SYNTHESIS OF HIGH-TEMPERATURE SUPERCONDUCTING YTTRIUM-BARIUM CUPRATE SINGLE CRYSTALS AND STUDY OF THEIR PROPERTIES

M.V. Bakuntseva, P.P. Gorbik, I.V. Dubrovin, G.N. Kashin, I.V. Laguta, and A.I. Nastasienko

Institute of Surface Chemistry, National Academy of Sciences
Gen. Naumov Str. 17, 03680 Kyiv-164, UKRAINE

Abstract

The method of synthesis of stack-plated single crystals of $YBa_2Cu_3O_{6+\delta}$ high-temperature superconductor has been improved. The method is based on combination of the processes of mass-nucleation and directional crystallization from the solution-melt by Czochralski. The single crystals with the natural cuts and plate habitus of 8 mm in length have been grown. Diffusion of silver from thin films (10-20 nm) into the $YBa_2Cu_3O_{6+\delta}$ single crystals has been studied in the temperature range 373-773K with the use of Auger electron spectroscopy. Diffusion activation energy and pre-exponential factor have been determined. The mechanism with participation of oxygen vacancies has been suggested as a principal diffusion mechanism.

1. Introduction

Development of new promising materials and processes is one of the major lines in fundamental and applied scientific studies. High-temperature superconductors (HTSC) belong among the class of promising materials that could play a significant role in the industries vitally important for the mankind: power engineering (improvement of the efficiency of power generation processes and long-distance power transmission with minimum losses), electronics, thin film applications and others. The works on development of the process for manufacturing the ceramic, single crystal, film or dispersed HTSC materials with improved critical parameters as well as the studies of their properties under various physical and chemical conditions play an important role in making and perfecting HTSC and various devices on their basis.

The fact that the high-temperature superconductivity was found not only in the conventional intermetallic compounds, organic and polymeric materials but also in oxide ceramics usually exhibited dielectric and semiconducting properties is of great importance.

About fifty distinct layered HTSC cuprates have been found. The $YBa_2Cu_3O_{6+\delta}$ compound is one of the leading high-T_c materials among them. The results obtained in the studies of the phase diagram for Y_2O_3–BaO–CuO quasiternary system [1] have allowed us to establish the general approaches to development of a method of growing the single crystals of $YBa_2Cu_3O_{6+\delta}$ high-temperature superconducting phase (YBCO). It is known that YBCO phase has incongruent melting behaviour therefore the growth of its single crystals may be performed only from the solution-melt of non-stoichiometric composition.

The analysis of liquidus surface for Y_2O_3–BaO–CuO system in the region of primary crystallization of YBCO compound has allowed us to determine three approaches that may result in its crystallization: cooling, evaporation and formation of temperature gradient. Decreasing the crystallization temperature used for growing crystals from the melts that are

saturated with YBCO compound at the most results in an increase in the melt viscosity. In its turn this leads to slowing down of diffusion of some components of the high-temperature superconductor to the growing crystals. Viscosity and reactivity of the melt complicate the processes of mass transfer to the crystal and impose more severe requirements to container resistance to interaction with the melt.

In many respects the basic properties and stability of HTSC materials are determined by stability and characteristics of interfaces (grain boundaries in polycrystals and sintered ceramic systems, interfaces in single crystal film systems). Composition and structure of interfaces in polycrystalline HTSC affect the magnitude of current that can be transported in power devices (current leads, wire for power transmission cables and others). The interfaces play a more important role in thin film systems intended for microelectronics (multilayer RF filters and transmitting lines, various active devices). Stability of composition and structure of interfaces are mainly determined by diffusion and chemical reactivity of materials that form such interfaces. Studies of states and properties of interfaces involve considerable experimental problems. For the purpose of determination of electrophysical properties it is reasonable to carry out all measurements with the use of single crystal specimens. In single crystals one can determine the quantitative relationships between surface and bulk electronic characteristics of solids. Studies of single crystal specimens are necessary for development of physicochemical models and elucidation of the nature of processes taking place in heterogeneous systems.

The purpose of this article is to report on the following:

1. optimal conditions for synthesis of YBCO single crystals with desired elecrophysical parameters and dimensions;
2. actual structure of the grown crystals;
3. chemical composition of the grown crystal surface and characteristics of the mass transfer processes at the interface "single crystal substrate/metal film" at varying temperature conditions.

