J MATER SCI 41 (2006) 1385–1390

Thermovaporous synthesis of complicated oxides

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In this paper the results of investigations of the mechanism and kinetics of reactions of formation of fine crystalline complicated oxides in thermovaporous and solvothermal conditions are presented. The processes of formation of complicated oxides, magnesian spinel ($MgAl_2O_4$), aluminate of lanthanum ($LaAlO_3$), gahnite ($ZnAl_2O_4$), barium hexaferrite ($BaFe_{12}O_{19}$), lithium metaniobate ($LiNbO_3$), and yttrium-aluminum garnet ($Y_3Al_5O_{12}$) were studied. Synthesis of complicated oxides carried out both in solvothermal (T = 250–350°C) and in supercritical conditions ($T > 380$ °C) in medium of water fluid. As raw materials were intermixtures of solid simple oxides or hydroxides and, sometimes, oxides with solution of compound containing doping component. It was found that process of complicated oxides formation proceeds into solid phase. In all cases the formation of complicated oxides has gone through a stage of existence of intermediate crystalline substance with $Me(OH)_n$ structure. The properties of synthesized complicated oxides mainly are determinated by peculiarities of this intermediate. It is possible to influence on properties of a finished product by changing conditions of formation of intermediate.

1. Introduction

The purpose of investigations was the establishment of general regularities of formation of crystal structure of complicated oxides in sub- and supercritical water and determining of dominant factors regulating rate of process and properties of synthesized compounds. Earlier, it was shown that reactions of formation of complicated oxides from solid simple oxides proceed intensive in water fluid [1]. The using of water fluid for activation of solid-phase processes clears the way to industrial production of new materials [2]. The authors of this paper investigated and developed the method of synthesis of series compounds in water fluid and in soft hydrothermal conditions up to a stage of the experimental-industrial production.

2. Experimental methods

Synthesis of complicated oxides was carried out in laboratory (18 ml) and experimental-industrial autoclaves (5 l). The intermixture of hydroxides or oxides of precursors and, sometimes oxides with solution of compound containing doping component, were carefully mixed and were placed into special container within an autoclave. The pressure of water vapor was created by water, filled between walls of autoclave and container with starting material, during heating of autoclave. The autoclave was heated up to design temperature in range of 380–400°C with an isothermal step at 200–270°C or without it during various times. The synthesized crystals products were investigated by X-ray analysis and electron microscopy. The electron microscopic photographies were carried out on the device «Cam Scan Series 2». For the X-ray analysis of the synthesis products was using a diffractometer DRON-3M (CuK_α-radiation). A size and form of crystals were determined using optical and electronic microscopes.

3. Results and discussion

The investigations of kinetics and mechanism of formation of fine crystalline complicated oxides ($MgAl_2O_4$, $ZnAl_2O_4$, $LaAlO_3$, $Y_3Al_5O_{12}$, $BaFe_{12}O_{19}$ and $LiNbO_3$) in water vapor in sub- and supercritical conditions (P = 2–25 MPa, T = 200–400°C) and in soft hydrothermal conditions shown that the process of synthesis of complicated oxides in these conditions is multistage. It proceeds through the formation of solid phase intermediate representing the hydrated forms of precursor. The

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DOI: 10.1007/s10853-006-7411-0

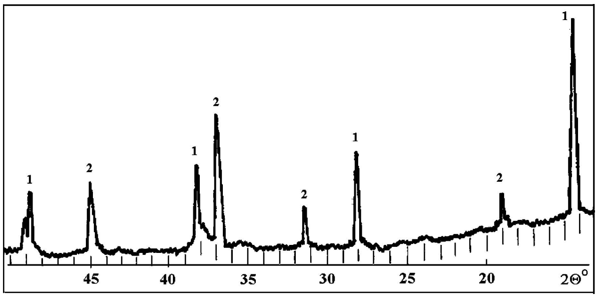

Figure 1 X-Ray diffraction pattern of the products of $MgAl_2O_4$ synthesis at T = 380°C, P = 18 MPa, t = 13 h. Phase 1—boehmite, phase 2 –magnesian spinel [3].

