Chemistry for Sustainable Development **20** (2012) 385–390

UDC 538.945:544.3.032.2

Modification of the Physicochemical Properties of $YBa_2Cu_3O_{6+\delta}$ by Means of Mechanochemistry

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(Received October 28, 2011; revised February 1, 2012)

Abstract

Physicochemical state of $YBa_2Cu_3O_{6+\delta}$ powder subjected to mechanochemical treatment was studied by means of thermogravimetry, X-ray diffraction, iodometry and X-ray photoelectron spectroscopy. It is demonstrated that the indicated treatment causes broadening of the range of variation for oxygen parameter (δ) and an increase in the chemical activity of yttrium/barium cuprate above the limit that can be attributed to a decrease in particle size. The discovered features are due to increased non-equilibrium character of activated $YBa_2Cu_3O_{6+\delta}$, including uncharacteristic combination of the oxidation numbers of copper and oxygen ions interacting with each other (Cu^{3+}, O^-).

Key words: mechanochemical activation, yttrium-barium cuprate, thermogravimetry, X-ray photoelectron spectroscopy

INTRODUCTION

Mechanochemical activation of metals and their oxides is the simplest method to enhance their reactivity, catalytic activity and to modify magnetic, electric, optical and other characteristics of materials [1–4]. At the same time, as the analysis of literature shows, the possibility of the mechanical activation of complex oxide $YBa_2Cu_3O_{6+\delta}$ as a method of regulating its functional characteristics has not been investigated yet. This compound is a high-temperature superconductor with layered perovskite structure, it contains CuO layer with oxygen defects in the (*ab*0) plane, and intense diffusion of anions is observed in this layer [5]. Due to the high diffusion characteristics, it was proposed to use yttrium-barium cuprate as ion conductor [6]. Mechanochemical action, in turn, is able to provide a substantial increase in the transport properties of oxides [1–4], which is of definite scientific and practical interest in the case of $YBa_2Cu_3O_{6+\delta}$ and requires experimental verification. It should also be stressed that consequences of the indicated treatment of materials during new studies remain almost unpredictable. This is why mechanical activation is increasingly frequently used as a method to make materials with unique properties.

The goal of the present work was to study the new physicochemical state of $YBa_2Cu_3O_{6+\delta}$ oxide subjected to mechanochemical treatment.

EXPERIMENTAL

The object of investigation was synthesized by stepwise annealing of a mixture of barium nitrate $Ba(NO_3)_2$ of kh. ch. grade, yttrium oxide Y_2O_3 and copper hydroxy carbonate

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$CuCO_3 \cdot Cu(OH)_2$ of os. ch. grade at 525–725–925 °C for 120 h. According to the data of X-ray analysis (Shimadzu diffractometer, Japan), the product contained 95 % of the major phase. The admixture phase is represented mainly by Y_2BaCuO_5 compound. The synthesized material was subjected to oxidative annealing by means of slow (with furnace) cooling from synthesis temperature to 585 °C and exposed at this temperature in the air for 3 h. The obtained value for the parameter of oxygen nonstoichiometry $\delta = 0.715 \pm 0.005$ was determined using the procedure developed by the authors of [7] by means of iodometric titration with Trilon B as the reagent binding Cu^{2+}. The reference value for parameter δ for the above-described conditions of oxidative annealing can also be obtained according to the $p_{O_2} - t - \delta$ diagram reported in [8]: $\delta|_{t\,=\,585\,°C;\;p_{O_2}\,=\,21\,kPa} \approx 0.71$.

Mechanical activation of $YBa_2Cu_3O_{6+\delta}$ powder was carried out using the ball planetary mill activator AGO-2 (with iron as the material of the fittings) developing the acceleration of milling bodies 60*g*. Two portions of initial powder were ground (activated) in the dry form for 0.5 and 10 min.

Thermogravimetric studies were carried out with the help of a STA 449F1 Jupiter thermoanalyzer (Netzsch, Germany) or by means of successive quenching and weighing. Electronic structure was studied with a Multiprob electron spectrometer (Omicron, Germany) by means of X-ray photoelectron spectroscopy (XPES).

