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KINETIC MODEL AND MECHANISM OF Y$_3$Al$_5$O$_{12}$ FORMATION IN HYDROTHERMAL AND THERMOVAPOROUS SYNTHESIS

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Kinetics and mechanism of fine-crystalline yttrium–aluminum garnet (YAG) formation under hydrothermal and thermovaporous treatment were investigated. It was synthesized from the stoichiometric mixture of oxides in the temperature range 200–400°C at pressures of water vapor 4.0–26 MPa. It was established that in quasi-equilibrium with water vapor conditions the synthesis of YAG proceeds with formation of intermediate substance with Y(OH)$_3$ structure and amorphous aluminous component. The diffusion of this aluminous component into the Y(OH)$_3$ matrix resulted in the reorganization of oxygen sublattice accompanied with dehydroxylation. The kinetics of YAG formation is described by the equation of solid-phase transformation with the limiting stage of nucleation. Synthesized YAG contains 5–7% of water, which corresponds to a hydrogarnet structure. The study of luminescence properties of YAG doped with Nd^{3+} or Cr^{3+} ions has allowed to determine the positions of hydroxyl groups and oxygen vacancies in the structure.

Keywords: Hydrothermal synthesis; Thermovaporous treatment; YAG; Solid-phase transformation

INTRODUCTION

The investigation of the processes of synthesis of fine-crystalline simple oxides at temperatures of 200–400°C in water vapour at 0.2–30 MPa

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pressures (conditions of thermovaporous treatment – TVT) showed [1, 2] that interaction of oxides with water vapors in the presence of special microadditive leads to a solid-phase transformation of oxides. On the other hand the synthesis of these oxides at the open air is carried out at temperatures higher than 1000°C. The synthesis of yttrium–aluminum garnet (YAG) in air proceeds in the temperature range of 1250–1750°C [3–5]. The works on YAG synthesis from oxides under hydrothermal conditions at temperatures of 500–600°C and pressures of 70–170 MPa in 6–10% carbonate solutions of K and Na are known [6–9]. Under such tough hydrothermal conditions, the processes of dissolving the oxides in fluid and crystallization of product play the main role.

The present work is devoted to the study of mechanism of solid-phase interaction of yttrium oxides and aluminum with YAG formation under thermovaporous and hydrothermal conditions: in the temperature range of 200–400°C and water vapor pressures of 1.5–26 MPa. The difference between hydrothermal and thermovaporous conditions of synthesis consists in that the hydrothermal process is carried out in a liquid and in a fluid, and in the second case – in an atmosphere of a water vapor at pressures is lower 30 MPa.

EXPERIMENTAL

The oxides of highest purity grade were used in the present work: yttrium oxide having particles with dimension less than 5 μm and aluminum oxide – feeble crystallized θ-Al_2O_3 with particles of no more than 3 μm. The oxides of neodymium (highest purity grade) or chromium ions (in $(NH_4)_2Cr_2O_7$ salt) were introduced into a mixture of yttrium oxides and aluminum. The content of neodymium or chromium in oxides mixture was 0.1–1% at. The ions Nd^{3+} and Cr^{3+} were used as luminescence sondes. The thermovaporous and hydrothermal treatment were carried out in stainless steel autoclaves with volume 16 cm^3. The oxides mixture (0.7 g) was introduced in a stainless steel container. This container with oxides was placed on a support inside the autoclave. The distilled water was added into the container or in the autoclave bottom outside of the container. In the latest case a mixture of oxide remained dry. The synthesis was done in the presence

of process activators (ammoniac salt of organic acids 0.5 – 5.0% mass). A degree of filling of autoclave by water was equated to 0.16. The autoclaves were treated in isothermal conditions under temperatures of 200 – 400°C. The time of autoclave heating to the needed temperature was of 0.7 – 1 h. The time of isothermal heating was calculated after getting the needed temperature. Then, after cooling the autoclave and condensing water vapors on the bottom of autoclave, the dry product was taken out and investigated by X-ray diffraction, IR-spectroscopy, thermal analysis, photoluminescence and electron microscopy. Quantitative analysis carried out on integrated intensities of XRD reflexes of phases YAG and $Y(OH)_3$ in select intervals. The XRD reflexes of boehmite were expressed indistinctly, in this connection the content boehmite determined by a method of a IR-spectroscopy on absorption band $1074 \, cm^{-1}$. IR-spectroscopical analysis of samples (1% in KBr tablets) was made using IR-75 spectrometer in a frequency range of $400 – 4000 \, cm^{-1}$. The photoluminescence was registrated on SDL-2M spectrometer in a range of 260 – 1200 nm. The crystal dimensions and habitus were measured by use of SEM Jeol JSM-35CF. Thermal analysis was performed on Q-1500D ("MOM") derivatograph in a dynamic regime at a heating rate of 7.5°/min in the temperature range 20 – 1200°C.

