Superconductivity with $T_c > 130$ K in $HgBa_2Ca_2Cu_3O_{8+x}$ and $HgBa_2Ca_3Cu_4O_{10+x}$

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Superconducting samples of the homologous mercury cuprate series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ with $n=3$ and $n=4$ have been synthesized at high pressure and studied. Superconducting transition temperatures $T_c=132$ K ($n=3$) and 131 K ($n=4$) have been obtained; these are the temperatures for the onset of the transition to the superconducting state in measurements of the magnetic susceptibility. The lattice constants of the compounds synthesized have been determined.

The family of layered cuprates $HgBa_2R_{n-1}Cu_nO_{2n+2+x}$which was recently produced holds promise for research on the nature of high-T_c superconductivity in the layered cuprates. The reason is that even the first member of this series, Hg-1201, has a high critical temperature along with a comparatively simple crystal structure (there are no modulations or statistical displacements of atoms; the symmetry of the cell is high).[1] As in the thallium family $TlBa_2Ca_{n-1}Cu_nO_{2n+3-x}$, in which T_c has been found to increase with increasing thickness of the perovskite block, from 10 K for $n=1$ to 110 K for $n=4$,[2,3] a T_c above 120 K has been found[4] for the second member of the series, Hg-1212, synthesized under high quasihydrostatic pressure. High-pressure mercury compounds must be used in the synthesis, since mercury oxide decomposes under ordinary conditions. In the present letter we are reporting preliminary results on synthesis under pressure of superconducting ceramics with $n=3$ and $n=4$, and the results of a study of these materials.

The synthesis was carried out at the Institute of High Pressure Physics, Russian Academy of Sciences, with the help of a toroidal quasihydrostatic pressure chamber made of the hard alloy VK-6, with a support. The working volume of the chamber could accommodate samples sealed off hermetically in platinum cylinders ($d=3$ mm). The test samples were a stoichiometric mixture of HgO and a precursor of the nominal composition $Ba_2Ca_{n-1}Cu_nO_x$ (with $n=3$ and $n=4$). This precursor was prepared by annealing a mixture of BaO_2, CaO, and CuO for 20 h in air at 920 °C. Pyrophillite was used to transmit the pressure and to seal the chamber. This chamber had a graphite heater and external water cooling. The synthesis parameters were 40 kbar, $T=700$ °C, and an exposure time of 1 h. The resulting samples consisted of a black powder in an amount up to 50 mg.

The test samples were studied by x-ray diffraction in order to identify the phases

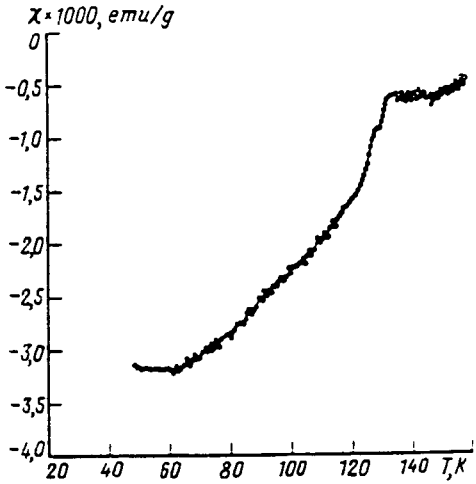

FIG. 1. Temperature dependence of the magnetic susceptibility of an $HgBa_2Ca_3Cu_4O_{10+x}$ sample.

present, in an FR552 focusing monochromator chamber (Cu $K\alpha_1$ radiation); germanium ($a=5.6574$ Å) was used as an internal standard. The resulting samples did not consist of a single phase. The x-ray diffraction pattern of a material corresponding to the composition Hg-1223 contained, in addition to lines of the Hg-1223 phase, some lines corresponding to the Hg-1212 phase and to small amounts of HgO and CuO. There were also some lines of unidentified phases. The same situation was observed for the composition Hg-1234. The x-ray diffraction pattern of an $HgBa_2Ca_2O_{8+x}$ sample was indexed in tetragonal symmetry with lattice constants $a=3.8553(7)$ and $c=15.806(5)$ Å. The compound $HgBa_2Ca_3Cu_4O_{10+x}$, with the lattice constants $a=3.852(1)$ and $c=18.960(9)$ Å, also crystallizes in a tetragonal symmetry.

The magnetic susceptibility was measured over the temperature range 12–160 K in an alternating external field with a frequency of 27 Hz and an amplitude of 1 Oe. Figure 1 shows a curve of the magnetic susceptibility.

These samples undergo a transition from a paramagnetic state to a diamagnetic state at $T_c=132$ K in the case of Hg-1223 and at $T_c=131$ K for Hg-1234. Annealing in oxygen for 10 h at 400 °C does not raise the transition temperature. The reason for the broad transition to the diamagnetic state may be the presence of several superconducting phases of a common homologous series in the sample, as has been observed in the cases of the Bi and Tl cuprates.

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