Extraction-Pyrolytic Method of Obtaining Functional Oxide Materials

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Abstract

Development of functional electronics as an alternative to the circuit engineering is tightly connected with solution of a number of problems in the field of material science and technology. Semiconductor complex oxides, magnetic, sensor and radiation-generating materials, ferro-, piezo- and pyroelectrics acquire a great importance in the modern world, since they play the role of "clever" materials. Their necessity is increasing as the most advanced branches of science and technology, in particular electronics, computer engineering, medicine, laser and photochemical engineering, are developing. Among the methods of obtaining complex oxide materials, very promising are those of solutions to which the sol-gel method belongs. Mixing the initial components in a solution and their subsequent thermal treatment result in obtaining homogeneous materials and decreasing the temperature and temporal parameters of synthesis. This makes it possible to introduce chemically active and easily fusible components, *e. g.*, lead and bismuth, into the complex oxide composition. An important role in the stabilization of the characteristics of functional materials is played by their purity factor. The absence of admixtures and the homogeneity of phase composition ensure the maximal characteristics and brusque transitions realized in the work of functional materials. In order to obtain homogeneous, pure and morphologically uniform functional oxide materials, the authors propose an extraction-pyrolytic technology.

INTRODUCTION

The increase in the role of functional (active) materials in the development of microelectronics is determined by the problems of minimization of the size of instruments and devices, heightening their efficiency and degree of integration. In active materials, transfer of charge carriers, waves, atoms or various kinds of radiation takes place. In the list of "clever" materials, a great part belongs to complex oxides whose circle is continuously enlarging. In complex systems of active dielectrics with a large portion of ionic bonds, a formation of large internal fields is possible. This permits producing on their basis a wide range of radioelectronic devices, in particular piezoelectric transducers, high-capacity memory units, various optical instruments, sensor and medical ultrasound diagnostic devices. The possible presence of practically useful properties in segnetomagnetics makes it possible to create on their basis multifunctional elements of radiocircuits.

Functional electronic devices combine the functions of input, processing and output of information by means of using various physical effects and dynamic non-uniformities in the functional materials. Production of functional electronic devices is an alternative to the use of complicated circuits in microelectronics. Such devices permit processing still larger massifs of information, decreasing the device dimensions and cost. Therein, the most important becomes the development of technologies for obtaining pure and homogeneous materials with replicable properties and maximal functional characteristics. Important for microelectronics are film materials in which boundary effects are manifested and the influence of orientation and texture on the anisotropy of properties is considerable.

FUNCTIONAL COMPLEX OXIDE MATERIALS

Functional materials include semiconductor oxides, materials that generate radiation for lasers, magnetic sensory materials, ferro-, piezo- and pyroelectrics *etc*., whose composition and application fields are presented in Table 1 drawn up on the basis of analysis of literature sources [1–30].

Usually, complex oxide materials are obtained by means of solid-phase synthesis from metal oxides and carbonates, which requires high temperature and temporal parameters of the process, since individual oxides and carbonates begin to interact at temperatures higher than 1000–1300 °C. Besides, commercial preparations usually contain admixtures. Admixture atoms are segregated on the border of grains of the obtained complex oxide products and change their resistance and other properties. This is especially important for materials consisting of small particles. Modern technologies are aimed at decreasing the grain size for obtaining materials with improved mechanical, optical and physical characteristics. It is known that nanoparticles give the materials new, sometimes unique, properties due to manifestation of quantum effects in them.

Small size particles can be obtained in low-temperature synthesis of complex compounds, and for this reason it is important to develop new technologies that would ensure obtaining admixture-free complex oxide materials and coatings with a decrease in energy expenditure. There exists the problem of high-temperature heating when the complex oxide compositions contain chemically active and volatile components, *e.g.*, lead and bismuth. One of the ways of solving this problem is the use of solution methods for material production.

EXTRACTION-PYROLYTIC METHOD AND ITS POSSIBILITIES

For preparation of chemically and morphologically homogeneous complex oxide compounds it is expedient to use solution technologies. For a sharp decrease in the presence of secondary phases in complex oxide compounds, stable and non-volatile precursor solutions are necessary. Metal alkoxides and other organometallic compounds used in sol-gel technology not always meet these requirements. Sufficiently stable, accessible and surface-active are metal carboxylates which can be mixed in any proportions to form true solutions. When obtaining metal carboxylates by the extraction method, purification of components of the future complex oxide from admixtures takes place, and the subsequent mixing of carboxylates in the solution ensures chemical homogeneity of the product. Therein, there are no purity limitations of the initial raw material.