2. Experimental

The YBCO single crystals were grown with the use of apparatus described in detail in the following section. Structure, phase composition and surface morphology of the grown single crystals were studied by scanning electron microscopy, X-ray microanalysis and X-ray spectroscopy [2]. The X-ray microanalyzer, ICXA-733 JEOL (Japan), and X-ray diffractometer DRON-2 with CuKα-source (NPO Burevestnik, St.-Petersburg, Russia) were used. The temperature dependence of electroconductivity of the grown crystals was studied with the use of the four-contact method under direct or alternating (f=1 kHz) current in the temperature range of 77 to 300K. Silver contacts with resistance of below 3 mΩ were fabricated by fusing. The temperature dependence of surface impedance was studied in the temperature range of 77 to 200K by using the inductive method [3].

The processes of mass transfer (diffusion) and chemical interaction at the interface "single crystal substrate/thin metal film" were studied by Auger electron spectroscopy (ESO-3 analyser, NPO Burevestnik, St.-Petersburg, Russia).

The stack-plated crystals of YBCO were fixed to the single crystal silicon substrates by inorganic glue. The metal (silver) films of 10 to 20 nm in thickness were deposited on the outer surface of the glued YBCO crystals by thermal evaporation at the residual pressure of about 10^{-5} Pa. The thickness of the deposited silver films was determined by using the profilometer (Tencor Instruments, USA). The specimens were annealed at the temperatures in the range from 373 to 773K. The optimal duration of annealing, which resulted in the well-defined changes in the Ag depth profiles (1000 s), was determined in the preliminary experiments with variation of annealing times in the range from 100 to 10000 s.

The Auger depth profiles for distribution of the constituent elements through the interface region were obtained by using the step-by-step Ar-ion sputtering (ion energy, 2500 eV; ion beam cross-section, 2 mm). At each step the Auger spectra of sputtered surface were recorded under the following operating conditions:

- residual pressure in the spectrometer's vacuum chamber: $<10^{-7}$ Pa;
- primary beam energy: 3000 eV;
- primary beam's cross-section: 20 μm
- mode of spectra recording: synchronous detection in the differential form (dN/dE);
- modulation voltage at the deflection cylinder: 5 V.

Table 1 shows the principal Auger peaks used in calculation of relative concentrations and plotting the depth profiles of corresponding elements through the interface region "Ag film/ YBCO substrate".

Table 1. Chemical elements and its Auger peaks used in analysis of specimens under study.

Chemical element (Auger electron transition)	Peak energy in the experimental spectra (eV)	Peak energy in the handbook [5] (eV)
Y ($M_{4,5}N_{2,3}V$)	122-124	127
Ba ($M_5N_{4,5}N_{4,5}/M_4N_{4,5}N_{4,5}$	586/600	584/600
Cu ($L_3M_{4,5}M_{4,5}$)	918	920
O ($KL_{2,3}L_{2,3}$)	510-511	503 (in MgO)
Ag ($M_5N_{4,5}N_{4,5}/M_4N_{4,5}N_{4,5}$)	347/352	351/356
C (KVV)	272	272
Cl (LVV)	179-181	181 (in KCl)

3. Synthesis of single crystals

At present the most widely used method of making the crystals and solid solutions on the basis of YBCO phase is their growing with the use of $BaCuO_2$–CuO flux combined with the method of slow cooling. In this method the nucleation and growth of crystals take place in the bulk of solution-melt due to decreased solubility of YBCO at lower temperatures. As a rule small crystals are formed in the bulk of solution and remain inaccessible. The other crystals that are free of a solvent and have natural cuts grow on the surface of shrinkage cavities. Thereof the experimenters often remove the flux by decanting at the last stage of the growth process. Our studies of morphology of ingots and crystals formed at shrinkage cavities have allowed us to suggest the preferred growth of crystal plates along the direction of liquid phase retreat. Thereof the essence of the method of growth of YBCO crystals used in the work is the creation of conditions needed for reliable nucleation, induced formation of cavities and continuation of oriented crystallisation as the melt is removed together with the simultaneous purification of the crystals formed. The containers of own design were used for growing the single crystals. They ensured slow pulling an alundum crucible off with holes in the bottom out of another one at the temperature gradient. Thus the method of growing YBCO single crystals was a combination of the method of mass nucleation and directional crystallization from solution-melt by Czochralski. Under conditions of supersaturation at the upper part of crucible held at lower temperature the spontaneous emergence of fine nuclei took place. Further reduction of temperature induced the growth of the nuclei and their fixation in the matrix of substance solidified at the crucible surface. Shift of the crucible resulted in the preferred growth of only such nuclei whose crystallographic axes *a* and *b* coincided with the temperature gradient as the rates of growth along these directions were the largest as

