

Synthesis and Superconducting Properties of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$

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The influence of precursor composition, nominal mercury vapour pressure (P_{Hg}) and reaction temperature (t) on the formation of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ have been studied. By reducing the empty space inside the quartz tube, we could increase P_{Hg} higher than 200 atm and obtain samples containing only $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ as the superconducting phase, with T_c (onset) = 134 K and T_c (zero) = 131 K.

Superconductivity above 130 K for Hg-containing cuprates was discovered recently by Shilling *et al.*¹ The $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ (Hg-1223) phase was known to be a response to 130 K superconductivity, but production of this single phase has not yet been successful. Several different methods have been suggested to prepare high-fractional Hg-1223 samples.

First, Antipov *et al.*² applied high pressure (50 kbar) at 950 °C in a belt-type apparatus. Hg-1223 was present as the main phase in the sample; however, some $\text{HgBa}_2\text{Ca}_1\text{Cu}_2\text{O}_{6+x}$ (Hg-1212) and other impurity phases were also detected. Moreover, the process requires complex equipment for sintering under high pressure and temperature. Compared with this, the synthesis of Hg-1233 in an evacuated quartz ampoule has several benefits owing to its simplicity.^{3,4} The most promising modification of this method was reported by Meng *et al.*⁵ The authors used the reactant pellet (R) with nominal composition $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (not a phase) as a composite Hg source for the precursor (P), $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, during heat treatment inside a quartz ampoule. Samples containing about 65% Hg-1223 were obtained within the temperature range 850–860 °C. However, the strong sensitivity of the phase composition to P:R ratio and possible interaction between the quartz and samples at high temperatures are the most serious problems of this method.

Here, we report a simple method for fabricating a high-quality superconducting sample with Hg-1223 as the main phase. For this sample, we tried every method to reduce the empty space inside the quartz tube, and increased P_{Hg} to

>200 atm, much higher than in the previously published sample used for the high-pressure study.⁶

The samples were synthesized by the following procedure. The precursors with Ba:Ca:Cu cation ratios of 2:1:2, 2:1.5:2.5 and 2:2:3 were prepared by mixing appropriate amounts of the nitrates $\text{Ba}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. The mixture of reagents was heated to 650 and 700 °C in air for 20 h with intermediate grinding. The resulting powder was then compressed into a pellet and heated in an oxygen atmosphere for 60 h at 900 °C with two intermediate grindings. A stoichiometric amount of HgO (yellow) was added to the precursor and mixed in a glove box under a nitrogen atmosphere. Pellets of nominal composition $\text{HgBa}_2\text{Ca}_1\text{Cu}_2\text{O}_y$, $\text{HgBa}_2\text{Ca}_{1.5}\text{Cu}_{2.5}\text{O}_y$ and $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ were placed inside an alumina tube and then inside a thick-walled quartz tube. The empty space inside the tube was reduced by packing it with quartz rods of different lengths. The volume of ampoule and amount of sample were adjusted to obtain the nominal 'mercury vapour pressure' during heat treatment. Here, 'mercury vapour pressure' means the calculated pressure inside the ampoule assuming that the HgO totally decomposes and all of the Hg remains unreacted. The value of this parameter for our experiments varied over the 80–300 atm range. The evacuated tube was sealed and placed in a steel container. The samples were heated at 160 K h⁻¹ to a temperature between 800 and 950 °C, kept at this temperature for 5 h and then cooled at 80 K h⁻¹ to room temperature. The oxygenation of the samples was carried out in flowing oxygen at 300 °C for 20 h.

Table 1 Estimated phase fraction according to XRD analysis in samples prepared under different conditions

sample number	$p^a / \text{g cm}^{-3}$	$t / ^\circ\text{C}$	estimated volume fraction (%)					
			Hg-1223	Hg-1212	Hg-1201	CaHgO_2	BaCuO_2	
				ref. 5				
Hg-91	0.19	800	—	—	30	40	30	
Hg-94	0.30	800	—	10	50	20	20	
Hg-95	0.33	800	—	50	10	20	20	
Hg-65	1.06	800	—	60	—	25	15	
				our results				
N1	1.02	800	—	40	—	25	35	
N2	1.25	800	25	30	—	—	45	
N3	2.00	800	25	35	—	—	40	
N4	2.00	830	35	20	—	—	45	
N5	2.00	850	45	15	—	—	50	
N6	2.00	900	55	—	—	—	45	
N7	2.50	900	70	—	—	—	30	
N8	2.50	930	50	20	—	—	30	

^a p = reactant mass per unit volume.

