High-pressure synthesis of an x-ray diffraction in the single-phase superconducting mercury cuprate $HgBa_2Ca_3Cu_4O_{10+x}$

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(Submitted 21 July 1995; resubmitted 10 August 1995)
Pis'ma Zh. Éksp. Teor. Fiz. **62**, No. 6, 491–493 (25 September 1995)

It is shown that a controllable high-pressure chamber can be used to obtain higher single-phase homologs of the high-T_c mercury cuprates. The single-phase superconducting ceramics $HgBa_2Ca_3Cu_4O_{10+x}$ are synthesized and corroborating x-ray diffraction data are presented. The synthesis parameters, the temperature, and the holding time are substantially different from the published values. It is shown that the next terms in the homological series can be obtained by using higher synthesis temperatures and longer holding times. © *1995 American Institute of Physics.*

The highest-T_c superconductors—mercury cuprates—discovered in 1993 constitute a homological series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$, where $n=1$, 2, and 3, and each cell of the tetragonal system with a definite value of n is structurally different from the cell with $n-1$ by an additional CuO_2 layer and a Ca atom between the neighboring CuO_2 layers. The highest terms of this series are synthesized mainly at high pressures of several tens of kilobars. The samples so obtained are multiphase materials, which makes it much more difficult to investigate their properties. The multiphaseness is associated mainly with the fact that imperfect pressure chambers with high temperature gradients are used for synthesis. Such chambers make it impossible to follow and control the synthesis process and, consequently, the synthesis process cannot be optimized. We synthesized a nearly single-phase mercury cuprate $HgBa_2Ca_3Cu_4O_{10+x}$ (Hg-1234 phase), which could be obtained only under a high pressure, using a program-controlled, high-pressure chamber,[1] by changing the synthesis parameters.

The Hg-1234 phase was first synthesized in 1993 at a pressure of 4.0 GPa and a temperature of 700°C.[2] The exposure time at the synthesis temperature was 1 h. The samples obtained were found to be multiphase materials and even contained unidentified impurities.

In the present work we synthesized the samples in a hermetically sealed gold container with a stoichiometric mixture of the required components. The container was inserted into a cylindrical graphite heater, which served as a reaction cell. The geometry and thermal insulation of the heater guaranteed that there were no appreciable tempera-

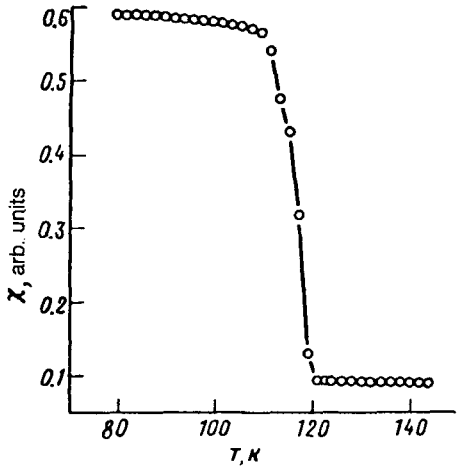

FIG. 1. Superconducting transition in a single-phase sample of $HgBa_2Ca_3Cu_4O_{10+x}$.

ture gradients in the reaction space, which made it possible to insert a thermocouple. The temperature was set and maintained automatically. The procedure employed in the present work for performing the synthesis experiments will be described in detail in Ref. 3 . Here we only report data on the results obtained by using this method.

The samples were synthesized at a pressure of 2.0 GPa and a temperature of 1000°C in a time of 3 h. The time for reaching the synthesis temperature and decreasing the temperature and pressure, just as the parameters of the synthesis itself, were determined from preliminary experiments and are substantially different from the published values. The thermograms showed that HgO, which is a component of the precursor (the corresponding initial mixture), decomposes at 725°C. Melting of the mixture was not observed, and the reaction was a solid-phase reaction.

Figure 1 shows the temperature dependence of the magnetic susceptibility with a transition into the superconducting state. This dependence was measured by an inductive method at a modulation frequency of 2 kHz upon heating the sample from the boiling point of liquid nitrogen.

