DECOMPOSITION OF HIGH TEMPERATURE SUPERCONDUCTORS IN WATER

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Changes of magnetic susceptibility and electrical resistivity of ceramic superconductors of nominal composition $YBa_2Cu_3O_{7-y}$ and $Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_{3.6}O_x$ observed during their soaking in water are reported. It was found that the $YBa_2Cu_3O_{7-y}$ superconductor is destroyed in few minutes by boiling water. At lower temperatures the hydrolysis reduces the volume of the superconductive phase, as seen from the susceptibility measurements. Reaction of $Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_{3.6}O_x$ with water causes a decrease of the relative volume of both superconducting phases at a rate substantially higher for the high temperature one (T_c = 110 K).

High-temperature superconductors YBaCuO and BiSrCaCuO are usually prepared by solid state reaction from oxides. Properties of the superconductors depend on the temperature, heating rate, pressure and atmosphere used during synthesis. Successful applications are stipulated also by their stability in the environment. One of the important factors is the influence of water on the superconductive properties of this material.

Changes of the chemical and physical properties of YBaCuO samples due to the reaction with water were studied by measurements of resistivity, magnetic susceptibility and X-ray diffraction and by the electron microprobe analysis[1 – 4]. The samples were decomposed by the action of water and nonsuperconducting phase have been produced.

Two different phases of BiSrCaCuO exist, the high temperature phase $Bi_2Sr_2Ca_2Cu_3O_x$ (2223, T_c = 110 K) and the low temperature one, $Bi_2Sr_2CaCu_2O_x$ (2212, T_c = 80 K). Partial substitution of Pb for Bi enhances the volume of the high temperature phase on account of the low temperature one. Stability of the low temperature phase in the water have been described[5,6]. This sample was much more stable in water than YBaCuO.

In this report we study the influence of water on both the phases of BiSrCaCuO as compared to that on YBaCuO.

EXPERIMENTAL

All samples were prepared by conventional solid state reaction from the powder reagents.

Appropriate molar amounts of p.a. Y_2O_3, $BaCO_3$ and CuO were mixed and ground. After the calcination of powder in oxygen for 6 h at 900 °C, the samples were reground, pressed into the pellets of 13 mm diameter and 1 mm thickness, sintered for another 6 h at 950 °C in O_2 atmosphere, then slowly cooled in the furnace.

Samples of BiSrCaCuO were prepared with the addition of Pb to promote the growth of the high-T_c phase. Powdered (p.a.) Bi_2O_3, Pb_3O_4, $SrCO_3$, $CaCO_3$ and CuO were mixed together in the molar ratio of Bi : Pb : Sr : Ca : Cu equal to 1.4 : 0.6 : 2 : 2 : 3.6 and ground. The resulting powder was calcinated in air for 20 h at 800 °C, reground and pressed into the pellets that were annealed for 116 h at 865 °C in air. Then they have been quenched into liquid nitrogen.

One set of experiments involved the isochronal soaking of samples in water of varying temperature and another the isothermal heating of the samples in boiling water.

Changes of critical temperatures after soaking were investigated by measurement of resistivity, a.c. and d.c. susceptibilities. The resistivity was measured by the standard four-probe technique. Voltage and current leads were connected to the samples with silver paste.

The Meissner effect was measured in the earth magnetic field frozen within a superconducting shield with the help of a SQUID. The S.H.E. mutual inductance bridge with the frequency of 160 Hz and the excitation voltage 5 V was used to measure the a.c. susceptibility. The temperature was determined by a calibrated Pt-termometer.

Samples were checked by X-ray diffraction (CuK_α line) with the help of a Geigerflex Rigaku Denki diffractometer and were analyzed by atomic absorption method with Perkin–Elmer 975 spectrometer.

RESULTS AND DISCUSSION

Y–Ba–Cu–O System

The superconducting transition temperature $T_c \sim 90$ K of the originally prepared samples $YBa_2Cu_3O_{7-y}$ has been determined from the resistivity. Samples were soaked in water of varying temperature t_w for 20 min. The results of measurement of the critical temperature are summarized in Table I.

The resistivity measurements have shown no change of T_c up to t_w = 80 °C. Above this temperature the superconductivity disappeared. The measurement of the susceptibility have indicated relative change of the volume of the superconducting phase during this soaking. When the temperature of water is below 30 °C there was no change of χ–T curve, between 30 – 80 °C the volume of superconducting phase decreased and the width of the transition increased. The onset temperature T_{ons} remained unchanged (Fig. 1).

The decomposition reaction of $YBa_2Cu_3O_{7-y}$ by water was described[7] as:

$$2\,YBa_2Cu_3O_7 + 3\,H_2O = 5\,CuO + 3\,Ba(OH)_2 + Y_2BaCuO_5 + 1/2\,O_2 \qquad (A)$$

The water in which our sample was soaked at 100 °C for an hour was analyzed to determine the amount of Y, Ba and Cu resolved. The atomic absorption analysis showed a presence of Ba and Cu atoms only, with a ratio Ba : Cu = 10^4 : 1. We have not detected Y atoms within the resolution of our equipment. The sample itself got covered by a very light grey surface layer after the drying process.