The extraction-pyrolytic technology of obtaining ceramic and film-forming materials developed by us [31] considerably lowers the phase formation temperature of complex oxides, because it includes mixing of components in solution and obtaining, as a result of heat treatment, ultradispersed highly active powders or particles on the substrate. The morphological homogeneity of the materials obtained is determined by the formation of a large number of crystallization centres of simple and complex oxide materials during heat treatment of extract solutions and pastes, wherein particles of submicron size having a great reserve of potential energy are formed. For this reason, phase formation in such systems takes place within a short time and at temperatures lower than those in solid-phase synthesis. In such structures, formation of a pattern with the help of laser and ion beams or of memory samples on backing from the precursor solution with its subsequent exposure through the mask, removal of unexposed sites and heat treatment is possible.

Thermal degradation (pyrolysis) in air milieu results in formation of simple and complex metal oxides and release of gases. In extraction systems with monocarboxylic acids, additional interactions take place, in particu-

TABLE 1

Composition and use of functional oxide compounds

Composition	Properties	Use	Ref.
$BaTiO_3$, $PbTiO_3$, $SrTiO_3$, $CdTiO_3$, $PbZrO_3$, $PbHfO_3$, $KNbO_3$, $BiFeO_3$, $PbBi_2Nb_2O_9$, $BaBi_2Nb_2O_9$, $SrBi_2Nb_2O_9$, $Na_{1/2}Bi_{1/2}Bi_2Nb_2O_9$, $PbBi_2Ta_2O_9$, $K_{1/2}Bi_{1/2}Bi_2Nb_2O_9$	Ferroelectrics	Development of nonvolatile memory devices, devices of dynamic memory with arbitrary sampling, capacitors, receivers of infrared radiation, optical processors, wave guides and delay lines, devices on surface acoustic waves, devices that change the spectral composition, amplitude and direction of the signal in the preset manner	[1–5]
In_2O_3/SnO_2, In_2O_3, $In_4Sn_3O_{12}$: Bi, SnO_2–Sb_2O_3, $BaCr_{1-x}In_xO_3$, $LiFeTiO_4$, Sr_2TiO_4, $Sr_2Ti_{1-x}In_xO_{4-2}$	Conductors	As conducing electrodes for liquid flat displays and solar cells, for realization of UV light-emission diodes working at room temperature	[6–10]
$SrCo_{0.5}Fe_{0.5}O_x$, Y_2O_3(8 %)+ZrO_2, CeO_2: Y, Gd, $La_{0.9}Sr_{0.1}GaO_3$, $La_{2-x}Sr_{2x}NiO_y$, $BaCe_{0.8}Cd_{0.2}O_3$, $BaCe_{0.9}Nd_{0.1}O_{3-x}$, $KMoO_4$: Mn, Zr, Zn..., ZrO_2 : Y_2O_3, Sc_2O_3, $LaGaO_3$: Sr, Mg, $SrCe_{0.99}Y_{0.05}O_{3-x}$, $SrYb_{0.95}(Ce_{1-x}Zr_x)_{0.95}O_{3-\alpha}$, $Sm_{0.1}Ce_{0.9}O_{1.95}$, $(Zr_{1-y}Mg_y)_{0.98}Al_{0.02}O_y$, $BaIn_{0.5}Sn_{0.5}O_{2.75}$	Solid electrolytes	In fuel elements considered as promising sources of energy for electric transport means, since they ensure a high efficiency and are ecologically clean; for obtaining solid electrolyte films (the resistance is linearly dependent on the electrolyte thickness). Ionic conductors can be used as indicators in potentiometric assay of Cu^{2+}, Fe^{2+} and Ni^{2+} in acid solutions	[11–15]
IrO_2, $Bi_4V_{12}O_{18-x}$, p-NiO/n-ZnO, CeO_2, $(Ca_{1-x}Sr_2)MnO_3$, RuO_2, $Nd_{1-x}Ca_xCr_{1-y}Cu_yO_3$, $Ba_{1-x-y}Sr_yY_xTiO_3$	Semiconductors	The width of the prohibited zone of about 2 eV makes these compounds close to typical electronic semiconductors CdSe and CdS. Thermoelectromotive force	[16–19]
135K, Hg–Ba–Ca–Cu–O, 94K, $YBa_2Cu_3O_{7-x}$, $NdBa_2Cu_3O_{7-S}$, 110K, $Bi_2Sr_2CaCu_2O_8$, $Bi_{2.2-x}Pb_xSr_{1.8}CaCu_2O_8$	Supercoductors	For magnetic separators, energy storage, water treatment, soil purification, improvement of polymer properties by means of polymerization in a strong magnetic field (high-temperature superconductive magnets consume very little energy: 400 W *vs.* 400 000 W in Cu electromagnets)	[20–22]
ZrO_2, $ZrTiO_3$, SiO_2, ZnO, $BaTiO_3$/M, Zn–Sn–O, $SiO_2 \cdot F/SiO_2$, TiO_2/SiO_2, MgO, $LiNbO_3$, $Bi_{12}SiO_{20}$, V_2SiO_5, SnO_2/In_2O_3, $(ZnO)_5In_2O_3$	Optical	Multilayer antireflection coatings, light guides, electrooptical modulators and gates, optical and colour multilayer compositions, thermooptical recording, optical sensors, transparent electrodes, for increase of illumination	[23–25]