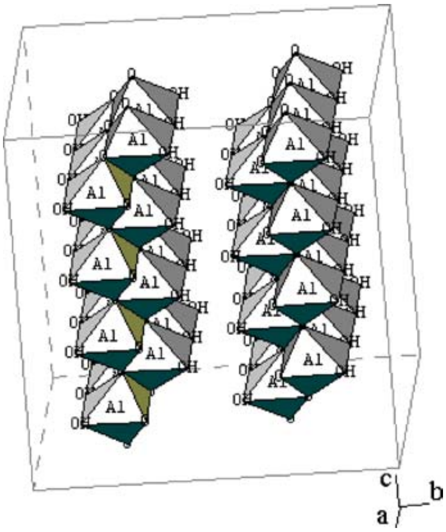

Figure 2 The local structure of boehmite (AlOOH).

conditions of intermediate formation influence on final stage of complicated oxides synthesis. The rate of the process, the properties of a final product, such as a habitus, degree of perfection and sizes of crystals depend on feature of structure of intermediate. The researches shown that the optimum realization of complicated oxides synthesis is two-stages, with isothermal exposure at the stage of the intermediate formation (200–300°C) and then at the stage of formation of the complicated oxide structure (350–400°C).

3.1. Magnesian spinel ($MgAl_2O_4$)

In the process of magnesian spinel formation during water vapor treatment of mixture of aluminium hydroxide and magnesia as intermediate phase was revealing the boehmite. It was shown by X-ray analysis that time magnesia was amorphous at the same. Fig. 1 presents the composition of products at intermediate stage (T = 380°C, t = 13 h).

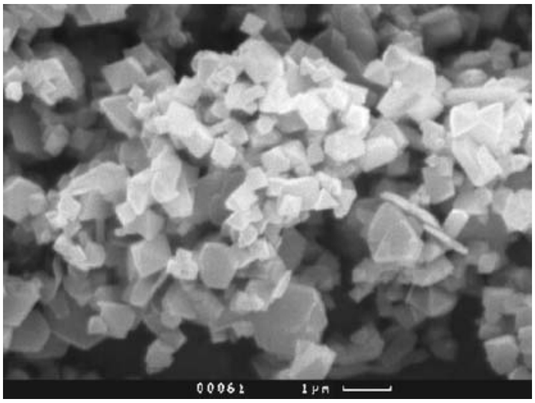

Figure 3 SEM photographs of crystals of $MgAl_2O_4$.

It shows that except the final product of synthesis, the spinel, only boehmite is formed [3]. Boehmite (γ-AlOOH) has bedded structure described by orthorhombic type of symmetry [4]. The magnesium cations diffuse in structure of boehmite. In reactionary system numerous acts of hydro-dehydroxylation occur. In these conditions the processes of diffusion and distribution of magnesium cations along the interlayer spaces and into lattice vacancies of boehmite are intensified. The crimped layers consisting from aluminum-oxygen octahedrons have a closest packing of oxygen (Fig. 2).

During dehydration of boehmite in water fluid from crimped layers of aluminum-oxygen octahedrons starts to be formed cubic anionic sublattice of spinel. At this time, the intensive diffusion of magnesium cations with the subsequent occupation tetrahedral and octahedral interstices in cubic oxygen packing is carried out. Magnesium ions stabilise the cubic oxygen sublattice of spinel structure. In result the fine crystalline (0.5−2.0 μm) magnesian spinel was generated (Fig. 3).

3.2. The gahnite ($ZnAl_2O_4$)

The crystalline structure of a gahnite is structural analog of a spinel $MgAl_2O_4$: the cubic symmetry of a lattice is featured by Fd3 m (Oh7) a space group of symmetry, ions Zn^{2+} (it is similar to ions Mg^{2+} in Mgspinel) occupy tetrahedral A—positions, the ions of aluminum are in octahedral B—positions [5].

The solvothermal method in combination with treatment in supercritical water fluid allows to obtain fine crystalline (0.2−0.5 μm) single-phase pure and doped gahnite (Fig. 4). As precursors for synthesis of gahnite were utilized aluminum hydroxide and zinc oxide. As doping compounds were salts: $Cu_2(OH)_2CO_3$ and $Ce(NO_3)_3{\cdot}6H_2O$. The designed by us method of gahnite synthesis consists in two-stage treatment of an intermixture of precursors: at first in hydrothermal, and then in supercritical conditions: under T = 200°C and then under T = 400°C and P = 260 MPa. This operation arises from the mechanism of formation of zinc aluminate in medium sub- and supercritical water. It was established that the

