INFLUENCE OF DOPANTS ON PROPERTIES OF SUPERCONDUCTING PHASES IN Bi–Sr–Ca–Cu–O SYSTEM

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Peculiarities of phase formation in Bi–Sr–Ca–Cu–O *system, caused by* Hf *impurity were investigated. It was established that* Hf *impurity corresponds to the formation of superconducting phases* $Bi_2Sr_2Ca_1Cu_2O_y$ *and* $Bi_2Sr_2Ca_1Cu_2O_y$. Hf *impurity increases superconducting transition start temperature of both phases, which reach 93 K and 127 K correspondingly. A number of anomalies of physical nature have been observed on these samples, in particular, diamagnetism at temperatures above 250 K.*

Studies of regularities of phase formation in oxide multicomponent systems started to evoke a special interest, when high-temperature superconductivity was discovered. The method of solid-state synthesis is one of the principal means of obtaining HTSC materials, and it is widely applied at synthesis of superconductive compounds in Bi–Sr–Ca–Cu–O system as well. It has been established that the formation of superconductive phases in this system takes place stage by stage, via double and triple compounds and is accompanied by competing processes [1,2]. Owing to this, a problem of obtaining single-phase samples seems to be quite complicated one. To solve this problem the long thermal treatments in sufficiently narrow temperature ranges [3,6] are necessary. It has been also established that an impurity of lead stabilizes the high-temperature phase $Bi_2Sr_2Ca_2Cu_3O_y$ (2223) [5]. Rather interesting results were obtained with a number of other impurities [6–8]. That's why we consider studies of phase formation peculiarities in Bi–Sr–Ca–Cu–O system, and a change of superconductive phases properties at the introduction of various impurities, very actual, alongside with the search of alternative methods of synthesis.

The present report deals with a study of how the hafnium dopants influence kinetics of phase forming in Bi–Sr–Ca–Cu–O system and with certain peculiarities of physical properties, brought about by the given dopants. The investigation was carried out on the samples containing either only Hf or Hf and Pb together with the main elements. The samples were synthesized in two stages, using oxides and carbonates with a purity not worse than 99,99 % in the air. The first stage included a thorough stirring of the initial components in agate cups of a spherical planetary mill and a thermoprocessing of mechanical mixture at 720–780 °C during 8 hours. Then the samples were grated again and pressed into tablets of 7 mm in diameter and 2 mm in height, which were annealed under various temperature and time conditions.

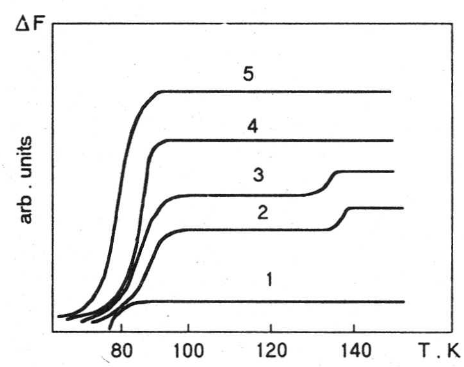
Characteristics of synthesized samples were studied by the following methods: *X*-ray analysis was carried out by means of diffractometer "DRON–3", using CuK_α -radiation, thermogravimetry and thermoanalysis — by the derivatograph *Q*–1500 with the heating rate of 7,5 °C/min in the air. Granular structure of ceramics was studied by means of the electronic microscope "Tesla BS-301". Temperature dependence of electroresistance was determined by the 4-point method on direct current of 10 mA, in the temperature interval of 77–300 K and on alternating current with frequency of F = 1.23 kHz, at 60–300 K. Superconductive transition was also registered by the method of radiofrequency field expulsion from the bulk of samples using a tunnel diode oscillator, $F = 1{,}5$ MHz at nitrogen temperature with stability not worse, than ± 0.2 Hz [9].