RESULTS AND DISCUSSION

According to the data of scanning electron microscopy (EVO 40 XVP electron microscope, Carl Zeiss, Germany), as a result of mechanical activation, the average size of the particles of powders under investigation decreased from 20 to ~0.3 μm; the particles formed agglomerates about 5 μm in size. The amount of extrinsic phases increased in both lots approximately similarly and reached (11±1) %. Measure-

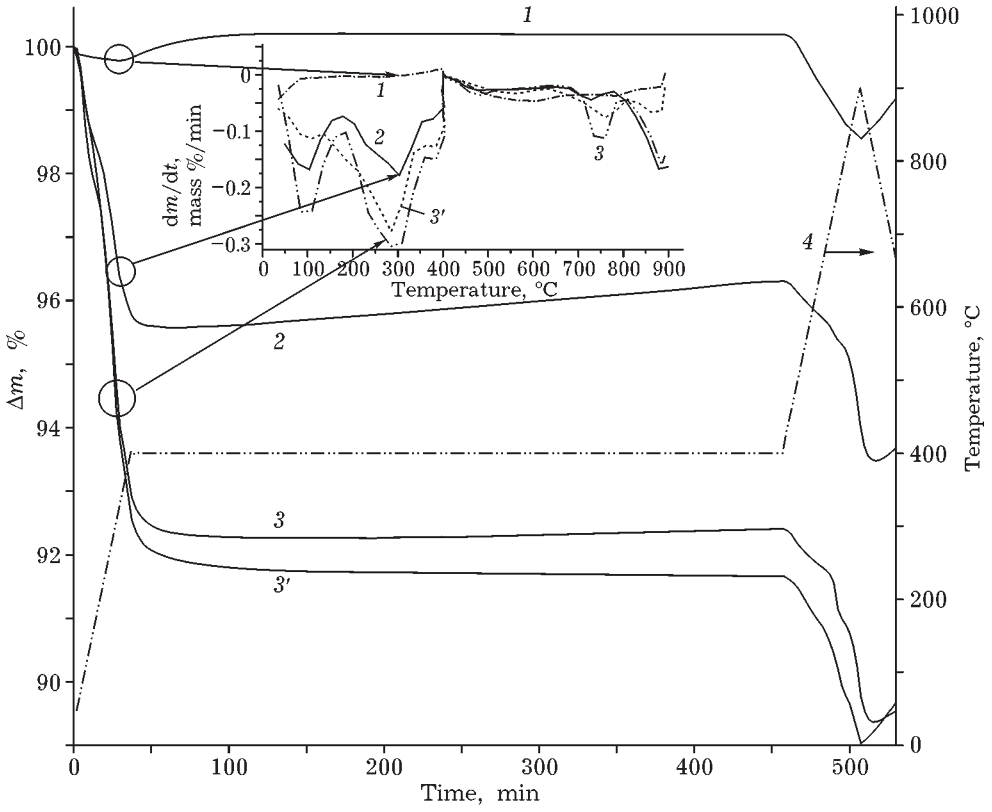

Fig. 1. Results of thermogravimetric analysis of $YBa_2Cu_3O_{6+\delta}$ samples studied in the mode of heating at a rate of 10 °C/min with exposure at a temperature of 400 °C for 7 h: *1* – initial, *2* – mechanically activated for 0.5 min; *3*, *3′* – mechanically activated for 10 min (*3*) and blown with artificial air with the composition 79 % N_2 + 21 % O_2 (*3′*); *4* – temperature change with time.

ment of parameter δ by means of iodometry showed that oxygen content in the samples remained at the prior level (0.70±0.01). Therefore, as a result of mechanical treatment (see also [9]) reduction of oxides did not occur though it is usually expected in the cases of this kind [1–4]. This is likely due to insufficiently high energy strain of grinding in AGO-2 mill.

The curves of thermogravimetric analysis (Fig. 1) are composed of four typical regions corresponding to the states of thermal treatment of the samples (curve *4*). At the first region (heating to 400 °C) mechanically treated samples exhibit a sharp substantial decrease in mass, while the change of the mass of initial sample is insignificant. Mass spectrometric analysis of emitted gases performed in some experiments with the help of the QMS 403C Aëolos attachment (Netzsch, Germany) allowed us to conclude that the observed decrease in mass is connected with the emission of water vapour from the samples. In addition, all curves show a fracture in the region of 300 °C. It is especially clearly pronounced in the differential form of these dependences (see insert in Fig. 1). This feature means that at ~300 °C there is a sharp change of the mode of mass exchange between the samples and the gas phase due to the activation of an additional process with mass increase. This process is represented in the explicit form in the TG curve of the initial sample for which intense desorption of H_2O during heating is not characteristic: according to the formal kinetic analysis, the kinetics of this process is controlled by diffusion with saturation at the mass gain of about 0.5 %. It is known [10, 11] that all the parameters indicated above correspond to the saturation of $YBa_2Cu_3O_{6+\delta}$ with oxygen with the limiting value of $\delta|_{t = 300\,°C;\, p_{O_2} = 21\text{ kPa}} = 0.93$.