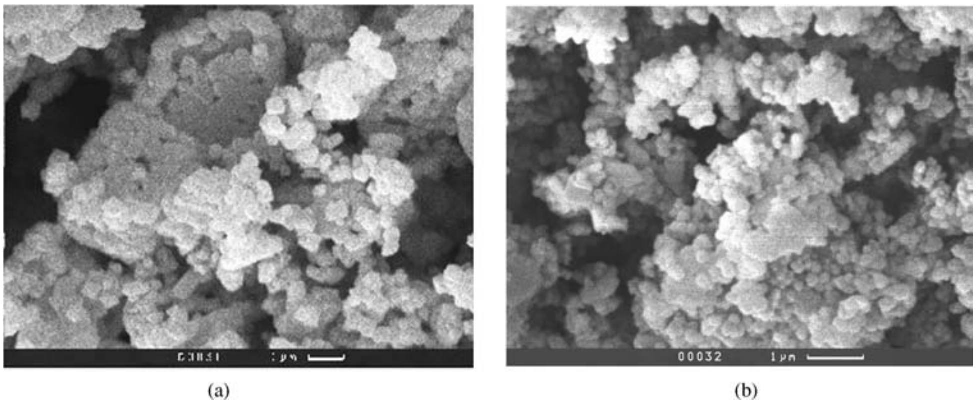

Figure 4 SEM photographs of gahnite crystals doped by copper (a) and by cerium (b).

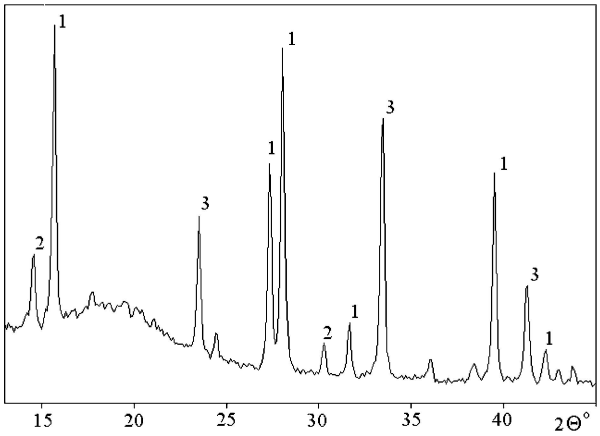

Figure 5 X-Ray diffraction pattern of products of hydrothermal treatment of mixture of hydrargillite with zinc oxide at of 200°C. Phase 1—AlOOH, phase 2—ZnO, phase 3—$ZnAl_2O_4$.

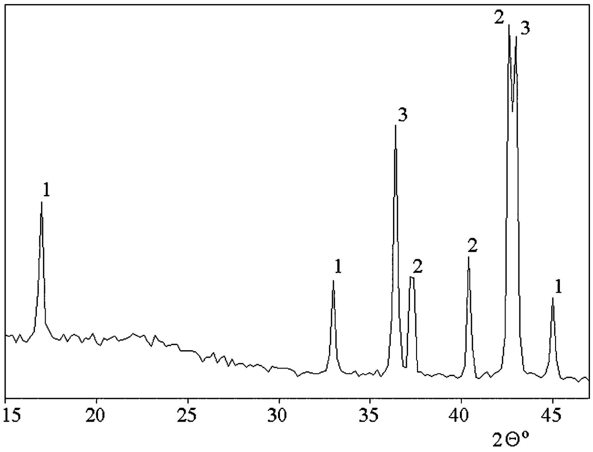

Figure 6 X-Ray diffraction pattern of products of $LaAlO_3$ synthesis from aluminium hydroxide and lanthanum oxide (at first under 200°C, 24 h and then under 380°C, 18 h). Phase 1—$La(OH)_3$, phase 2—LaOOH, phase 3—$LaAlO_3$ (44%).

formation of aluminate structure proceeds two-stage, just as in case of magnesian spinel. At first at $T = 200°C$ will be mainly formed solid intermediate - boehmite (γ-AlOOH) and a few gahnite (Fig. 5). At higher temperatures $T = 380–400°C$ and pressures $P = 2-26$ MPa the implantation and diffusion of the second component (zinc ions) into aluminous matrix of boehmite increase and arises of spinel. The mobility of oxygen skeleton and presence of considerable amount of the generated defects such as oxygen vacancies at a stage of dehydration boehmite promote also the diffusion of a doping component in a matrix of formed gahnite.