according to the habitus. The crystals whose orientation did not comply with these terms were behind development and torn of the melt.

In the process of crystal growing the mixture with the molecular ratio of initial components of about 1:4:10 (the composition with the melt temperature of about 1273K that fell into the upper part of liquidus surface of YBCO compound upon cooling) was used as a feeding medium. The powders of Y_2O_3, $BaCO_3$ and CuO, "SC" grade, were used as the mixture's initial components. Decarbonization and annealing of the mixture preformed as pellets was carried out in the alundum container at 1123K for 10 hours. After grinding and second preforming the mixture was annealed in a similar way.

The rates of heating and cooling as well as the temperature of the synthesis were controlled to an accuracy of ±0.1K with the use of the precision programmed regulator of RIF-101 type.

The proposed method allowed us to grow the single crystals of YBCO compounds, which had the natural cuts and plate habitus of 8 mm in length. The crystals grew along the directions of the crystallographic axes *a* and *b* as the crystallization front moved to the lower part of the crucible. As the solution-melt was depleted of YBCO compound the rate of crystal growth decreased and the liquid phase was torn off the crystallisation front.

4. Structure of crystals and surface morphology

X-ray analysis data showed that the grown single crystals had the tetragonal structure and low oxygen saturation ($\delta \approx 0.5$). The transition to the orthorhombic syngony was onserved upon saturation by oxygen in the flow-type system under the mode of linear reduction of temperature from 773 to 693K for 10 hours.

The measurements of the lattice parameters for thin plate crystals showed that the maximal value of $\delta \cong 1.0$ was restored in the crystals for the period of saturation. At that the distribution of oxygen content across the plate area was rapidly became even so the crystal peripheral areas and central zone were similar with respect to the oxygen content. We have suggested that oxygen is supplied to the crystal mainly along the normal to the plane (001). X-ray rocking patters of thin plate crystals with recording the 001 reflection have shown the mosaic structures of various types:

−   coarse mosaic structure with an angle of block misalignment of 1 to 1.5°;
−   fine mosaic structure with the more fractional blocks (<0.01–0.001 mm) which are mutually disordered within the angles of 0.05 to 0.5°.

One shall take into account that the block boundaries have served as channels through which oxygen have penetrated into the crystal. Since the mosaic blocks are distributed evenly across the surface of plates the crystal is saturated evenly. However this does not mean that within the boundaries of a particular block there is no gradient of oxygen content.

As the process of saturation of YBCO crystal plates proceeds they display twinning that is well observed on the plane (001). One can discern some stages in development of the twinning structure:

−   fine lattice twinning, poorly pronounced ($\delta=0.7 \div 0.85$);
−   well-pronounced twin lattice ($\delta=0.85 \div 1.0$);
−   great (broad) twin domains with a trend towards a formation of a single domain ($\delta=1.0$).

A specific feature of the twin structure of thin plate crystals is the dependence of twinning scale on the location on the plate surface. The twin lattice may be visually observed, in the first turn, at the plate corners then along the perimeter and in the last turn at the crystal's centre. At that the degree of oxygen saturation (δ) of the plates is the same across the plate's whole area. Upon increasing the time of annealing in oxygen the twin structure develops