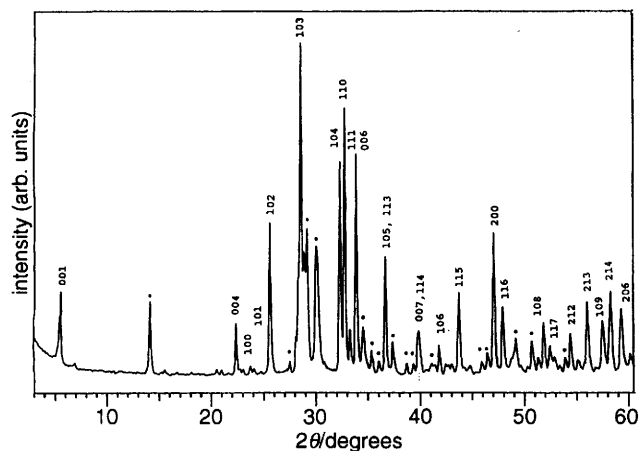


Fig. 1 X-Ray diffraction pattern for sample N7. Indexed XRD intensities correspond to Hg-1223. Impurity phases are marked by ●

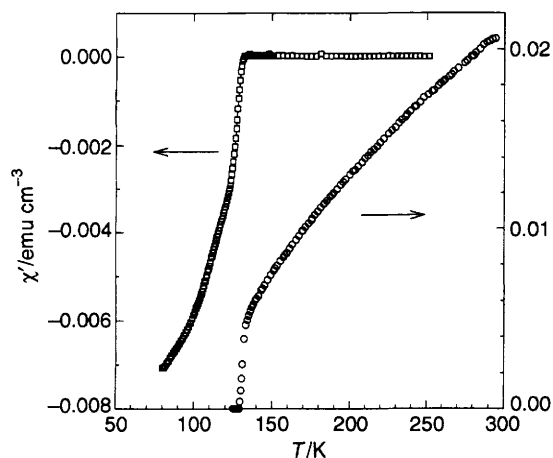


Fig. 2 Resistance and ac magnetic susceptibility vs. T for sample N7 with Hg-1223 as the major superconducting phase. T_c (onset) = 134 K and T_c (zero) = 131 K

The results of XRD analysis for our samples in comparison with ref. 5 are summarized in Table 1. We used the ratio of the intensities of the (103) line for Hg-1212 and Hg-1223, to estimate the approximate amounts of these phases. The (442) and (012) lines were chosen for the main impurity phases of BaCuO_2 and CaHgO_2 , respectively.

For a pellet composition of $\text{HgBa}_2\text{Ca}_1\text{Cu}_2\text{O}_y$, and a reaction temperature of 800°C , Meng *et al.*⁵ found that at low Hg vapour pressure, associated with a low reactant concentration in the ampoule (p), only Hg-1201 was formed, together with a larger amount of CaHgO_2 and BaCuO_2 . The fraction of

Hg-1212 increased to 60% by increasing p to 1.06 g cm^{-3} . However, the Hg-1223 phase could not be found in their experiments. This is also confirmed in our sample N1. However, by further increasing p up to 1.25 g cm^{-3} we successfully made sample N2 containing Hg-1223 phase together with Hg-1212 and BaCuO_2 . We could not detect CaHgO_2 in sample N2 with high p , while in sample N1 with low p the amount of this phase was quite high. The data were confirmed by ac susceptibility measurements, which indicated the presence of two phases, Hg-1223 and Hg-1212, with superconducting transitions at 130 and 126 K, respectively, in an oxygenated bulk sample.

The effect of temperature on the formation of Hg-1212 and Hg-1223 in samples with a nominal chemical composition of $\text{HgBa}_2\text{Ca}_{1.5}\text{Cu}_{2.5}\text{O}_y$ was studied. Four different temperatures, 800°C , 830°C , 855°C and 900°C , were chosen to study the temperature effect (samples N3, N4, N5 and N6, respectively). p was kept constant at 2.0 g cm^{-3} in all the experiments. It is important that Hg-1212, which was reported⁵ to be unstable above 820°C , still exists in the sample at 830°C and 855°C and disappears only at 900°C .

The best samples were obtained by using a stoichiometric $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ composition at 900°C (sample N7). It contained Hg-1223 as the main superconducting phase with no traces of Hg-1212 (Fig. 1). At 930°C (sample N8) the total amount of superconducting phases remained constant, but Hg-1212 was present as a second superconducting phase. A further increase of temperature up to 950°C led to a rupture of the quartz ampoule in the present experiment. A possible reason for such a rupture is the decomposition of the Hg-containing phases and an increase in the mercury vapour pressure inside the ampoule. So, according to our data, Hg-1223 starts to decompose above 900°C and the optimum temperature for Hg-1223 formation is about 900°C . However, the optimum temperature may change for another p value. The resistance and ac susceptibility measurement data for sample N7 (Fig. 2) confirmed its high quality.

References

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