TABLE 1 (end)

Composition	Properties	Use	Ref.
Cr_2O_3, $BaFe_{12}O_{19}$, $LaM_xMn_{1-x}O_3$, $Ln_{1-x}Nd_xTiO_3$, $LaCo_{1-t}Cr_tO_3$, $Fe_8V_{10}W_{16}O_{85}$, $(Y,Sc)_3Fe_5O_{12}$, $Co_{0.7}Fe_{2.3}O_7$	Magnetic	For creation of magnet-controlled optical devices, electrically erasable and user-programmable devices based on thin films absorbing the radar radiation (toroics, magneto-optical recording materials)	[26–30]

lar the formation of dimeric carboxylates of copper, nickel, cobalt, trinuclear iron (III) compounds *etc.* In joint extraction of different metals or in mixing their extracts, in some cases heteronuclear compounds, *e. g.*, heteronuclear carboxylates of Fe(III) with Ni(II), Co(II), Cr(III), Mn(II) are formed [32]. The formation of heteronuclear coextractable compounds contributes to obtaining materials with a uniform distribution of components in pyrolytic synthesis. For example, the thermogram of Li and Co carboxylates has demonstrated that a transition of components to a solid state takes place at 200–290 °C. The considerable difference in the thermal behaviour of individual carboxylates and their mixture (Fig. 1) witnesses to formation of a compound in organic solution from which a complex oxide is obtained directly in the process of pyrolysis of the organic part.

According to the gas-chromatographic study of pyrolysis products, the degradation of the organic part goes by a complicated mechanism with ultimate formation, to a great degree, of CO_2 (88 %), CO (8 %) and volatile hydrocarbons. After pyrolysis, the complex oxide or separate oxides are in amorphous phase. The analytical assay of carbon in pyrolysis products annealed at temperatures higher than 500 °C failed to detect its presence within the limits of measurement sensitivity (up to 0.1 %).

The morphology of pyrolysis products is characterized by uniformity and submicron particle size (Fig. 2). The growth of crystallites

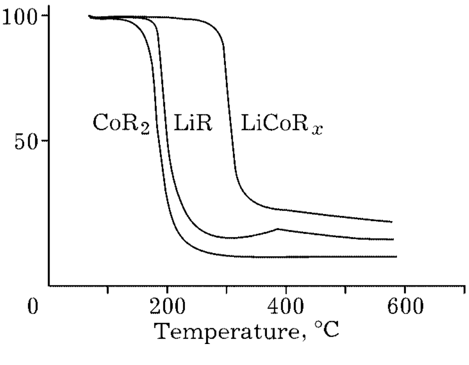

Fig. 1. Thermograms of carboxylates of lithium (LiR), cobalt (CoR_2) and mixture of lithium and cobalt carboxylates ($LiCoR_x$).