The X-ray diffraction spectra of samples showed peaks of $BaCO_3$ and CuO and confirmed the appearance of a new nonsuperconducting phase Y_2BaCuO_5.

TABLE I
Superconductive properties of the resistivity of water treated $YBa_2Cu_3O_{7-y}$ sample. Duration of each treatment 20 min

t_w, °C	R, mΩ	T_{50}, K	T_0, K	ΔT, K
–	21	90.0	89.5	1.5
5	20	90.9	89.3	1.5
15	20	90.6	89.3	1.7
25	20	91.2	90.1	1.8
35	21	91.2	90.0	1.7
44	19	91.0	89.4	1.8
51	19	91.0	89.6	1.4
66	18	92.1	91.1	1.8
85	$3.85 \cdot 10^6$	no superconductivity observed		

t_w Temperature of water, R resistance at room temperature, T_{50} midpoint of the resistive transition, T_0 zero resistance point, ΔT width of the transition.

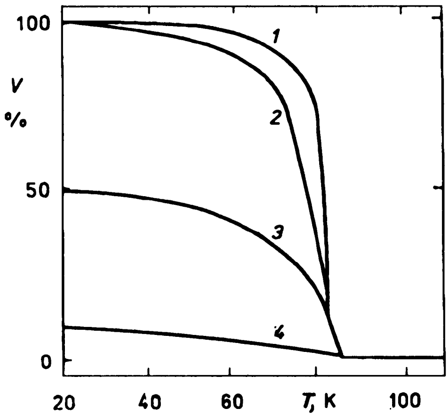

FIG. 1
Relative changes of the volume of the superconducting phase YBaCuO during isochronal soaking (20 min). *1* originally prepared sample, *2* at 44 °C, *3* at 51 °C, *4* at 66 °C

Bi–Sr–Ca–Cu–O System

Bi based superconductors are expected to be much more stable[5,8] in water. To accelerate the reaction the samples have been soaked in boiling distilled water.

After a sample soaking at 100 °C for 45 min pH value rose to 10. Contrary to the case of soaking $YBa_2Cu_3O_{7-y}$, there was no gas bubble rising up in the soaking water. After being filtered, the soaking water was analyzed and the results of the atomic absorption analysis are shown in Table II. The presence of large amount of Ca and Sr manifests in the alkaline reaction of aqueous solution which indicates the formation of both $Ca(OH)_2$ and $Sr(OH)_2$. Both hydroxides are gradually transformed into the corresponding carbonates under the influence of atmospheric CO_2.

The X-ray diffraction pattern of the initial sample (Fig. 2*a*) showed presence of both superconducting phases as expected. The reaction residue after 45 and 120 min soaking was analyzed by the X-ray diffraction method (Fig. 2*b*, 2*c*). The relative intensities of peaks of the high-T_c (2223) phase have decreased more than those of the low-T_c (2212) one in the presented part of spectra.

New peaks appeared in the spectra. Clearly visible peaks (Fig. 2*c*) were identified as $CuBi_2O_4$, a product of decomposition of the superconductive phases. CuO peaks were identified, too (2 θ > 35°). This results supported the reaction of the phase 2212 with water[9]:

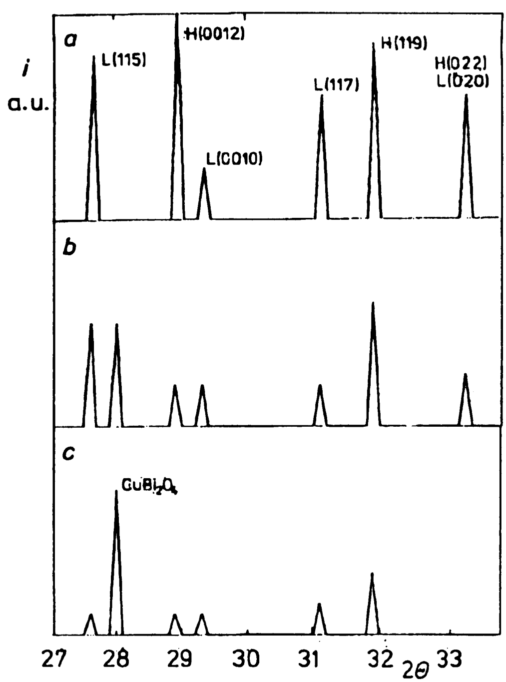

FIG. 2
Evolution of X-ray diffraction spectra BiSrCaCuO during water exposure at 100 °C. *a* originally prepared sample, *b* 45 min exposure, *c* 120 min exposure. H high-T_c and L low-T_c phases, respectively

$$Bi_2Sr_2CaCu_2O_8 + 3\,H_2O = 2\,Sr(OH)_2 + Ca(OH)_2 + CuBi_2O_4 + CuO \qquad (B)$$

No other products were found in our experiment.

