (179.55°) and [5] (178.0°), and also less than the value of 176.40° obtained by refinement from x-ray diffraction for the Pb-free sample [6]. These differences may also relate to the increase of T_c .

The valence of copper can be estimated for mercury-based homologous series compounds. The formula can be represented as follows if full occupation is assumed for all cations:

$$\bar{V}_{\text{Cu}} = \frac{(2n + 2 + \delta)V_{\text{O}} - V_{\text{Hg}} - 2V_{\text{Ba}} - (n - 1)V_{\text{Ca}}}{n} \quad (1)$$

where V is the valency of corresponding atoms with the value of 2, n is the number of $\text{Cu}\text{--O}$ layers, and δ is the content of oxygen in the $\text{Hg}\text{--O}$ plane. For the Pb-free Hg-1223 superconductor, the average valency for each copper atom is 2.28, which is deduced from the refined structure parameters of Chmaissem *et al* [8]. For our Pb-doped sample, $V_{\text{Hg}} = 0.7V_{\text{Hg}} + 0.3V_{\text{Pb}} = 2$ (the valency of 2 is assumed for Pb), $\delta = 0.450$, and the average valency of 2.30 for each copper atom is obtained. This value is consistent with that for YBCO superconductor [13], where $\bar{V}_{\text{Cu}} = 2.29$ for the sample with the highest transition temperature $T_c = 92$ K.

Table 2. Refined structure parameters for Pb-doped (Hg,Pb)-1223 and Pb-free Hg-1223 [8] superconductors.

		(Hg, Pb)-1223	Hg-1223 [5]	Hg-1223 [8]
Hg/Pb	Position	$(0, 0, \frac{1}{2})$	$(0, 0, \frac{1}{2})$	$(0, 0, \frac{1}{2})$
	B (\AA^2) for Hg	0.02(2)		3.9(2)
	B (\AA^2) for Pb	0.24(4)		
	Occupancy for Pb	0.382(6)		
Ba	Position	$(\frac{1}{2}, \frac{1}{2}, 0.3167)$	$(\frac{1}{2}, \frac{1}{2}, 0.3265)$	$(\frac{1}{2}, \frac{1}{2}, 0.3227)$
	B (\AA^2)	2.12(8)		2.2(3)
Ca	Position	$(\frac{1}{2}, \frac{1}{2}, 0.0992)$	$(\frac{1}{2}, \frac{1}{2}, 0.1027)$	$(\frac{1}{2}, \frac{1}{2}, 0.1046)$
	B (\AA^2)	0.13(5)		0.0(2)
Cu(1)	Position	$(0, 0, 0)$	$(0, 0, 0)$	$(0, 0, 0)$
	B (\AA^2)	2.86(9)		1.2(2)
Cu(2)	Position	$(0, 0, 0.1998)$	$(0, 0, 0.2012)$	$(0, 0, 0.2021)$
	B (\AA^2)	1.20(7)		1.2(2)
O(1)	Position	$(\frac{1}{2}, 0, 0)$	$(\frac{1}{2}, 0, 0)$	$(\frac{1}{2}, 0, 0)$
	B (\AA^2)	1.52(4)		0.1(1)
O(2)	Position	$(\frac{1}{2}, 0, 0.1928)$	$(\frac{1}{2}, 0, 0.1991)$	$(\frac{1}{2}, 0, 0.2006)$
	B (\AA^2)	0.30(7)		0.3(1)
O(3)	Position	$(0, 0, 0.3823)$	$(0, 0, 0.3755)$	$(0, 0, 0.3764)$
	B (\AA^2)	1.74(8)		0.9(2)
O(4)	Position	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
	B (\AA^2)	4.22(7)		1.2(fixed)
	Occupancy	0.450(2)		0.41(2)
a (\AA)		3.8457(1)	3.8460(1)	3.8502(1)
c (\AA)		15.8252(7)	15.7730(5)	15.7829(9)
R_I (integrated intensity)		8.40		5.09
R_F (structure factor)		7.08		4.65

4. Conclusion

In summary, Hg in the Hg-1223 superconductor can be partially substituted for with Pb, resulting in the increase of T_c . The structure parameters were determined by neutron powder diffraction refinement for the Pb-doped Hg-1223 phase. The increase of T_c may be related to the increase of the valency of copper and the change of some kinds of cation–oxygen bond distance and/or the bond angle in the Cu–O plane.

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