It has been established that the sizes of crystals, of which a ceramic sample is composed, change at variation of synthesis temperature and time, and of sample's pressing degree. Crystals average sizes can vary in the range from 3–5 to 100–140 μm at thickness of 1–2 μm. Introduction of Hf does not sufficiently influence crystals sizes.

A comparison of thermographs of synthesized samples shows that the presence of Hf reduces temperature of incongruent melting of the phase 2223, for instance, in case of sample of $Bi_{1.7}Pb_{0.3}Hf_{0.5}Sr_2Ca_2Cu_3O_y$ compound, the peaks are present on the thermogrammes at 825, 885 and 960 °C , and each of them goes along with sample's weight loss 0,44; 0,74 and 1,48 % correspondingly. The sample's weight begins to reduce at 780 °C .

Considering these data, sample synthesis optimal temperature have been chosen.

Studies of the samples phase composition revealed, that the 2223 phase in only Hf impurity-containing samples form already after 30–hours long firing. Concentrations of Hf impurity, stimulating formation of 2223 phase have been determined. Thus, in Fig. 1 one can see the temperature dependence of a change of oscillator $\Delta F(T)$ frequency of samples of nominal compound $Bi_{2-x}Hf_xSr_2Ca_2Cu_3O_y$ synthesized at 850 °C during 70–hours session. It should be stressed that, like in case of Pb-containing samples, the increase of synthesis duration leads to the growth of 2223 phase's content.



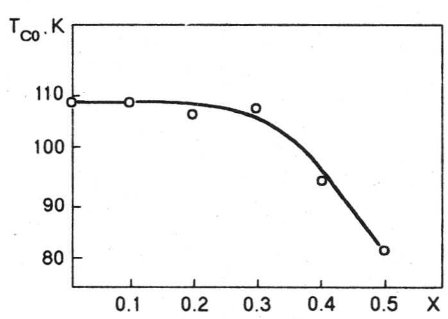


Fig. 1. Temperature dependence of the radiofrequency field expulsion from the bulk of samples $Bi_{2-x}Hf_xSr_2Ca_9Cu_yO$: (*1*) $x = 0.5$; (*2*) $x = 0.1$; (*3*) $x = 0.2$; (*4*) $x = 0.3$; (*5*) $x = 0.4$

Fig. 2. Critical temperature, T_{c0} , vs Hf concentration, x, in the samples $Bi_{1.7}Pb_{0.9}Hf_xSr_2Ca_2Cu_9O_y$

Increase of Hf concentration leads to the growth of $Bi_2Sr_2CaCu_2O_y$ (2212) phase content at minimal synthesis time, i.e. Hf impurity can shorter considerably the one-phase samples preparation time. At joint introduction of Hf and Pb impurities the similar regularities may be observed. It may be stated that in the given case a summing of hafnium and lead impurities has a stimulating effect on formation of superconductive phases.

Studies of $R(T)$ dependence have shown that the temperature of the superconductive transition onset, determined as the $R(T)$ dependence linear deviation point, with the introduction of Hf impurity increases by 7 K in comparison with nominally clean samples. Much stronger changes of superconductive transition end temperature T_{c0}, determined as temperature of sample resistance with a precision not worse than 10^{-5} Ohm. In Fig. 2 each point corresponds to the T_{c0} maximal value of the given compound samples, synthesized under different temperature and time conditions. Thus T_{c0} is mostly responsible for the width of superconductive transition. As it can be seen in figure, the width of $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ compound samples superconductive transition does not change sufficiently up to values of $x = 0.3$ whereas at higher values of $x - T_{c0}$ it decreases considerably, which leads to the widening of the superconductive transition.

Apart from the abovementioned peculiarities in Hf-containing samples, the following anomalies were observed. Diamagnetic anomalies at temperatures above 250 K were observed in $\Delta F(T)$ dependence curves of a number of samples (Table, Fig. 3). These phases were stable at 300 K, but degraded at thermocycling from 77 to 330 K.