towards the domain coarsening. Very often the single domain areas (non-twin) are formed at the plate's corners. The fact that sometimes the twin structure is not observed at the crystal's central region (the optically isotropic area under polarized light) does not mean that the crystal's structure is tetragonal. The value of δ is about 1.0 in these areas so the lattice is orthorhombic.
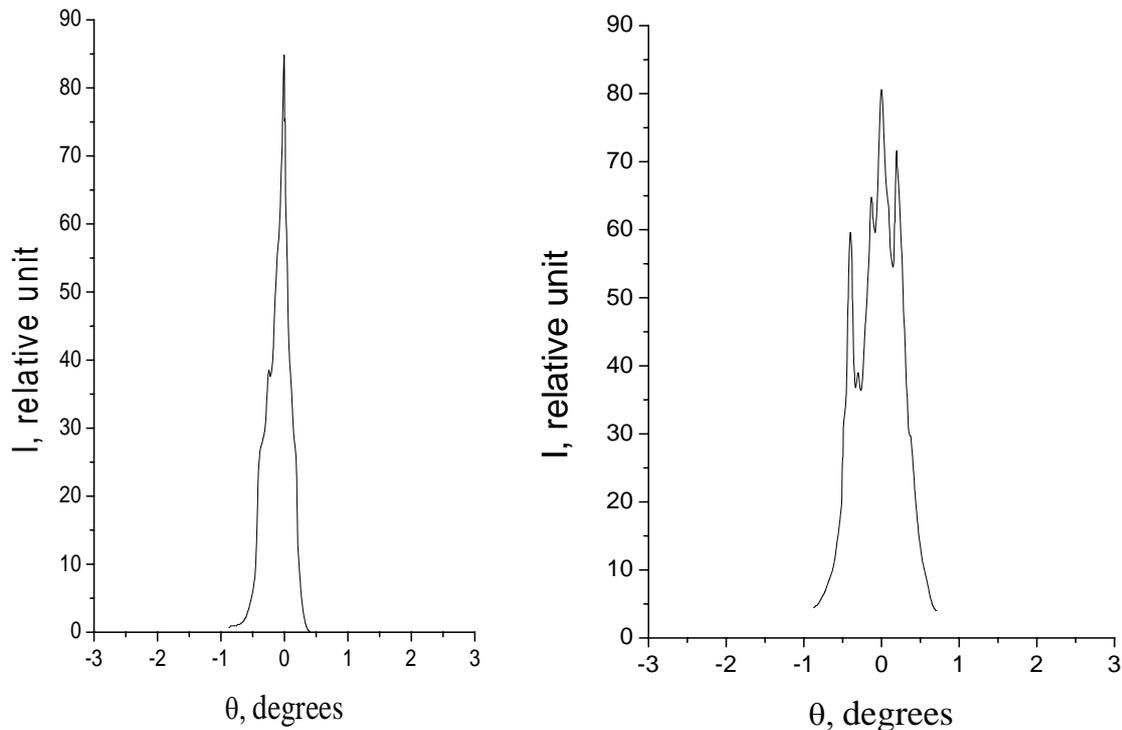

Fig. 1. Preferred development of twin lattice at the sides and corners of (001) crystal plane.

The absence of the observable twin structure is solely due to submicroscopic sizes of twin domains. This has been confirmed by the X-ray diffraction data. The angular separation of doubled reflections of h01 and 0k1 types (h=k) depends on degree of structural orthorhombicity and scale of the twin lattice [3]. The maximum angular separation, $\Delta 2\theta$, for the 0.3.10 and 3.0.10 pair of reflections is about 1.85° for CuK_α-radiation (Fig. 1). However this angle is observed only for the crystals with δ=1.0 and the well pronounced large-scale twin lattice. A wide range of $\Delta 2\theta$ values has been recorded for the crystals under study (0.3 to 1.65) while the minimal values are specific only for the optically isotropic regions. It should be noted that these regions are highly saturated with oxygen (δ=0.9÷1.0). Thus we have concluded that a small-scale twin structure has been developed at the crystal's central region with domain sizes below the wavelength of visible light.

Upon increasing the annealing time (at 723K) the twin lattice is enlarged in some extent. However we suppose that the "nature" of lattice is formed at higher temperatures and related to the distribution of mechanical stresses in the crystal and kinetics of oxygen diffusion.

Measurements of temperature dependencies of crystal resistance and surface impedance (Fig. 2) have shown the transition to the superconducting state at 90K (T_c) with ΔT=1.0 K.