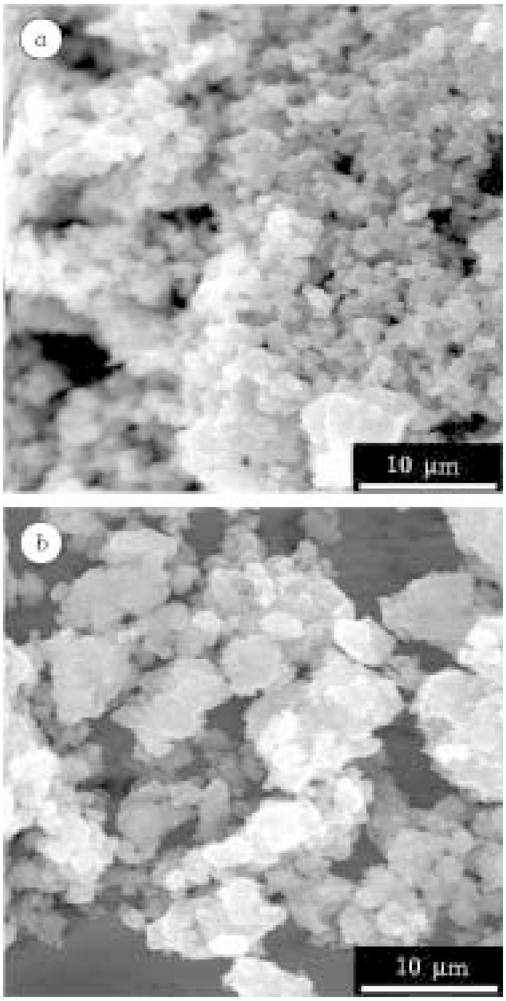

Fig. 2. REM images of $LiCoO_2$ powder obtained by extraction-pyrolytic method at the heating rate of up to 27 (*a*) and 5 °C/min (*b*).

in the process of annealing and caking of materials is regulated by the kinetic of the processes with participation of factors of velocity of rise and fall of the annealing temperature. It has been established that a slow rise of temperature, as compared to a rapid one, promotes the formation of larger grains, wherein the product is also characterized by a single phase composition.

EXPERIMENTAL

In accordance with the possibility of an efficient separation of metals for obtaining extracts of various metals, α-ramified monocarboxylic acids with 5–9 carbon atoms, solutions of inorganic metal salts (chlorides, nitrates of barium, strontium, titanium and other metals) and an alkaline reagent (sodium hydroxide solution) were used. It has been demonstrated in previous studies that the best extracting capacity is characteristic of a mixture of higher isomers of carboxylic acids (HIC). As a result of 2–3 steps of extraction, the obtained metal carboxylates are practically free from admixtures and can be purified by washing from the alkaline reagent.

The preliminarily calculated concentration of carboxylates was checked using the method of atomic absorption of re-extracts. Further on, the metal carboxylate solutions were mixed in desired stoichiometric proportions and used for obtaining homogeneous pastes and powders or films, according to wetting technology. It is noteworthy that the removal of the solvent and of the excess of the extractant in organic solutions is not accompanied by fractional crystallization like in aqueous solutions, and homogeneous pastes are obtained.

Thermogravimetric measurements were carried out on a Paulic–Paulic–Erdey derivatograph in air milieu at the temperature rise rate of 5 °C/min. For identification of metal carboxylate degradation products, gas chromatography, X-ray phase analysis and carbon analyzer AN 7529 were used.

X-ray phase analysis was carried out on a DRON-4-07 diffractometer with a GUR-9 goniometer (IBM PC-compatible horizontal goniometer with the radius of 180 mm and with focusing according to Bragg–Brentano, equipped with a graphite monochromator). Photography of samples was carried out in filtered CuK_α radiation with the specimen rotation around the normal to its plane (in order to increase the number of atomic planes getting under the X-ray beam, which heightens the accuracy of the method).

The morphology of powdered specimens and films was studied using a PEM-202 electron microscope.