RESULTS AND DISCUSSION

The test performed showed that the lowest temperature of YAG formation under hydrothermal conditions is ca. 260°C. At the temperature below, the synthesis product contains yttrium hydroxide, boehmite traces and X-ray amorphous aluminum oxide. In this case, a wide halo is registrated in a diffractogramm in the range of $2\theta = 13 – 25°$ with a maximum at 18°. During 40 h at 270°C formation of YAG is about 50% and at 300°C the formation is completed. The main amount of aluminum containing component stays amorphous during reaction. The synthesis under water vapours is going in the same way. The synthesized crystals of YAG have dimensions of 1 – 5 μm. After the synthesis under thermovaporous conditions the crystals have clear rhombododecahedral habitus. Crystals of YAG synthesized under hydrothermal conditions have no defined form.

The kinetics of transformations under hydrothermal conditions was investigated at temperatures 270°C and 300°C (Fig. 1). The YAG formation is preceded by the induction period of 1 h at 300°C and 6 h at 270°C. During induction period, only X-ray reflexes of yttrium hydroxide lattice are registrated. The presence of induction period indicates the complicity of YAG initial formation, which is going on base of intermediate product with yttrium hydroxide structure. A kinetics of transformations can be described (Fig. 1) by the equation of solid-phase process with a constant nucleation rate [10, 11] $\alpha = 1 - \exp(-kt)$, where α – degree of transformation, k – a constant of rate. The rate of reaction is controlled by nucleation. The estimation of activation energy on base of temperature dependence of k gives the amount of 162 kJ/mol.

The specifics of oxides interaction under conditions mentioned is an intensive hydroxylation of their structures. In the absence of aluminum oxide, at 300°C yttrium oxide completely transforms into yttrium hydroxide, which does not change after isothermal treatment. In the absence of yttrium oxide, during 5 h of hydrothermal treatment at 300°C aluminum oxide completely transforms to boehmite. The influence of additive of yttrium oxide onto boehmite formation from aluminum oxide is shown in Figure 2. With yttrium oxide content up to 0.66% by weight in a mixture with aluminum oxide, the boehmite
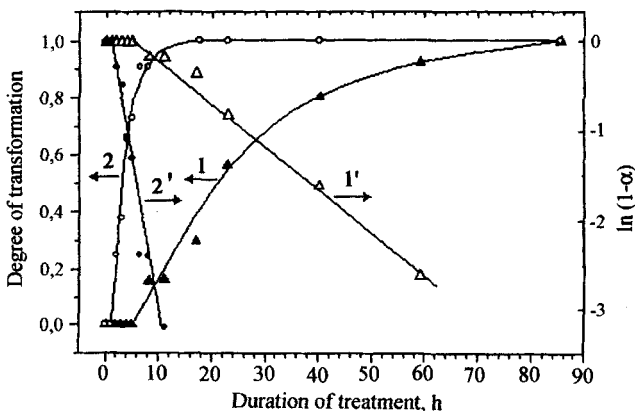