5. Mass transport processes at the interface single crystal /metal film

5.1. Diffusion model

The model of diffusion out of a thin layer of finite thickness has been described in detail in our work [4]. According to the model the diffusing component initially presented as a thin layer on the specimen's surface is distributed along the specimen's depth in accordance with the following equation:

$$N(x,t) = \frac{N_0}{2}\left[\text{erf}\left(\frac{h-x}{2\sqrt{Dt}}\right) + \text{erf}\left(\frac{h+x}{2\sqrt{Dt}}\right)\right] \tag{1}$$

where h is the thickness of the initial film of diffusing component; $N(x,t)$ is the content of the diffusing component at the depth of x in the bulk of specimen at the time t; N_0 is the initial distribution of the diffusing component at the time t=0; erf(z) is the error function,

$$\text{erf}(z) = \frac{2}{\pi}\int_0^z \exp(-t^2)dt .$$

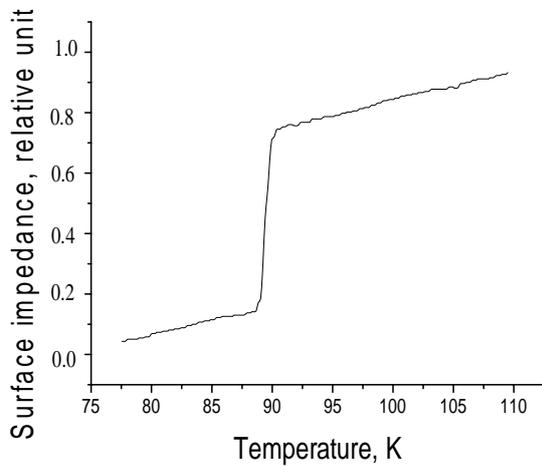Fig. 2. Temperature dependence of surface impedance for the YBa$_2$Cu$_3$O$_{6+\delta}$ single crystals.
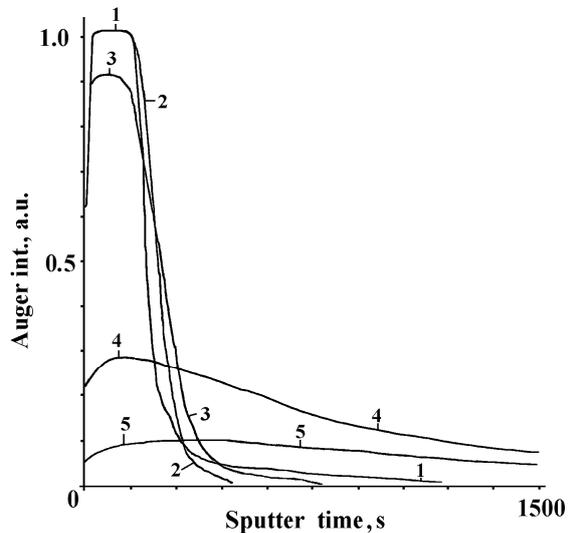
Fig. 3. Auger depth profiles for silver through the interface "Ag film/YBCO substrate": *1* - initial state; *2* - 373K; *3* - 473K; *4* - 573K; *5* - 773K.

The changes in the content of the diffusing component on the specimen's surface are described by the following equation:

$$N(0,t) = N_0\left[\text{erf}\left(\frac{h}{2\sqrt{Dt}}\right)\right] \tag{2}$$

By using this equation amd with the use of $N(0,t)/N_0$ ratio for surface concentration after annealing the specimen for the time t as well as with the use of numerical values of the error fuinction one can determine the error finction's argument, $[h/2(Dt)^{1/2}]$. Then it is possible to calculate the diffusion coefficient D substituting the measured values for h and t.

5.2. Silver diffusion into YBa$_2$Cu$_3$O$_{6+\delta}$

As it has been mentioned earlier the study of diffusion properties of single crystalline yttrium barium copper oxide, YBa$_2$Cu$_3$O$_{6+\delta}$, known as YBCO, has been carried out with the use of specimens consisted of thin silver films (10-20 nm in thickness) deposited onto the surface of YBCO single crystal plates with c-axis directed along the normal to the plane of the

crystal. In this work silver has been chosen as a material of thin metal films due to the following reasons: silver does not react with YBCO, it is a promising material for fabrication of electric contacts to the systems on the basis of YBCO, it can be used as a protective coating as well as a component in composite materials.

