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The thermal effect of oxygen subsystem reorganization in ceramics $YBa_2Cu_3O_{6+\delta}$ at 300–400 K

S.Yu. Glazkov*, L.V. Glazkova, Z.I. Semenova, N.F. Zakharchuk

Institute of Inorganic Chemistry, Russian Academy of Science, Siberian Branch,
3 Acad. Lavrent'ev, Ave., Novosibirsk 630090, Russia

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Abstract

Study of the thermal effect, oxygen content and electronic states of elements in ceramics $YBa_2Cu_3O_{6+x}(0.40 \geq x \geq 0.50)$ by differential scanning calorimetry, chemical analysis and voltammetry of solids has showed that the relaxation phenomena observed in closed-on oxygen system connects with redistribution of oxygenic vacancies and it is accompanied by the reorganization of electronic state of copper settled in the chain. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

On studying the superconducting properties of 1 2 3-ceramics the relaxation phenomenon was found. This phenomenon consists in restoration of the superconducting transition temperature during 3–4 days exposure of sample at room temperature after their reduction in a heating–cooling cycle [1–9]. Some researches explain the relaxation by high mobility of oxygen in a basic plane Cu–O, and by the reorganization of an oxygen subsystem.

For example, the authors of the work [6,7] studied the relaxation process measuring temperature dependences of electrical resistance and magnetic susceptibility of $YBa_2Cu_3O_{6.42 \pm 0.02}$. A sample was heated to 420 K and quenched in liquid nitrogen. After quenching it had the superconducting temperature $T_c \approx 20$ K. For 120 h at room temperature T_c had increased to 33 K. This effect repeated many cycles of heating — quenching — isothermal hold was explained by the authors as a process of ordering the oxygen vacancies. From the literature [10–16] it is known, that this process results in redistribution of electronic states of the elements: in a chain of Cu–O for phases 1 2 3 [10,12,16] or in a layer of Bi–O for phases 2 2 1 0, 2 2 1 2, 2 2 2 3 [13–15]. As a rule these redistributions are accompanied by the formation of oxygen holes, O^-. The latter create conditions for realization of the resonant valency model [17]. The holes are easily identified as a signal of electrochemical reduction ($O^- + e^- = O^{2-}$) on voltammetric curve for researched sample [12,14,15].

The reorganization of an oxygen subsystem should be accompanied by some thermal phenomena. Authors [18] have defined the activation energy for removing mobile oxygen (about 4 kCal mol^{-1} at 313 K) in ceramic $YBa_2Cu_3O_{6.85}$ using the mass-

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[*] Corresponding author. Fax: 7-3832-344489
E-mail address: boy@casper.che.nsk.su (S.Y. Glazkov)

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spectrometric method. The activation energy of oxygen diffusion process was determined for $YBa_2Cu_3O_y$ at temperature 630–830 K by the differential scanning calorimetry (DSC) method [19]. It has appeared equal to 1.6 eV, that will be well coordinated with the data received with the differential thermogravimetric (DTG) method — 1.7 eV [20]. In [21] the measurement of the thermal effect for oxygen absorption in ceramics 123 was carried out with the DSK method at 530–830 K. The sample was annealed in an atmosphere of argon for 5 min at 1000 K to remove the oxygen. After that it was cooled to 720 K at 20 K min^{-1} in an atmosphere of oxygen. The heat released in this case was equal to ca. 65 J g^{-1}. Under the second heating of the sample to the same temperature in the same condition the thermal effect was not found. The authors assumed that the given exothermic effect was connected with the absorption of oxygen.

In [18–21] the system with changeable oxygen content during investigation were considered. At the same time there are data [6] that the oxygen index remains constant during the relaxation process.

In the given work attempt was made to define the thermal effect of reorganization of the closed oxygen subsystem in ceramics $YBa_2Cu_3O_{6+\delta}$ at temperature 300–420 K and to connect this reorganization with the change of valency states of copper and oxygen.

2. Experimental

As a initial material for the investigation the ceramic tablets $YBa_2Cu_3O_{6.97}$ ($T_c = 92$ K) prepared using standard technology were used. Tablets were annealed in air at 1020 K for 4–5 h. According to X-ray data single-phase samples of $YBa_2Cu_3O_{6.40}$–$YBa_2Cu_3O_{6.50}$ were obtained. The temperature of superconducting transition was determined by the contactless method of electrical conductivity measuring [22]. It was 30–40 K depending on the content of oxygen in a phase. The oxygen index was calculated from data of iodometric titration with precision ±0.02 [23].

A differential scanning calorimeter DSK-111 was used for measurement of the thermal effect. The rate of temperature change was 5–10 K min^{-1}. Measurements were carried out both with heating, and with cooling in an interval of temperature, 300–420 K. Maximum temperature of 420 K was chosen, because greater heating results in irreversible changes of samples shown by an increase of the superconducting transition width.

During the experiment the sample was in flowing atmosphere of air, argon or oxygen at 0.5 ml s^{-1}.