FIGURE 1 The kinetics of YAG formation and anamorphose of kinetic curves in coordinates $\ln(1 - \alpha) - \tau$. 270°C – 1, 1', 300°C – 2, 2'.
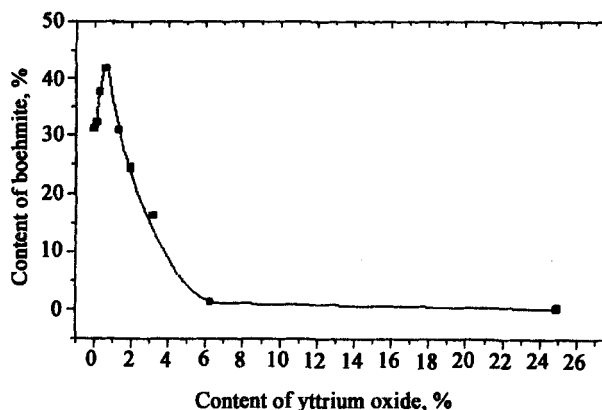
FIGURE 2 The influence of yttrium oxide addition onto boehmite formation during hydrothermal treatment of aluminum oxide: 1 h, 300°C.
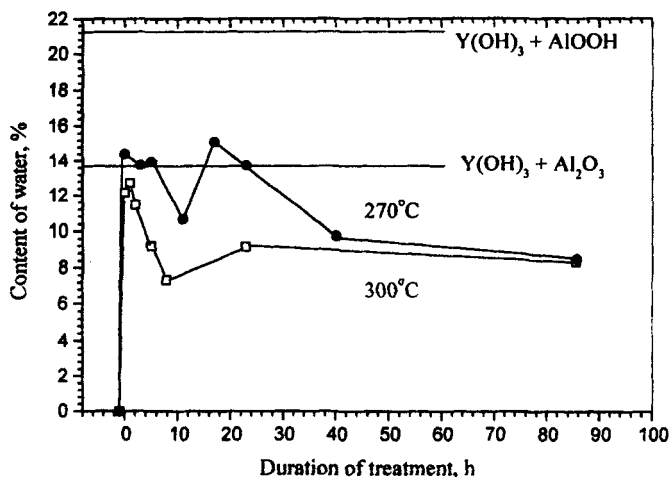
FIGURE 3 A change of water content in synthesis products in dependence from the duration of hydrothermal treatment of oxides mixture at 270°C and 300°C.

formation accelerates, and with Y_2O_3 amount of more than 6% by weight it goes slower. Thus, the hydroxylation of aluminum oxide into boehmite stops in stoichiometric mixture (57.06% Y_2O_3) of yttrium and aluminum oxides. The amount of structural water in products of oxides mixture treatment decreases after rising of the synthesis temperature from 270 to 300°C (Fig. 3), but after long treatment at

270 and 300°C this amount becomes quasi equal. The calculated amount of water, that is needed for hydroxylation of aluminum oxide into boehmite and yttrium hydroxide (line above), and also of yttrium oxide into yttrium hydroxide (line below) is indicated in Figure 3. One can see that at temperature 270°C the maximal water amount in samples is in accordance with total hydroxylation of yttrium oxide and partial hydroxylation of aluminum oxide. At the same time, at 300°C the maximal amount of water in samples is lower than needed even for hydroxylation of yttrium oxide to hydroxide. Relative maximum of water content corresponds to the end of induction period (1 h at 300°C and 6 h at 270°C). The beginning of YAG formation is accompanied with strong dehydroxylation. Then, the amount of water in samples passes through its maximum again. Strong decrease of water content in samples changes into secondary hydroxylation after formation of about 20% YAG at 270°C and 90% at 300°C.

The changement of structural water distribution in various forms during treatment of oxides at 300°C is shown in Figure 4. In the beginning of treatment, more than 80% of water is removed during thermal analysis at temperatures below 510°C, having maxima at 300°C and 460°C. This character of water elimination is known [12] for
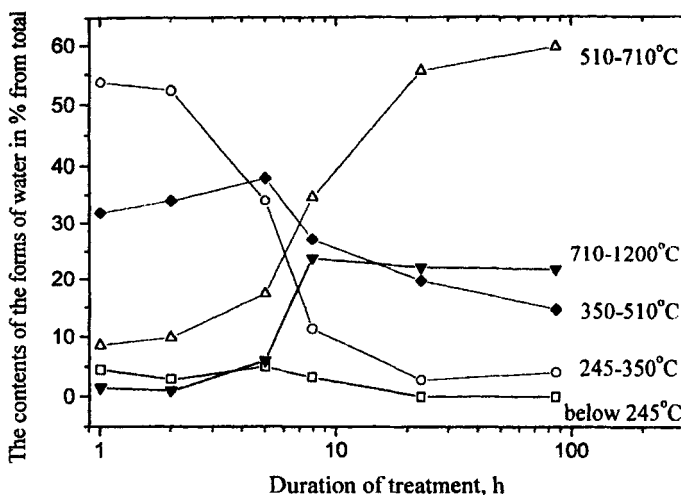

FIGURE 4 Dependence of water distribution into various forms from synthesis time at 300°C.

$Y(OH)_3$ decomposition in yttrium oxide with intermediate formation of YOOH and two maxima of dehydroxylation at 314° and 474°C. From Figure 4 it is visible, that the increase of transformation is accompanied by reallocation of hydroxyl groups into forms with higher bond energy. The character of changement in total water content in product structure (Fig. 3) says about a different water capacity of these forms.