Table. Compositions and synthesis of samples

	Initial composition	Synthesis condition*			
		stage 2		stage 3	
		T, °C	t, hour	T, °C	t, hour
1	$Bi_{1.6}Pb_{0.3}Hf_{0.1}Sr_2Ca_2Cu_3O_y$	800	10	800	20
2	$Bi_{1.69}Pb_{0.3}Hf_{0.01}Sr_2Ca_2Cu_3O_y$	800	10	800	20
3	$Bi_{1.5}Pb_{0.3}Hf_{0.2}Sr_2Ca_2Cu_3O_y$	830	20		
4	$Bi_{1.9}Hf_{0.1}Sr_2Ca_2Cu_3O_y$	830	40		
5	$Bi_{1.9}Hf_{0.1}Sr_2Ca_2Cu_3O_y$	800	10	800	20
6	$Bi_{1.9}Hf_{0.1}Sr_2Ca_2Cu_3O_y$	830	20		
7	$Bi_{1.9}Hf_{0.1}Sr_2Ca_2Cu_3O_y$	830	20		

* Synthesis conditions for stage 1 — T = 780 K, t = 10 h.

Next type of peculiarities is presence of three superconductive phases in samples at the temperature range of 80–110 K. As it can be seen in Fig. 4, besides the superconductive transitions, corresponding to phases of 2212 and 2223, a transition

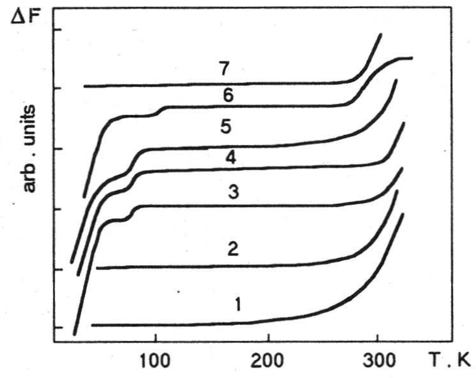
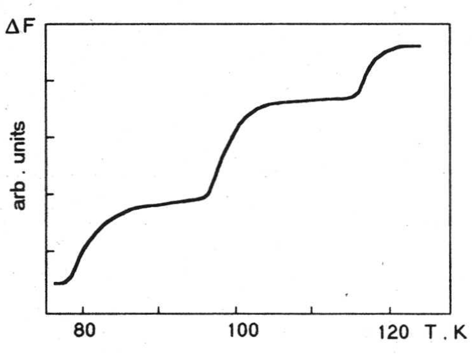


Fig. 3. $\Delta F(T)$ for samples of various composition. The numbers of the curves correspond the number of the samples in the table

with $T_{c0} \sim 95$ K is present in the curve. This transition may correspond to both phase 2234 and the modified state of one of the usual phases.

Another peculiarity of Hf-containing samples was a certain increase of radiofrequency field absorption on the superconductive transition tail (Fig. 5), observed in $\Delta F(T)$ curves. There may be several explanations for this fact, so the only way to verify a nature of the observed phenomena is to continue the investigations in this direction.



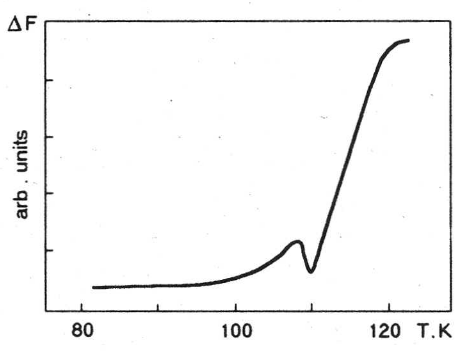


Fig. 4. Three superconducting transitions in Hf-containing sample at temperature range of 80–120 K

Fig. 5. Radiofrequency field absorption on the superconductive transition's tail

In conclusion we'd like to note that accounting of discovered peculiarities of phase formation in Bi–Sr–Ca–Cu–O system with Hf impurity can be useful for the synthesis of monocrystals of Bi-containing superconductors.

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