As equation (*2*) shows the thickness of the initial film is one of the experimental parameters needed for calculation of diffusion coefficient. The thickness shall satisfy a number of requirements. In the first turn such a film shall not be very thick in order that the diffusion processes result in noticeable changes during annealing the specimen for the selected time. In the next turn this film shall no be very thin and shall cover the whole surface of the single crystals that is it shall be continuous. The preliminary experiments have shown that taking into account the method of film deposition (thermal evaporation in vacuum) the films of 10 to 20 nm in thickness comply with the above-mentioned conditions. The film thickness was measured by the profilometry. The thickness of the reference film was determined by the height of a step formed on the reference specimen together with the films on the studied specimens. Even at the minimal load on the profilometer's diamond stylus (3 mg) a significant depression of the evaporated silver films was observed. Therefore the additional measurements aimed to the determination of necessary corrections were performed. In these measurements the profilometer stylus was moved perpendicular to the primary track of the stylus left after the measurements of the step height. The following results were obtained: the step height on the reference specimen was 7 ± 1 nm; the depth of the diamond stylus track was 8 ± 1 nm. Thus the thickness of the silver film was considered to be 15 ± 2 nm.

Annealing of the specimens consisted of single crystals with deposited silver films was carried out at temperatures of 373, 473, 573, and 773K in the inert atmosphere (argon). The annealing time was varied from 100 to 10000 s. After some preliminary experiments on studying the effect of annealing time on the Ag depth profiles the optimal annealing time was determined, 1000 s.

Fig. 3 shows the Ag depth profiles for the specimens under examination: before annealing and after annealing at temperatures of 373, 473, 573, and 773K. The normalized Auger intensities (the ratio of Ag intensities for the annealed specimens to the intensity of Ag Auger peak for the initial film without annealing) are represented as a function of sputter time. The normalized intensity is proportional to the ratio N/N_0 in equations (*1*) and (*2*) above. Before annealing the compact layer of silver with an abrupt interface between the film and underlying YBCO single crystal substrate is observed. Upon increasing the temperature of annealing the silver content on the specimen surface decreases and the interface region is broadened.

Substituting the data represented in Fig. 5 (N/N_0) into equation (*2*) we have calculated the diffusivity of Ag (D) in YBCO single crystals and obtained the following results.

As Fig. 3 shows the Ag depth profile for annealing temperature of 373K is similar to the initial Ag depth profile. This means that the rate of diffusion of Ag in YBCO is very low at 373K and its effect is not observable for the chosen time of annealing (1000 s).

In the temperature range from 474 to 773K the Ag diffusivity is varied from 6×10^{-16} cm^2/s to 8×10^{-14} cm^2/s. These values are significantly lower than the diffusion coefficients for other metals in sintered ceramic specimens of YBCO [6]. For the purpose of presenting the diffusion coefficient as a function of temperature in the form $D=D_o\times\exp[-E_a/kT]$, the values of Ea (the diffusion activation energy) and preexponential factor D_o have been determined as 0,5 eV and $1,75\times10^{-10}$ cm^2/s correspondingly.

With the aim of finding the most probable mechanism of Ag diffusion in YBCO single crystals we have performed the detailed analysis of changes in the Auger spectra for the major constutent elements upon annealing and subsequent depth profiling of the specimens under examination.

5.3. Analysis of Auger-spectra structure

As it had been indicated earlier in Table 1 there were carbon and chlorine impurities in the specimens under examination. Carbon was located only on the surface of specimens. Its origin was due to adsorption of gases from the residual atmosphere in the high-vacuum chamber of the Auger spectrometer. This carbon layer may be easily removed by Ar-ion sputtering for a short time (some seconds). Chlorine was presented in all specimens under examination. We can not establish its origin with certainty. Most probably its presence is due to the processes of YBCO single crystals making.