The band in IR-spectrum at $3600\,cm^{-1}$ are typical for a hydroxyl-group in structure of $Y(OH)_3$. The changement of concentration of hydroxyl-group during synthesis of YAG is shown in Figure 5. The time of transformation is normalized to duration of induction period. Two relative maxima in the beginning and in the middle of transformation are related to a change of $Y(OH)_3$ into intermediate product and following formation of YAG. The change in hydroxyl state in coordination sphere of yttrium ions is evidently connected with the modification of yttrium hydroxide by aluminum ions. The diffusion of aluminum ions into yttrium hydroxide is also indicated by increase in unit cell parameters of $Y(OH)_3$ (Tab. I) during induction period. At the same time, the initial values are the same as characteristics of pure yttrium hydroxide phase, which was synthesized under the same conditions, but in the absence of Al_2O_3.
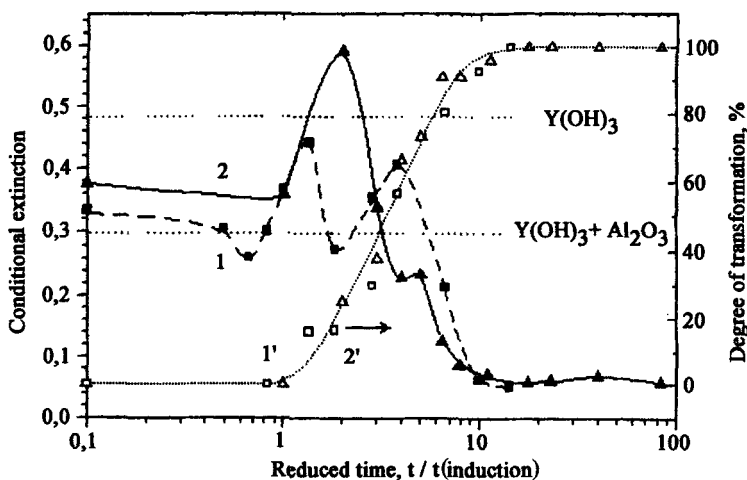

FIGURE 5 Dependence of hydroxyl groups content showing IR band at $3600\,cm^{-1}$ from reduced time of hydrothermal treatment. The time is normalized onto duration of induction period. 270°C − 1, 1', 300°C − 2, 2'.

TABLE I The change of the unit cell parameters of $Y(OH)_3$ during synthesis of $Y_3Al_5O_{12}$

	$Y(OH)_3$		
Sample	$a, \AA$	$c, \AA$	Volume
*$Y(OH)_3$, hydrothermal treatment of Y_2O_3 at 300°C, 85 h	6.2670(4)	3.5467(3)	120.63(2)
Product of hydrothermal synthesis, 300°, 0 h	6.2666(5)	3.5463(4)	120.61(2)
Product of hydrothermal synthesis, 300°, 2 h	6.2694(6)	3.5487(5)	120.80(2)

*The synthesis of $Y(OH)_3$ from Y_2O_3 is carried out in the same way as the synthesis of $Y_3Al_5O_{12}$.

TABLE II The unit cell parameters of $Y_3Al_5O_{12}$

	$Y_3Al_5O_{12}$	
Sample	$a, \AA$	Volume
YAG, 300°, 85,3 h	12.0516(8)	1750.4(3)
YAG 300°, 85,3 h after heating at 1200°C	12.0224(7)	1737.7(3)

The structural water partly remains in formed $Y_3Al_5O_{12}$. Its amount decreases with the synthesis temperature rise, for YAG samples, which are synthesized at 400°C during 40 and 400 h it is equal to 5.44%. The presence of hydroxyl groups in synthesized samples of YAG is a result of substitution of a part of tetrahedra $[AlO_4]$ onto tetrahedra $[OH]_4$ with a formation of hydrogarnet [13–15]. This substitution should lead to the increase in unit cell parameter without changement of its symmetry (Ia3d) [13]. The hydroxyls in tetrahedra strongly influence each other, and wide band in IR-spectrum at $3300 \, cm^{-1}$ is related to these hydroxyl groups. The unit cell parameters of synthesized YAG are increased (Tab. II), and boehmite is present in the products of long treatment of oxides mixture at 270°C and 300°C (6% and 4.2% of boehmite relatively). The forming of boehmite is a result of a presence of hydroxyl groups protons in the structure of YAG, which are not substituted by aluminum ions. The heating of YAG sample up to 1200°C is accompanied by water release. In this connection, the unit cell parameters decrease (Tab. II) and in IR-spectrum the band at $3600 \, cm^{-1}$ disappears and intensity of band at $3300 \, cm^{-1}$ decrease. Then the impurity of Y_2O_3 appears. The elimination of hydroxyl groups leads to changement of stoichiometry of hydroxylated YAG and formation of water-free YAG. Moreover, the elimination of hydroxyl groups has an influence onto neodymium luminescence. The