Al_2O_3 was used as comparison sample. The masses of investigated sample and that of comparison were selected to equalize their heat capacities.

The voltammetry of solids was used for identification of the valency state of the oxygen and copper. Voltammograms were registered with universal polyarograph OH-105 (Hungary). The sample was added to a graphite powder and silicon oil. The homogeneous paste was filled into holder which was a paraffin-impregnated graphite rod in a Teflon tube several millimeters longer than the rod, forming a cup. A concentration of samples in the paste was 2×10^{-4} M g^{-1} every time. Saturated calomel electrode (SCE) and a graphite rod (for spectral analysis) served as a reference and auxiliary electrodes, respectively.

3. Results and discussion

Fig. 1 shows the calorimetric curve of thermal effect versus temperature for the sample $YBa_2Cu_3O_{6.42}$($T_c \approx 32$ K). The curve 1 corresponds to the first heating. In the second cycle the thermal effect decreases approximately twice, in the third — ca. 80%, in the fourth it was not observed any more (curve 3), and calorimetric experiment was considered as finished.

The endothermic thermal effect was found for all samples $YBa_2Cu_3O_{6.40}$–$YBa_2Cu_3O_{6.50}$ in the temperature interval 320–380 K. Its value has formed ca. 0.6 J g^{-1}. It should be mentioned that both in our researches and in the works [19,21] the forms of calorimetric curves are similar. Nevertheless, the intervals of temperatures where these effects are observed strongly differ: 320–380 and 530–830 K, accordingly. Besides the calculated values of thermal effects differ approximately on two orders.

The critical temperature decreased 3–4 K after calorimetric experiment. The general content of oxygen remained constant within analytical accuracy.

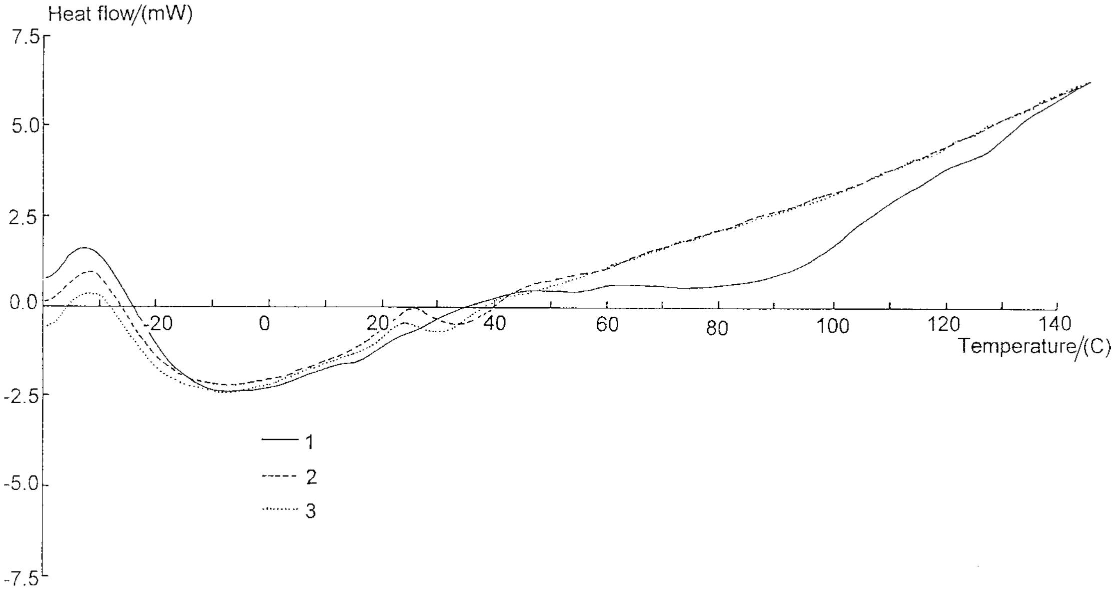

Fig. 1. Temperature dependence of thermal effect for $YBa_2Cu_3O_{6.42}$: 1 — first heating; 2 — second heating; 3 — fourth heating.

Keeping of the samples during 3–4 days at room temperature (as in atmosphere of dry chamber under P_2O_5, and in a flow of argon or oxygen) causes the critical temperature removing to its initial value (30–40 K depending on structure), without any changes of an oxygen index as well.

The same thermal effect was observed on carrying out the calorimetric experiments with the samples after keeping. This is evidence that the observed thermal effect is connected not to loss of oxygen during heating a sample, but to reorganization of a oxygen subsystem. Actually, the thermal effect can be caused by the desorbtion of carbonic dioxide or water. However mass-spectrometric analysis have shown that no signals connected with evolving water or carbonic dioxide are found within temperatures 300–420 K. In accordance with [24], appreciable CO_2 and H_2O evolving from samples is not observed up to 930 K. For an additional check of the hypothesis that present system is closed-on oxygen, we carried out thermogravimetric measurement. Data of this analysis showed that masses of samples before and after calorimetric experiment had not changed within analytical accuracy (±0.02). The constancy of an oxygen index during our calorimetric experiment is another difference from [19,21] where the oxygen content varied.