The most prominent changes have been revealed in the Auger spectra of oxygen, one of the principal components of YBCO. Oxygen plays an important role in high-temperature superconductors of oxide-types ensuring their superconducting properties together with copper. In the structure of YBCO high-temperature superconductor the oxygen atoms occupy four different sites (Fig. 4).Two sites in the Cu-O plane, O(2) and O(3), one site – in the Cu-O chains directed along the b axis, O(1), and the last one – O(4), which connects Cu atoms along the c axis. Conduction in YBCO is understood to arise due to the motion of holes in the Cu-O sheets, although conduction due to carriers on some the other layers (for example, the chains Cu-O) is not ruled out [7]. In any case the changes in oxygen content affect the conductive properties of YBCO and one may expect that such changes will also affect the Auger spectra of oxygen in YBCO.
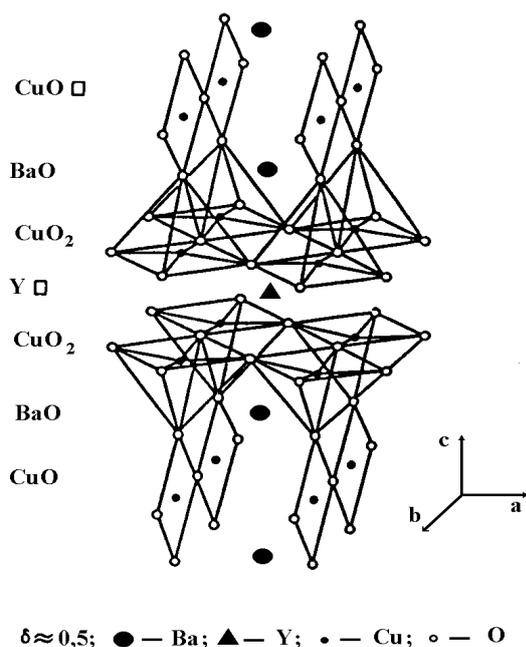

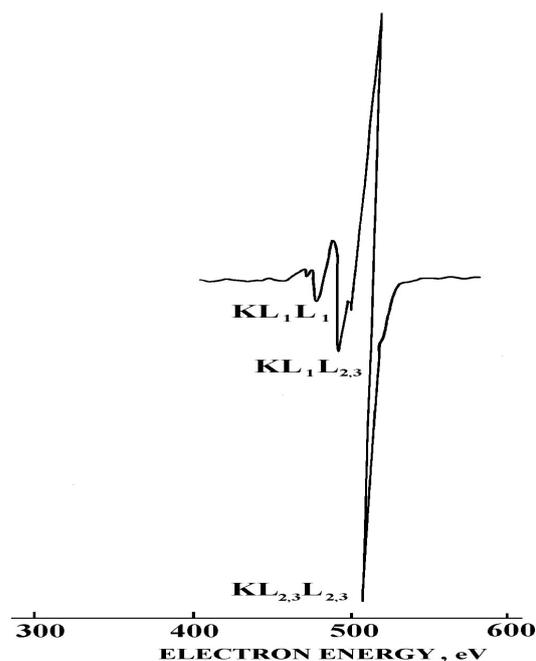**Fig. 4.** Structure of $YBa_2Cu_3O_{6+\delta}$.

Fig. 5. Auger spectra of oxygen [5].

There are three major peaks in the oxygen Auger spectra in the energy range from 470 to 530 eV (Fig. 5), due to the KL_1L_1, $KL_1L_{2,3}$, and $KL_{2,3}L_{2,3}$ transitions. The most intensive is the Auger-peak due to the $KL_{2,3}L_{2,3}$ transitions. Its intensity strongly depends on charge transfer to the oxygen atom as the $L_{2,3}$ level in oxygen is valent. On the contrary electron occupation of L_1-level does not depend on charge transfer processes. Thus the ratio of $KL_{2,3}L_{2,3}$ intensity to one of the two other Auger-peak may serve as an indicator of changes in charge transfer processes due to motion of carriers from neighbour atoms to the oxygen atom.

Taking into account the above-mentioned we have studied the changes in the values of the ratio of $KL_1L_{2,3}$ and $KL_{2,3}L_{2,3}$ peak intensities ($K=KL_1L_{2,3}/KL_{2,3}L_{2,3}$) in the oxygen Auger-spectrum for the following specimens:

a) original single crystals YBCO;

b) YBCO single crystals with deposited silver film;

c) YBCO single crystals with silver film after annealing at 773K.

The following results have been obtained: for the specimens *a* and *b* the values of K are practically the same (0.175 ± 0.002 and 0.173 ± 0.005 correspondingly), for the specimen *c* this ratio is equalled to 0.196 ± 0.004.