changement are well seen, when comparing (Fig. 6) the spectra of luminescence and spectra of luminescent excitation of synthesized samples of hydroxylated YAG and powdered water-free monocrystal of YAG having 1% at. of neodymium, which have been grown by means of high-temperature synthesis. In presence of hydroxyl groups in YAG, the width of luminescence bands of Nd^{3+} increases and some bands in a spectrum of luminescent excitation of Nd^{3+} disappears. Neodymium substitutes yttrium ions in a structure of YAG, and Cr^{3+} ion substitutes octahedral aluminum ions [16]. The Cr^{3+} luminescence indicates two types of luminescent centers. The first is related to chromium ions in a structure of YAG [16] (luminescent bands at 687.3 nm and 688.3 nm), the second – to chromium ions in ruby (bands at 692.4 nm and 693.9 nm). Bands of ruby luminescence are absent in a spectrum of monocrystal YAG: Cr, but they appear after mechanical grinding together with the bands of F-centers (wide bands at ca. 370 nm and 460 nm [17]) due to a forming of oxygen vacancies during destruction of structure. The presence of ruby bands and bands of F-centers in luminescence spectra of synthesized samples of YAG proves the appearance of oxygen vacancies during dehydroxylation of matrix in YAG structure formation. Luminescent properties of neodymium and chromium ions allow to conclude that hydroxyl
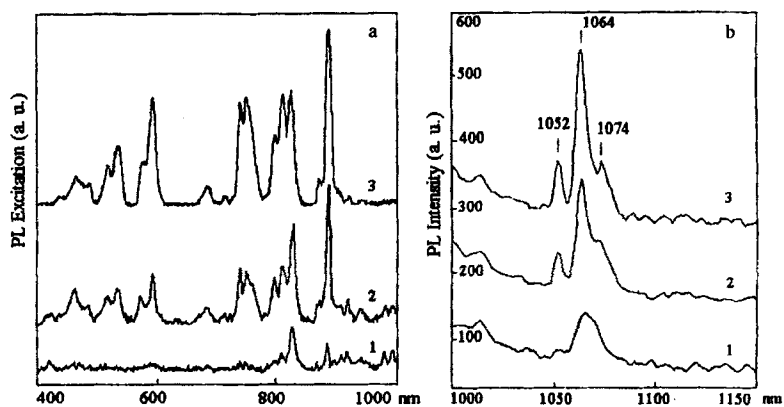

FIGURE 6 Spectra of luminescence excitation 1064 nm (a) and luminescence spectra (b) of YAG samples doped with Nd: 1 – synthesized YAG sample with hydroxyl groups, 2 – the same sample, treated 4h at 1100°C, 3 – powder of water-free monocrystal.

groups are located in the tops of tetrahedra (Fig. 7), having joint side with dodecahedra of yttrium, and that a part of position in joint tops of octahedra and of second type tetrahedra is vacant.

The results obtained can be explained on a base of views [1, 2, 19] about quasiequilibrium hydroxylation of oxides under conditions of high temperatures and water vapor pressures. In the beginning of transformation a hydroxylation process dominates. Then, with a raise of hydroxyl groups content, the rate of dehydroxylation stage becomes comparable to hydroxylation. In the conditions of quasiequilibrium of hydroxylated oxides with water medium, a solid-phase transformation and structural ordering are the result of the selection and accumulating of position with highest bond energies during breakage and appearance of bonds Me —O —Me and Me —OH in acts of hydroxylation–dehydroxylation. These processes provide high solid-phase mobility. Aluminum ions diffuse into the structure of yttrium hydroxide, forming intermediate product with the increased content of hydroxyl groups. The aluminum ions begin to participate in a selection of structural positions at the end of an induction period. It leads to the dehydroxylation of intermediate product. Thus the aluminum ions occupy octahedral positions and part of tetrahedral positions with structure formation of hydroxylated YAG. In this case the
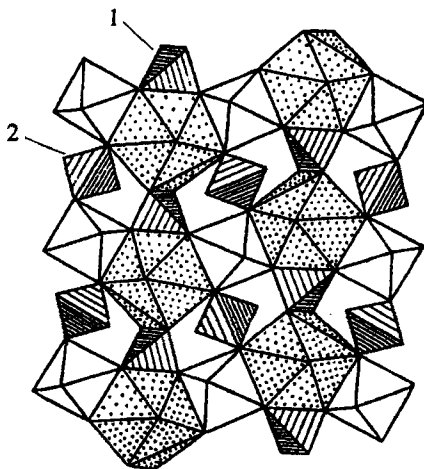