The results of the x-ray-phase analysis for one of the best samples, which was synthesized with an initial composition corresponding to the stoichiometry of the 1223 phase, are given in Table I. The synthesized cuprate crystallized in the tetragonal system with unit cell parameters $a=3.8492$ Å and $c=18.939$ Å. The x-ray-phase analysis was performed and the cell parameters were determined in a focusing chamber — FR552 monochromator $CuK\alpha_1$ radiation), using germanium ($a=5.6574$ Å) as an internal standard. The presence of such a large number of indexed lines with intensity I/I_0 ranging from 1 to 100 allowed us to assume that this is a single-phase sample. Analysis showed that this sample consists of 95% Hg-1234. The remaining lines correspond to impurities which collectively amount to 5%: $Ba_2Cu_3O_{5+x}$ (3 lines), CaO (1 line), and one unknown impurity (1 line).

TABLE I. Diffraction pattern of sample No. 27, mercury cuprate, 1234 phase.

hkl	I/I_0, %	*d*, measured	*d*, calculated
001	10	18.882	18.939
100	1	3.848	3.849
005	2	3.785	3.788
102	8	3.564	3.568
	5	3.3544	
103	40	3.288	3.287
006	1	3.154	3.157
104	90	2.9874	2.9868
$Ba_2Cu_3O_5$	2	2.8194	
CaO	1	2.7843	
110	100	2.7236	2.7218
007	80	2.7014	2.7057
105	80	2.7014	2.6999
111	40	2.6942	2.4961
112	3	2.6153	2.6159
$Ba_2Cu_3O_5$	2	2.5915	
	5	2.49547	
106	30	2.4395	2.4408
008	5	2.3646	2.3675
$Ba_2Cu_3O_5$	1	2.132	
009	2	2.1010	2.101
116	8	2.0613	2.0613
200	60	1.9241	1.9246
117	5	1.9174	1.9189
109	1	1.8451	1.8465
118	6	1.7863	1.7863
123	20	1.6612	1.6608
124	25	1.6179	1.6178
125	40	1.5671	1.5672
126	25	1.5112	1.5113
028	10	1.4935	1.4934
1012	5	1.4599	1.4603
220	30	1.3608	1.3609

It should also be noted that increasing the temperature to 1000–1200°C and the synthesis time to 3 h with the initial composition of the mixture for synthesis corresponding to the stoichiometry of the 1234 phase made it possible, in addition to giving a higher percentage yield of the high-T_c phases Hg-1223 and Hg-1234, to obtain a mixture of phases of the higher homologs, right up to Hg-1256. Each of these phases was present in amounts of severals tens of percent. This suggests that the synthesized phases of the mercury cuprates are not necessarily formed from the phases of the lower precursor-homologs which do not correspond to the given stoichiometry. From our data we determined the lattice parameters for second through the sixth terms of the homological series of the mercury cuprates.[3] It is interesting to note that, within the experimental error, the

lattice constants a do not depend on the synthesis parameters and are approximately identical in all phases from Hg-1212 to Hg-1256, inclusively.

This work was performed as part of the direction "Superconductivity" of the State Scientific and Technical Program Urgent Directions in the Physics of High-T_c Superconductors" (project 93080).

We wish to thank E. V. Antipov and N. A. Bendeliani for a discussion of this study. We also thank S. M. Kazakov for assisting in the x-ray analysis.

[1] T. I. Dyuzheva, N. A. Bendeliani, L. N. Dzhavadov *et al.*, Alloys and Compounds (to be published).
[2] S. M. Kazakov, E. S. Itskevich, and L. V. Bogachev, JETP Lett. **58**, 343 (1993).
[3] E. S. Itskevich, T. I. Dyuzheva, I. G. Kuzemskaya, and K. A. Lokshin, Neorganicheskie materialy [Inorganic materials] (in press).

Translated by M. E. Alferieff