RESULTS AND DISCUSSION

Synthesis of ferroelectrics $BaTiO_3$, $SrTiO_3$ and $ZrTiO_2$ from extract solutions has been carried out. Extraction of barium, strontium, zirconium and titanium was performed by the cation exchange mechanism. The metal carboxylates obtained with the preset concentration, after the analytical confirmation of concentration with respect to the metal, were mixed in stoichiometric proportions and exposed to heat treatment. X-ray phase analysis of annealing products showed that the synthesis of single phase specimens took place at 700–800 °C within 1 h (Fig. 3).

In pyrolysis of carboxylates of Sr, Ti, a complex oxide $SrTiO_3$ is already formed at 500 °C. This product is rather well crystallized, but the extended peaks witness to a small size of particles. This permits making a conclusion that the structure of the material is nanocrystalline. An increase in the annealing temperature enhances the phase formation process and decreases the amount of admixture phases. A pure product with a high crystallinity was obtained at 800 °C within 1 h.

The product $ZrTiO_3$ is also already formed from carboxylate precursors at 500 °C. An increase in annealing temperature results in an increase in its crystallinity. It has been noted that even high annealing temperatures do not lead to any considerable increase in the particle size, which is witnessed by the extended peaks, *i. e.*, the product annealed and caked at a high temperature remains nanocrystalline.

The process of $BaTiO_3$ crystallization and phase formation becomes intensified only at 800 °C, and its annealing for 1 h at 800 °C

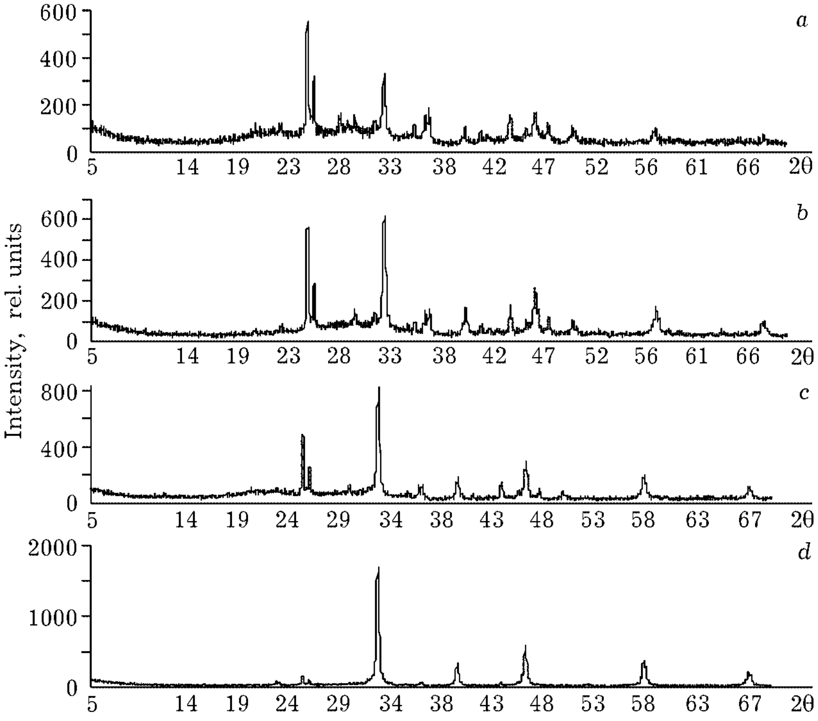

Fig. 3. X-ray photograph of pyrolysis products of strontium and titanium carboxylates annealed at the temperature of 500 (*a*), 600 (*b*), 700 (c) and 800 °C (*d*).

results in the 100 % yield of the phase. Therein, the intensity of peaks increases from 140 to 2000 conventional units due to the increase in the product crystallinity.

In comparison with the solid-phase synthesis of oxide mixture, the phase formation temperature is by 500 °C lower. Besides, the solid-phase synthesis requires a long heating period, whereas the pyrolysis products of organic pastes easily interact within 0.1–1 h. Fine-granular and homogeneous dielectric ceramics obtained by the proposed method ensures the stability of the temperature coefficient of capacity and a low value of the coefficient of scattering.

Homogeneous ceramic and film high-temperature superconductor materials in $YBa_2Cu_3O_{7-x}$ and $Bi_2Ca_2Sr_2Cu_3O_8$ systems with a sharp superconductive transition at a temperature maximally possible for these compositions have been obtained by the extraction-pyrolytic method [33].