The way of incorporation of doping cation in structure of zinc aluminate depends on a chemical nature of a doping component (radius of cations, valent state etc.). Therefore, the chrome isomorphously substitutes aluminum in aluminum-oxygen octahedrons and larger cations place in structure of spinel interstitially. The doped by Cu and Ce gahnite was utilized as three way catalysts (TWC), providing simultaneous conversion of hydrocarbons, of monoxide of carbon and oxides of nitrogen [6].

3.3. The lanthanum aluminate ($LaAlO_3$)

In case of the synthesis of lanthanum aluminate the mechanical mixture of aluminium hydroxide and lanthanum oxide was used as precursor. Thermovaporous treatment was designing in range of 200–400°C and pressure of 2–26 MPa. As intermediate were revealing oxyhydroxide LaOOH and hydroxide $La(OH)_3$ with a dominance of the last one. The aluminous component is fixed by X-ray analysis as a small amount (~3 %) of boehmite. The main part of the aluminous component was amorphous for X-ray. The presence of the amorphous aluminous component in the sample was confirmed by availability of halo on the diffraction pattern near of angle $2\theta = 20°$ (Fig. 6).

The halo disappears completely at the synthesis final stage. The formation of aluminate proceeds by diffusion of aluminium ions into a matrix of lanthanum hydroxide. At this stage the reorganisation of hexagonal oxygen sublattice of $La(OH)_3$ in cubic $LaAlO_3$ happens [7].

This process is facilitated due to mobility of La-O matrix in quasi-equilibrium conditions of dehydration

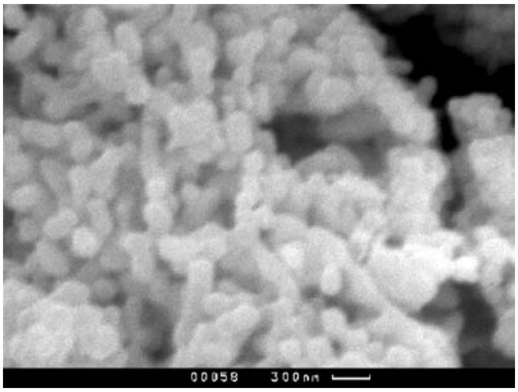

Figure 7 SEM photographs of crystals of $LaAlO_3$.

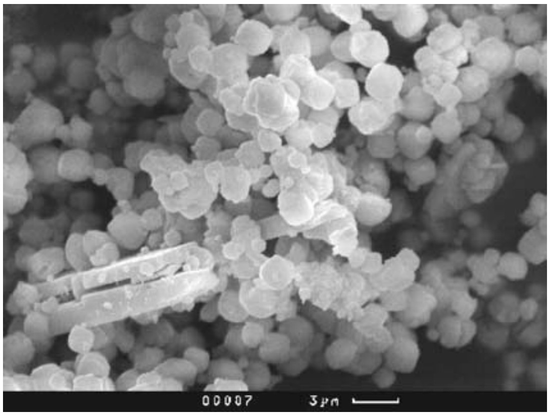

Figure 8 SEM photographs of synthesized crystals of $Y_3Al_5O_{12}$ with residual crystals of $Y(OH)_3$.

in water fluid. At higher temperature (>370°C) the complete formation of the new phase-$LaAlO_3$ was realized. The obtained lanthanum aluminate was fine crystalline powder with size of crystals from 200 to 300 nm (Fig. 7).

3.4. The yttrium–aluminium garnet ($Y_3Al_5O_{12}$)

Mechanism of formation of fine crystalline yttrium-aluminum garnet (YAG) in hydrothermal and thermovaporous conditions was similar to the mechanism of formation of lanthanum aluminate. In both cases the formation of aluminates begins from appearance of crystalline intermediate with structure—Me(OH)n and amorphous alumina [8]. For example, yttrium-aluminum garnet ($Y_3Al_5O_{12}$) was synthesized from stoichiometric mixture of yttrium and aluminum oxides in the temperature range 200–400°C under pressure of water vapor 2−26 MPa. It was established by X-ray that in quasi-equilibrium with water vapor conditions the synthesis of YAG proceeds with formation of intermediate $Y(OH)_3$ and amorphous aluminous component. The diffusion of aluminium ions into $Y(OH)_3$ matrix resulted in the reorganization of oxygen sublattice accompanied with dehydration [9]. In products of synthesis were revealed by SEM the prismatic crystals of $Y(OH)_3$ and isometric crystals of YAG (Fig. 8). The obtained powder of YAG consists of isometric crystals with size in interval 1–3 μm.