Thus, the above-mentioned values show that annealing causes the reduction of $KL_{2,3}L_{2,3}$ intensity with respect $KL_1L_{2,3}$ intensity and this may be due to decrease in the effective electron density on the $L_{2,3}$ valence level in oxygen atoms. Such decrease in effective electron density may be explained by reduced mobility of holes generated in oxygen atoms as a result of Auger transitions. $KL_{2,3}L_{2,3}$ transition leaves the oxygen atom with two holes on the $L_{2,3}$ valence level. So the next Auger transition in the same oxygen atom is possible only if these holes will be filled as a result of charge transfer due to the motion of carriers. If the mobility of carriers is reduced then the lesser number of oxygen atoms will contribute to the $KL_{2,3}L_{2,3}$ Auger peak intensity). So we may consider that taking into account that conduction in YBCO high temperature superconductors is due to the overlap between the Cu and O atomic orbitals the reduction in the conducting properties (decrease in hole mobility) may be connected with the partial removal of oxygen atoms from conducting layers and generation of oxygen vacancies.

Thus we may suggest that the most probable mechanism of silver diffusion in YBCO single crystals is a vacancy mechanism at which the Ag atoms from the deposited film diffuse in to the bulk of single crystal substrate along the oxygen vacancies.

6. Conclusions

According to the results of studies of the physical and chemical processes of crystallisation of YBCO compound the optimum condition of HTSC single crystal synthesis from solution melt have been determined. The proposed technique allows to fabricate YBCO single crystals of prefect structure with the rather large dimensions (8x4x0.05 mm) in small volume containers (<20-30 mL). The mechanism of saturation of crystals by oxygen and the stages of development of twin structure *vs.* saturation of YBCO by oxygen and condition of synthesis have been studied.

Diffusion of silver into YBCO single crystals along the *c*-axis has been studied in the temperature range from 373 to 773K. The detailed analysis of Auger spectra for the components of silver film and HTSC substrate has revealed the most prominent changes in the oxygen Auger spectra. We have related these changes in the relative intensities of constituent peaks with the variation of effective valence electron density in the oxygen atoms. Upon annealing of single crystals the are atoms depleted of some oxygen atoms. The vacancies formed as a result of such depletion reduce the conduction with participation of oxygen atoms and change the relative peak intensities in the Auger spectra of oxygen. At the same time these vacancies may serve as a route of diffusion of silver atoms from the deposited film into the YBCO single crystalline substrate (vacancy mechanism).

Acknowledgement

References

1. Bashkirov Yu.A. and Fleishman L.S. Massive high-temperature superconductive materials for the powerful current application // Sverkhprovodimost: Fiz., Khim., Tekh. - 1992. – V.5. - N8. – P.1351-1382.
2. Ustinov A.I. and Olikhovskaya L.A. // Metallofizika. - 1991. – V.13, N10. - P.41-48.
3. Voloshin I.V., Gaponov S.V., Il'yn N.V., Strikovsky M.D., and Fisher L.M. Radio frequency impedance of epitaxial films YBaCuO // Sverkhprovodimost: Fiz., Khim., Tekh. - 1989. – V.2. - N5. - P.94-96.
4. Gorbik P.P., Kashin G.N., Ogenko V.M., Slesarevsky S.O., and Chuiko A.A. Diffusion of Ag in single crystals of high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ // Doklady NAN Ukrainy. - 1997. - N5. - P.134-137.
5. Handbook of Auger Electron Spectroscopy. Second Edition /L.E. Davis, N.C. McDonald, P.W. Palmberg, G.E. Riach, and R.E. Weber. – Eden Praire: Physics Electronic Ind. Corp., 1976.
6. Gorbik P.P., Dyakin V.V., Ogenko V.M., Chuiko A.A., Alfeev V.N., Gorshkov A.V., Zaitov F.A., and Shalyapina G.M. Studies of nickel diffusion in $YBa_2Cu_3O_{7-\delta}$ and $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_y$ sintered ceramics // Doklady AN UkrSSR. - 1990. - Ser. A. – N7. - P.50-53.
7. Beasley M.R. High-temperature superconductive thin films // Proceedings of the IEEE. - 1989. - V.77, N8. - P.1135-1163.