The extraction-pyrolytic technology has many applications, since it is possible to carry out reduction of oxide compounds both in the process of pyrolysis and in separate operations, and to obtain fluorine-, phosphorus- and sulphur-containing compounds and halogen-containing complex oxides.

We have obtained ionic conductors in the Bi – Sr – Cl – O system which differ from purely oxide compounds by their properties, colour, and synthesis temperature. X-ray studies of materials of this system with different stoichiometry has permitted establishing that a single phase product can be obtained with a component ratio of 1 : 1.5 : 2. However, the use of alcohol solutions of chlorine salts leads to sol formation with subsequent obtaining a xerogel and a mesoporous structure of the annealing product with regular pore sizes.

For obtaining films on various plates (dielectric, metallic or semiconductor), extraction-pyrolytic technology was used. Organic solutions easily form wetting films on various substrate materials due to low values of the coefficient of surface tension. The wetting films deposited by the method of submersion, centrifugation or spraying were exposed to heat treatment after drying for evaporation and pyrolysis of the organic component. The wetting and heat treatment processes were repeated 5–30 times for obtaining a film of necessary thickness. Therein, the film thickness can

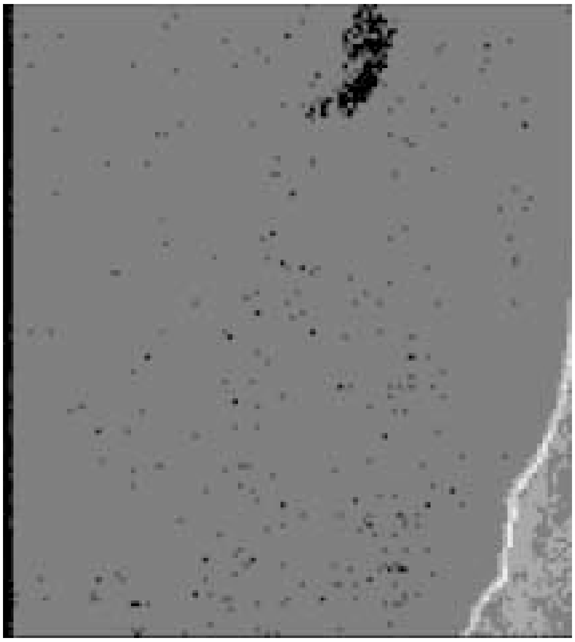

Fig. 4. Morphology of a ZnO film obtained from extract solutions on a Ni substrate (×400).

be calculated on the basis of the theory of wetting by the value of the disjoining pressure determined by the surface tension of the solution under study.

The conditions of obtaining homogeneous layers the most important of which is the use of solutions with a concentration of no less than 1–2 %, were estimated experimentally. Under these conditions, heat treatment does not lead to film swelling or cracking.

Differences in the structure of oxide films (islet or layer structure) were observed depending on the character of the material applied and of the substrate. For example, a ZnO film on a metallic nickel plate has a layer morphology (Fig. 4), and an SnO_2 film shows an islet character of coating, which leads to formation of pores (Fig. 5). Therein, subsequent layers of wetting films contribute to covering the defects in the preceding layers.

The film formation process consists in evaporation of the solvents and of the excess of carboxylic acid at room temperature or in hot drying. As the evaporation goes on, the particles converge to the state of critical packing. A great stretching tension arises in the capillaries which compresses the particles in the whole film. A quantitative estimation of this tension associates the surface tension of the fluid with the size, module and strength of the particles [34]. As a result of coalescence, only two situations are possible. If the arising capillary pressure is sufficiently high to provoke a plastic flow of particles, then the final film will consist of particles packed into structures which are mostly free from cavities. If, however, the particles are so hard and strong for being able to withstand the capillary compression, then a porous fragile film of compressed particles will be formed.

Self-organization processes on the surface of various materials ensure the structural orientation of coatings. These processes are manifested in liquid crystals and in thin films of liquids on orienting surfaces. In films of high-temperature superconductors a high degree of orientation of the *c* axis perpendicularly to the substrate plate has been obtained (Fig. 6), which is determined by the organization of wetting films of solvents on the substrate and by the texturing of the films in the process of their synthesis by the method of drawing out from the solution.