Synthesized garnet contains 5–7% of water that corresponds to hydrogarnet structure. The water was removing after annealing at 1200°C and garnet with regular structure was formed.

The kinetics of garnet formation is describing by the Avrami–Erofeev equation of solid-phase transformation [9]: $\alpha = 1-\exp[-(kt)^n]$; where k is the rate constant and n is the crystalline seeds nucleation mechanism parameter, which characterizes dimensional growth of crystals (Fig. 9).

3.5. The barium hexaferrite ($BaFe_{12}O_{19}$)

Barium hexaferrit (BHF) is magnetic medium, carrier for vertical magnetic high compact record and for storage of the information. Optimal shape of used BHF crystals for this purpose is thin fine plates (∼1 μm). The single-phase BHF with the required performances would be obtained under treatment in supercritical conditions (T = 400°C, P = 26 MPa) dry intermixture of γ—ferric oxide and barium hydroxide at the relation Fe_2O_3/BaO in an interval 3.2–4.0. The formation of plates of ferrite starts already at temperatures above 200°C. The investigations of products of transformation at low temperatures have allowed assume that the process goes through formation of intermediate FeOOH, in which structure diffuses the second component Ba^{+2}. Really, at usage FeOOH as precursor, the process of formation BHF completely flows past at 300°C. However, it is established that the magnetic performances are improved with increase of temperature of

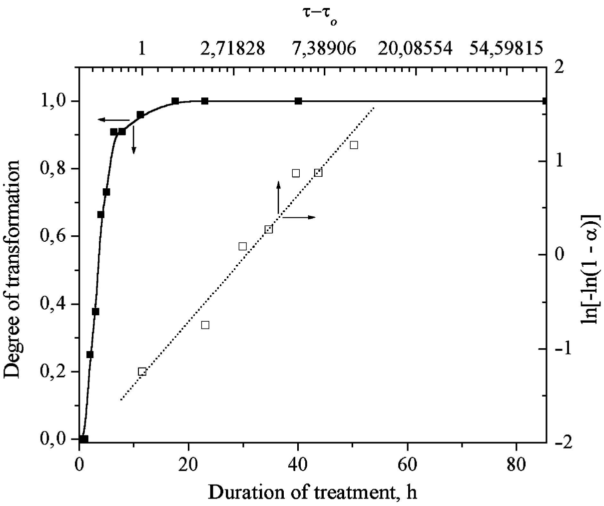

Figure 9 The kinetics curves of YAG formation at T = 300°C, P = 8.5 MPa and Avrami—Erofeev plots for this process.

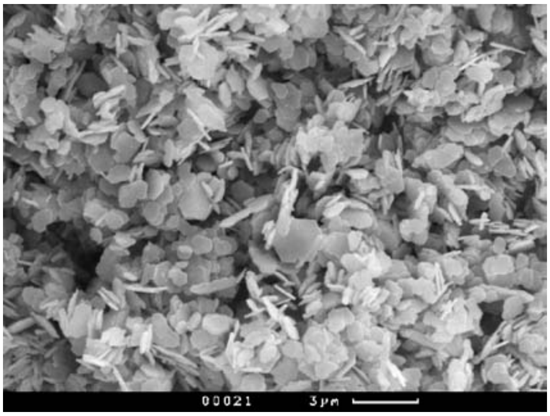

Figure 10 SEM photographs of synthesized crystals of $BaFe_{12}O_{19}$.

synthesis, transiting through a maximum at 400°C (P = 26 MPa).

Obtained in these conditions BHF represents of hexagonal plates by a diameter less than 2 microns and thickness 0.1–0.2 microns (Fig. 10) with the good magnetic performances: coercive force 1.7–2.0 KOe, specific saturation magnetization 50–60 emu/g the squareness of hysteresis curve 0.7–0.8 [10].