Visualization of oxidation for mechanically activated samples was carried out with the help of their preliminary annealing in the mode: 250, 300 and 400 °C for 20, 20 and 10 min, respectively. Water was removed from the material under this kind of treatment in the most time-optimal mode being brought to the equilibrium with $YBa_2Cu_3O_{6+\delta}$ at the final stage 10 min long. In addition, the chosen mode provided minimal uncontrolled oxidation of powders, which could occur only during a short-time exposure at 400 °C. After this treatment, the kinetic curves of the interaction of samples with the environmental atmosphere were recorded (Figs. 2, 3). The initial region (10 minu long) of uncontrollable process was obtained by extrapolation of the trend from two nearest experimental points to this region.

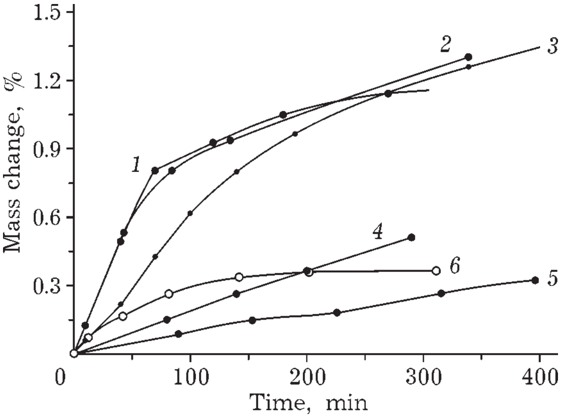

Fig. 2. Kinetic curves of the interaction of $YBa_2Cu_3O_{6+\delta}$ mechanically activated for 10 min with the components of environmental air at 400 °C, recorded by means of sequential quenching and weighing. Sample mass, mg: 16 (*1*), 37 (*2*), 57 (*3*), 275 (*4*), 507 (*5*), 30 (*6*) (initial sample).

The results of the kinetic study obtained for one lot of powder for different mass of weighted portion are shown in Fig. 2. One can see that the limiting stage of the interaction under investigation for the mass of weighted portion more than 30 mg is the access of gaseous reagent to the particles of the material rather than its transport in the solid. In agreement with the data

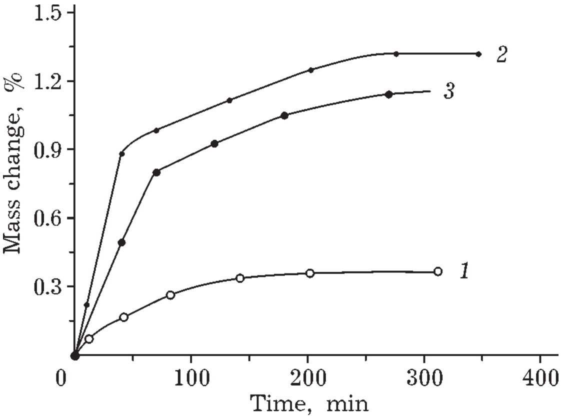

Fig. 3. Kinetic curves of the interaction of $YBa_2Cu_3O_{6+\delta}$ with the components of environmental air at 400 °C, recorded by means of sequential quenching and weighing: *1* – initial sample; *2*, *3* – samples mechanically activated for 0.5 and 10 min, respectively.

obtained, similar studies of other lots of $YBa_2Cu_3O_{6+\delta}$ powders were carried out using the weighted portions of (16±1) mg (see Fig. 3).

Comparative analysis of the kinetic curves (see Fig. 3) showed that mechanical activation promotes a substantial increase in the rate of the interaction of the oxide with the components of the atmosphere; this interaction becomes two-stage. The rate of the slow stage is close to the rate of mass increase at the isothermal region of TGA curves in Fig. 1, which is due to similar conditions of thermogravimetric experiments.