A most important property of wetting consists in the fact that it is determined not by the individual properties of the liquid and of the solid body, but their interaction. A flat film is within the sphere of influence of the surface

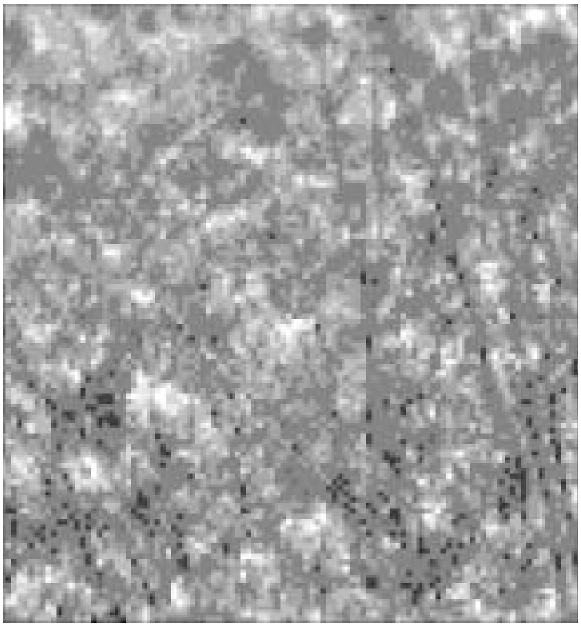

Fig. 5. Morphology of a SnO_2 film obtained from extract solutions on a Cu substrate (×250).

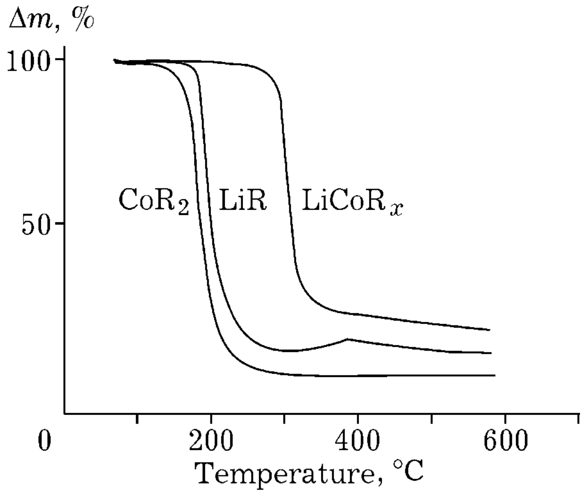

Fig. 6. X-ray photograph of a $YBa_2Cu_3O_{7-x}$ film (*a*) and $YBa_2Cu_3O_{7-x}$ powder (*b*) obtained by extraction-pyrolytic method.

forces of the substrate. An oriented monolayer of adsorbed polar molecules can change the structure of the adjacent layers of the nonpolar solvent at a large distance from the substrate – up to several hundreds layers of molecules, which has permitted hypothesizing [35, 36] the possibility of formation of liquid crystal boundary structures for polar liquids with asymmetric flat molecules in thin liquid films. Numerous experimental data [37] point to the existence of boundary liquid layers with a structure altered as compared to the volumetric one. The extension of the boundary layers exceeds by far the monolayer thickness and increases as so does the lyophilic nature of the hard substrate and the temperature decreases, when the thermal motion of molecules does not weaken the structuring influence of the substrate surface. This can account for the appearance of structural orientation in the films obtained by the wetting technology; however, in each concrete case additional studies are necessary.

CONCLUSION

The use of metal extract solutions is the most promising for obtaining films of ferroelectrics and other functional oxide materials which are progressively more needed in microelectronics. The unusually high dielectric constant of ferroelectrics is important for creation of high-capacity multilayer capacitors and memory units. The extraction-pyrolytic method decreases the synthesis temperature by 400–500 °C, and the temporal parameters from 20–24 h to 1 h. This makes it possible to obtain stoichiometric compositions of complex oxides with Bi, Pb and other low-melting elements. Heightening of purity of functional materials due to extraction processes is very important for functional thin-film materials used in microelectronics. Structural orientation processes in thin films that influence the service parameters of microcircuit engineering are possible in wetting films of organic solutions.

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