3.6. Lithium metaniobate ($LiNbO_3$)

The lithium metaniobate is a perspective material due to high piezoelectric, optical and mechanical characteristics [11]. The lithium metaniobate crystallizes in a ditrigonal-pyramidal class of rhombohedral syngony.

In conditions of hydrothermal (T = 300°C) and thermovaporous (T = 400°C, P = 26 MPa) treatments of an intermixture of lithium hydroxide and oxide or hydroxide of niobium the synthesis metaniobate proceeds through intermediate stages of niobates formation with various stoichiometric composition. Depending on kind of used raw material, oxide or hydroxide of niobium, in structure of intermediate the relation Li_2O/Nb_2O_5 from 3 up to 1/14 varies (equation 1 and 2). In the just same conditions, the generation rate of metaniobate from niobium hydroxide (equation 2) in some times exceeds the generation rate of metaniobate from niobium oxide (equation 1). It is necessary time for hydration of precursor before interaction with the second component Li^{+1} and by formation of new phase. This new phase ($3Li_2O{\cdot}Nb_2O_5$) is labile intermediate preceding formation of lithium metaniobate. During hydration of oxide niobium the diffusion of ions of lithium was facilitating that results in formation labile intermediate ($3Li_2O{\cdot}Nb_2O_5$) with the excess content of lithium. The rate of process in this case was determining by hydration of oxide niobium. In case of usage as precursor of niobium hydroxide this stage is absent and process was determined directly by diffusion of ions of lithium in crystals of niobium hydroxide and formation of labile intermediate ($Li_2O{\cdot}14Nb_2O_5$) with impurity ($Li_2O{\cdot}3Nb_2O_5$) (equation 2).

$$\mathrm{LiOH} + \mathrm{Nb_2O_5} \xrightarrow[\mathrm{H_2O}]{400^{\circ}\mathrm{C},\,26\,\mathrm{MPa}} 3\mathrm{Li_2O}\cdot\mathrm{Nb_2O_5}(\mathrm{Li_3NbO_4}) \rightarrow \mathrm{Li_2O}\cdot\mathrm{Nb_2O_5}(\mathrm{LiNbO_3}) \qquad (1)$$

$$\mathrm{LiOH} + \mathrm{HNbO_3} \xrightarrow[\mathrm{H_2}O]{400^{\circ}C,\,26\,\mathrm{MPa}} \frac{\mathrm{Li_2O}\cdot 14\mathrm{Nb_2O_5}}{\mathrm{Li_2O}\cdot 3\mathrm{Nb_2O_5}(\mathrm{LiNb_3O_8})} \rightarrow \mathrm{Li_2O}\cdot\mathrm{Nb_2O_5}(\mathrm{LiNbO_3}) \qquad (2)$$

The final product was the powder of lithium metaniobate with crystals from 1 to 10 μm, depending on conditions of synthesis (Fig. 11a and b). The analysis of kinetics of formation lithium metaniobate has shown that process satisfactorily is described by the equation typical for processes in solid phase: $-\ln(1-\alpha) = \mathrm{k}t^{n}$, where $n = 1.1$, $k = 0.135$.

Figs. 12 and 13 demonstrate kinetics of processes. This kinetics corresponds to kinetics of formation of fine crystalline yttrium-aluminum garnet and some fine crystalline oxides in these conditions of synthesis.

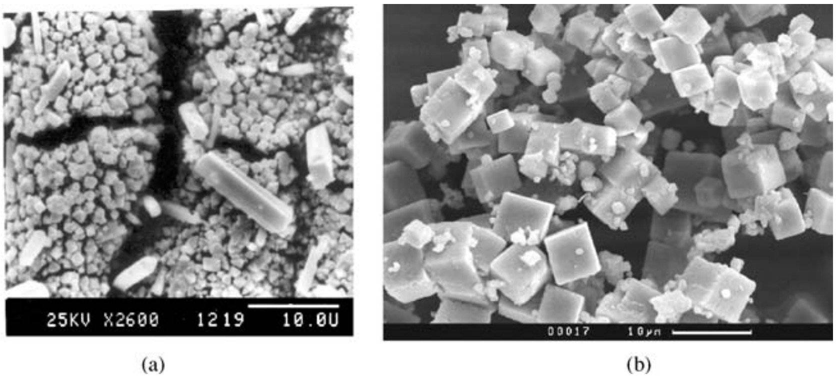

Figure 11 (a) Intermediate, conditions of synthesis: niobium hydroxide into container in autoclave, solution of lithium hydroxide on the outside of container in autoclave, 400°C, P = 26 MPa, (b) lithium metaniobate, conditions of synthesis: Niobium hydroxide and lithium hydroxide into container in autoclave, 400°C, P = 26 MPa.