The internal reorganization of an oxygen subsystem should be accompanied by change of valency states of not only oxygen, but also other elements within the phase. Voltammograms of the sample $YBa_2Cu_3O_{6.46}$ before (curve 1) and after (curve 2) calorimetric experiment are shown in Fig. 2. Curve 3 represents the voltammogram of the same sample being kept in dry chamber under P_2O_5 at room temperature within 3 days after the calorimetric experiment. The conditions (composition of electrolyte) were chosen so that the electrochemical conversion of copper ions located only in a chain was possible. As it can be seen from Fig. 2, after the calorimetric experiment the signal of reduction of "active" (O^-) oxygen (the signal A) decreases approximately twice in comparison with initial, and increases again after keeping a sample at room temperature. At the same time the general oxygen content remains constant within analytical accuracy. A signal B characterizes electrochemical conversion of copper ions in a chain. Before calorimetrical experiment this signal represented a sharp maximum of a current (half-width of peak is not more then 60 mV), appropriating to the reduction potential of Cu^+-ions [12]. Thus the chain $[Cu{-}O_{2+\delta}]_{\infty}^{3-}$ can be presented as $[Cu^+O^{2-}_{(2-\delta)}O^-_{2\delta}]^{3-}$ according to [25]. As a rule, half-width of peak is

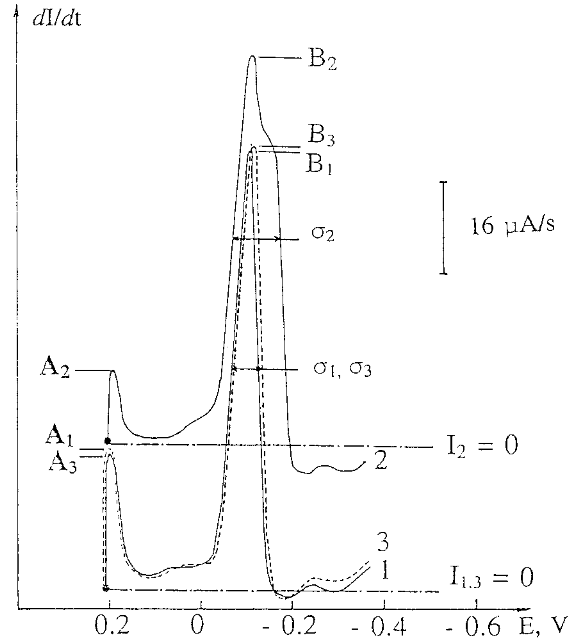

Fig. 2. Voltammograms of the sample $YBa_2Cu_3O_{6.42}$ before (curve 1) and after (curve 2) calorimetric experiments. Curve 3 — after 3 days keeping at room temperature in dry chamber.

increased almost twice after calorimetrical measurements. On a descending branch of voltammogram a knee or in some cases even bifurcation of a signal B is shown up. In the latter case the maximum of a current appropriates to reduction potential of bivalent ions of copper. The similar results were received for other above-mentioned samples, too. All this is evidence that the decrease of a signal A (reduction O^-) for the sample after calorimetrical experiments is accompanied by occurrence in a chain of copper atoms in a state Cu^{2+}. Taking into account that the general content of oxygen remains constant, it is need internal reorganization of all oxygen subsystem for electroneutrality of crystal lattice. The part of "active" oxygen (O^-) is spent for neutralization of an additional positive charge because ions Cu^{2+} was appeared in a chain. It is easy to show that in such situation, the structure of the chain can be presented as: $[Cu^+_{(1-\delta)}Cu^{2+}_{\delta}O^{2-}_2O^-_{\delta}]^{3-}$. At the time it is occurred the opportunity to explain the thermal effect by transition of a type: $[Cu^+O^{2-}_{(2-\delta)}O^-_{2\delta}] \Leftrightarrow [Cu^+_{(1-\delta)}Cu^{2+}_{\delta}O^{2-}_2O^-_{\delta}]$.

4. Conclusion

Thus, the data of calorimetric, thermogravimetric, voltammetric investigations and chemical analysis of the ceramics $YBa_2Cu_3O_{6.40}$–$YBa_2Cu_3O_{6.50}$ are evidence that observed relaxation phenomenon occurred in the system closed-on oxygen. The thermal effect found out in an interval of temperature 320–400 K is connected to reorganization in an oxygen subsystem. Proceeding from the voltammetric data, the mechanism of reorganization can be described as: $[Cu^+O^{2-}_{(2-\delta)}O^-_{2\delta}] \Leftrightarrow [Cu^+_{(1-\delta)}Cu^{2+}_{\delta}O^{2-}_2O^-_{\delta}]$.

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