Temperature dependence of the d.c. susceptibility of the sample soaked for various times in boiling distilled water is presented in Fig. 3. In this case we observe the Meissner effect and in a one-phase homogeneous superconducting sample the diamagnetic shift is proportional to the volume of the superconducting phase. The relative changes of apparent volumes of both superconducting phases during soaking of the sample, assumed to be proportional to relative heights of corresponding diamagnetic

TABLE II
The results of the atomic absorption analysis of the $Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_{3.6}O_x$ as prepared and of the solution after soaking

Element	Content of the element		
	as prepared, mg	solution	
		mg	%
Bi	27.60	0.123	0.4
Pb	11.73	0.076	0.7
Sr	16.50	3.600	21.8
Ca	7.56	0.580	7.7
Cu	21.60	0.048	0.002

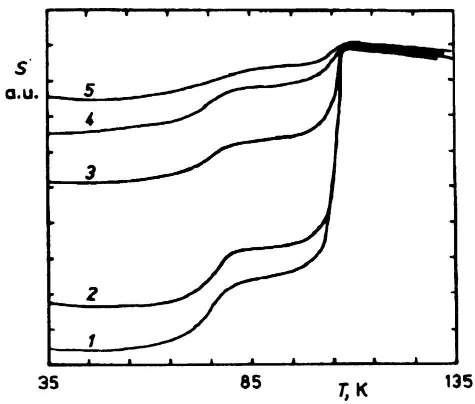

FIG. 3
Temperature dependence of the d.c. susceptibility (*S*) of the BiSrCaCuO sample after soaking in boiling water. *1* originally prepared sample, *2* 2 min, *3* 12 min, *4* 18 min, *5* 27 min

shifts in Fig. 3, are presented in Fig. 4 as a function of soaking time t_s. It can be seen that the high-T_c phase is rapidly destroyed by reaction with water while the volume of the low-T_c phase remains nearly constant.

The results of the isochronal soaking of the sample in boiling water are summarized in Fig. 5. It is worth noting that all these substantially differing curves have been obtained subsequently on the same sample. To be able to present them in one picture (the normal state resistance of the sample increased during the experiment by more then three orders of magnitude) the resistances have been normalized to their respective values at T = 140 K.

The originally prepared sample (Fig. 5, curve *1*) exhibits a sharp one-step resistive transition with T_c = 105 K and T_0 (R = 0) = 92 K. Presence of the low-T_c phase, detected by susceptibility measurement, is thus completely disguised by the high-T_c one, which is characteristic for the Pb-substituted samples[10,11]. Above the onset of the superconductivity resistance increases up to room temperature.

On the curve *3* (Fig. 5) one can see two qualitatively new features. First, there appears a second step on the $R(T)$ curve which indicates the presence of the low-T_c phase and second, the normal state resistance takes a semiconducting character with $dR/dT < 0$.

The two-step character of all curves unambiguously demonstrates the presence of both superconducting phases in the sample in accord with susceptibility data.

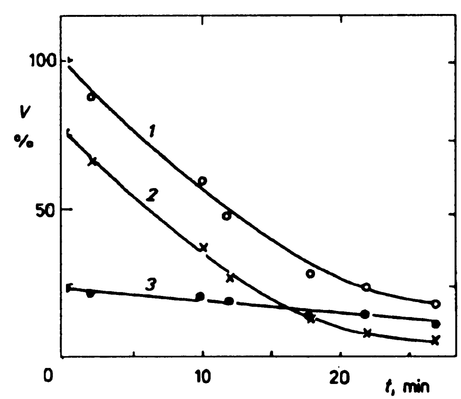

FIG. 4

Relative changes of the volume of the superconducting phases of BiSrCaCuO as a function of total soaking time t_s. *1* V_s, total superconducting volume; *2* V_H, high-T_c and *3* V_L, low-T_c phases, respectively

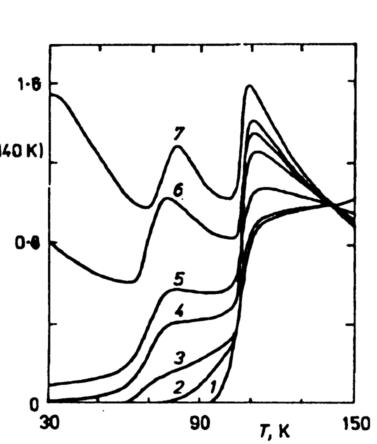

FIG. 5

Changes of the resistance of BiSrCaCuO sample after soaking in boiling water. *1* originally prepared sample, *2* 20 min, *3* 40 min, *4* 60 min, *5* 80 min, *6* 100 min, *7* 120 min

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