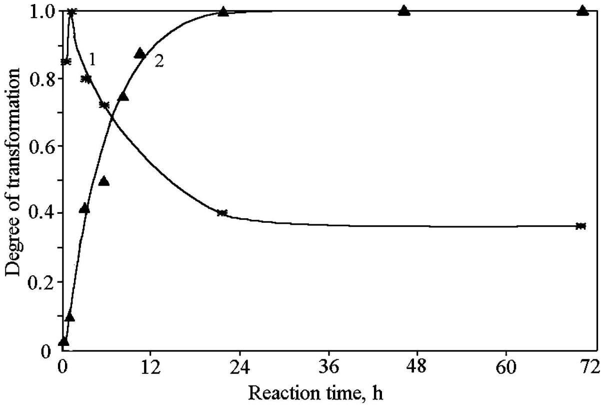

Figure 12 Dependence of degree of precursors transformation into $Li_2O{\cdot}14Nb_2O_5$ (1) and into $LiNbO_3$ (2) on time thermovaporous treatment (400°C, 26 MPa).

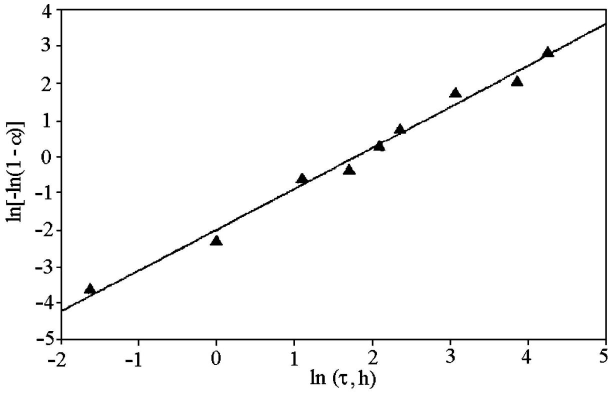

Figure 13 Avrami—Erofeev plots for process of formation $LiNbO_3$ ($T = 400°C$, $P_{H_2O} = 26 MPa$).

4. Conclusions

The investigations were designed to establish general regularity of formation of fine crystalline complicated oxides in sub- and supercritical water. The results have shown that the synthesis of lanthanum aluminate and yttrium–aluminium garnet in sub- and supercritical water occurs in solid phase with formation of intermediate solid phases, accordingly, lanthanum and yttrium hydroxides in crystalline form. An aluminous component is X-ray amorphous. It diffuses in matrix of crystalline intermediate and results to reorganization of oxygen sublattice and dehydration of intermediate with formation of these complicated oxides. During of synthesis of magnesium spinel and gahnite, the intermediate was the solid-phase aluminium oxyhydroxide (boehmite) and the amorphous components of Mg and Zn. These ions diffuse along interlayer spaces of boehmite. During synthesis of barium hexaferrite and lithium metaniobate as intermediates were solid-phase hydroxides of niobium and ferric iron, second components (hydroxides of lithium and barium) were in amorphous state.

By summing results of investigations of the mechanism of complicated oxides formation in water vapor, it is possible to mark out the following general regularity:

- The process of formation of complicated oxides under thermovaporous treatment is multistage and occurs in solid phase.
- At the first stage the hydration of precursors results in origin of hydroxylated intermediate substance—hydroxide or oxyhydroxide of one of components. The second component will be hydrated and amorphous.
- The formation of complicated oxide structure carried out due to diffusion of the second component ions in solid intermediate. At that happens reorganization and dehydration of structure of intermediate and starts formation of a new phase—complicated oxide.
- At introduction into a reactionary medium of doping ions, they will be diffused together with ions of the second component into structure of intermediate and the doped complicated oxide will be obtained.
- The doping ions facilitate the embedding of the second component into structure solid intermediate, due to what the process of formation of complicated oxide is accelerated. The doping during the synthesis allows to modify purposeful the characteristics of obtained complicated oxides.

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Received 19 August 2004
and accepted 11 April 2005