Along with oxygen, surrounding air also contains CO_2 entering the interaction with the surface layer of $YBa_2Cu_3O_{6+\delta}$ particles with the formation of $BaCO_3$ [12], During grinding and/or temperature rise, the rate of this reaction increases sharply. It is likely that the initial region of kinetic curves in Fig. 3 corresponds to carbonization and oxidation proceeding simultaneously (curves *2*, *3*). At the inflection point oxidation stops, and the extended gently sloping region of the curves corresponds to carbonization of yttrium/barium cuprate. To confirm this, we carried out additional TGA experiment using mechanically $YBa_2Cu_3O_{6+\delta}$ powder mechanically treated for 10 min that was blown with artificial air of the composition 79 % N_2 + 21 % O_2; H_2O and CO_2 content was at a level of 0.0001 % (see Fig. 1, curve *3′*). Comparative analysis of curves *3* and *3′* in Fig. 1 shows that an extended nearly linear region of mass increase during isothermal treatment of the sample in the atmosphere of surrounding air (curve *3*) is connected exactly with the presence of CO_2 in the gas phase. Carbon dioxide accumulated at this region is emitted by the sample heated above 800 °C, which is expressed as a sharp decrease in the mass of the oxide within this temperature range (see insert in Fig. 1) and the appearance of the component with m/z 44 detected by the mass spectrometric analysis of exhaust gas.

The results of XPES studies of initial and mechanically activated powders are shown in Fig. 4. One can see that the spectral lines of oxygen included in the structural positions of $YBa_2Cu_3O_{6+\delta}$ (lines I and III) after mechanical activation were observed to shift to higher bond energies. For other lines corresponding to carbonate groups (II) and organic impurities (IV) [13–15] that are localized on the surface of oxide particles, no noticeable shifts are observed.

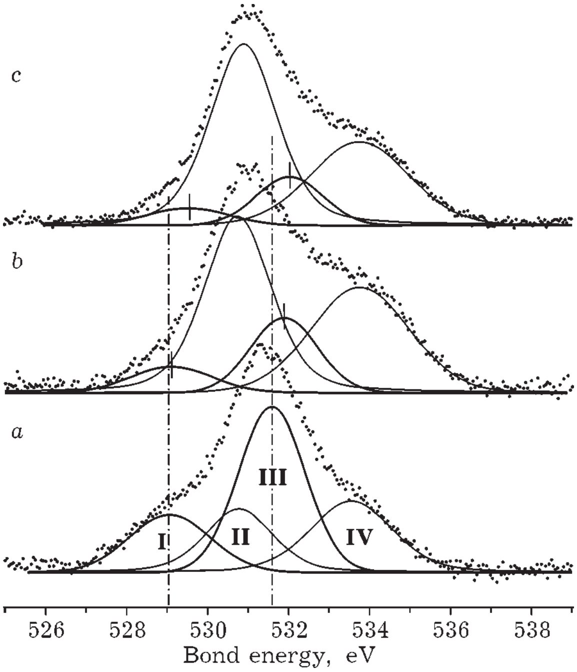

Fig. 4. Photoemission spectra of oxygen O 1*s* recorded for initial sample (*a*) and the samples mechanically activated for 0.5 (*b*) and 10 min (*c*): **I–IV** – peaks.

Let us consider the TGA dependencies (see Fig. 1) in more detail at the region corresponding to sample heating from 400 to 900 °C. According to the data published in [8, 10], within this temperature range $YBa_2Cu_3O_{6+\delta}$ should lose the major part of oxygen incorporated in the basic structural plane (*ab*0) and possessing high mobility within it. At the final point of heating, the equilibrium value

$$\delta|_{t\,=\,900\,°C;\ p_{O_2}\,=\,21\ \text{kPa}} = 0.25$$

should be reached [8]. Comparing mass changes during heating due to oxygen evolution alone, we may conclude that oxygen content in mechanically activated samples before heating was higher in comparison with its content in initial samples (see Fig. 1, curves *1* and *3′*). Similarly, it follows from the data shown in Fig. 3 that d for mechanically activated samples was changing during heating at 400 °C more substantially than for initial sample. Quantitative analysis allowed us to determine more accurately that for initial sample after annealing $\delta \approx 0.88$, while for mechanically activated samples $\delta \approx 1.03$ and 1.08 for activation time 10 and 0.5 min, respectively. While δ value for initial sample corresponds to the equilibrium parameter of oxygen nonstoichiometry for temperature and p_{O_2} involved in experiments [8], δ for mechanically activated samples is higher.

Relying on the results of oxidation-reduction experiment, we evaluated the valence states of copper and oxygen situated in the lattice points of the basic plane of $YBa_2Cu_3O_{6+\delta}$. According to the data published in [16–18], in the initial sample (usual yttrium-barium cuprate) copper and oxygen in the basic plane are present in the states Cu^{2+} and O^-. In this situation, copper (in the amount of 1 atomic unit) forms one valence bond with oxygen in the basic plane and one valence bond with the rest lattice. This defines the limiting amount of oxygen δ_{max} that can enter $YBa_2Cu_3O_{6+\delta}$ during low-temperature oxidative annealing (300–400 °C): $\delta_{max} = 1$. In reality, for a number of reasons the maximal value of parameter δ does not exceed 0.93 and is achieved at 300 °C in the atmosphere of pure oxygen. Then, increased maximal values of the parameter of oxygen nonstoichiometry in mechanically activated samples are explained by an increase in the number of valence bonds in 10–15 % of copper atoms in the basic plane of $YBa_2Cu_3O_{6+\delta}$. In other words, the indicated fraction of copper atoms in the basic plane should have oxidation degree +3.

The authors of [19] proved that a definite fraction of the hole charge concentrated in the basic plane of $YBa_2Cu_3O_{6+\delta}$ and localized at oxygen O^- or copper Cu^{3+} gets into the neighbouring structural plane (CuO_2) forming conduction band, or – at low temperatures – superconducting pairs. The larger hole charge is present in the basic plane, the larger it is in the CuO_2 plane. Then, under increased concentration of O^- or/and Cu^{3+} in the basic structural plane the major part of all oxygen in $YBa_2Cu_3O_{6+\delta}$ oxide concentrated near the CuO_2 plane turns out to be affected by the increasing positive potential. As a consequence, a shift of oxygen lines to higher bond energy must occur in the O 1*s* spectrum, which is observed in the case of mechanically activated $YBa_2Cu_3O_{6+\delta}$ samples (see Fig. 4).

Let us consider the kinetic features of the interaction of mechanically activated yttrium-barium cuprate with O_2 and CO_2. According to Fig. 2, the determinant part in the kinetics of gas exchange between the weighted portion of the powder and the gas phase at a temperature of 400 °C is played by the slow diffusion of the gaseous reagent in the space between the particles. Therefore, the size of pores along which the gas is transported has enormous importance. Taking into account the hierarchic structure of the porous space in mechanically activated samples, one should expect that the major flux of gas reagent passes through the space between the conglomerates of $YBa_2Cu_3O_{6+\delta}$ particles, while only small its part passes inside these conglomerates. Indeed, judging from the initial regions of curves in Fig. 3 that depict mainly the kinetics of oxidation process, the intensity of this process for mechanically activated samples is only 4–5 times higher than its intensity for initial sample. This ratio shows the ratio of the average size of conglomerates to the average size of particles in the initial material (correspondingly, the factor by which the specific surface areas of these structural elements differ). In other words, in the case of mechanically activated oxides, reaction surface is the surface of conglomerates rather than separate particles, Diffusion into the conglomerate volume proceeds through the solid phase.

The degree and kinetics of the saturation of mechanically activated powders with gaseous CO_2 are also higher in comparison with the initial sample (compare Figs. 1 and 3), however, this excess is more substantial than 4–5 times, and so it cannot be explained by the size factor alone. Mechanically activated samples are likely to exhibit increased chemical affinity to carbon dioxide, which can be connected with the special electronic structure of this material as revealed in the present work.

CONCLUSION

We demonstrated that mechanochemical treatment does not change the diffusion characteristics of yttrium/barium cuprate but broadens the range of oxygen parameter δ variations in $YBa_2Cu_3O_{6+\delta}$ powders and increases their chemical activity above the limit that can be assigned to the factor of particle size reduction. The discovered features can form the ground for further studies of the new state of

$YBa_2Cu_3O_{6+\delta}$ caused by mechanical activation, for the purpose of creating a material with unique properties.

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