FIGURE 7   The YAG structure [18]: a joint location of YO_8 – dodecahedra (pointed with points) with AlO_4 – octahedra and with two types of AlO_4 – tetrahedra.

formation of intermediates as $Y_4Al_2O_9$ and $YAlO_3$ is not observed. At the same time, these compounds are common for high-temperature processes of synthesis. The hydrothermal treatment of mixture of yttrium oxide and aluminum oxide (ratio $1:1$) under conditions used does not lead to $YAlO_3$ formation. Thus, the mechanism of hydrothermal synthesis YAG differs from the mechanism of high-temperature synthesis in that the formation of a finished product occurs through hydroxylated intermediate compounds.

Acknowledgements

References

[1] Lazarev, V. B., Panasyuk, G. P., Voroshilov, I. L., Boudova, G. P., Danchevskaya, M. N., Torbin, S. N. and Ivakin, Yu. D. (1996). New Ecologically Pure Technologies of Fine-Crystalline Materials, *Ind. Eng. Chem. Res.*, **35**, 3721.

[2] Danchevskaya, M. N., Panasyuk, G. P. and Lazarev, V. B. (1991). Fine-Crystalline Materials Producing, *Zh. Vsesojuzn. Khim. Obsch. Imeni D.I. Mendeleeva*, **36**, 706.

[3] Glushkova, V. B., Krzhizhanovskaya, V. A., Egorova, O. N., Udalov, Yu. P. and Kachalova, L. P. (1983). Vzaimodeistvie oksidov ittriya i alyuminiya, *Izv. Akad. Nauk SSSR Neorg. Materialy*, **19**, 95.

[4] Neiman, A. Ya., Tkachenko, E. V., Kvichko, L. A. and Kotok, L. A. (1980). Usloviya i makromehanizm tverdofaznogo sinteza alyuminatov ittriya, *Zh. Neorg. Khim.*, **25**, 2340.

[5] Zinoviev, S. Yu., Krzhizhanovskaya, V. A. and Glushkova, V. B. (1989). Osobennosti tverdofaznogo sinteza scandiisoderzhaschih alyuminievyh i gallievyh granatov, *Izv. Akad. Nauk SSSR Neorg. Materialy*, **25**, 808.

[6] Mill, B. V. (1967). Gidrotermalnyi sintez alyuminievyh i gallievyh granatov, *Crystallografiya*, **12**, 158.

[7] Puttbach, R. C., Monchamp, R. R. and Nielsen, J. W. (1967). Hydrothermal Growth of $Y_3Al_5O_{12}$, *J. Phys. Chem. Solids (GB)*, **1**, 569.

[8] Kolb, E. D. and Laudise, R. A. (1975). Phase equilibria of $Y_3Al_5O_{12}$ hydrothermal growth of $Gd_3Ga_5O_{12}$ and hydrothermal epitaxy of magnetic garnets, *J. Cryst. Growth*, **29**, 29.

[9] Takamori, T. and David, L. D. (1986). Controlled nucleation for hydrothermal growth of yttrium–aluminum garnet powders, *Am. Ceram. Soc. Bull.*, **65**, 1282.

[10] Delmon, B., *Introduction a la cinétique hétérogéne* [Éditions Technip. 7 rue nélaton, Paris 15e, 1969].

[11] Brown, M. E., Dollimore, D. and Galwey, A. K., *Reactions in the solid state*, In: *Comprehensive chemical kinetics*, **22** [Elsevier Scientific Publishing Company, Amsterdam–Oxford–New York, 1980].

[12] Klevtzov, P. V. and Sheina, L. P. (1965). Termo i rentgenograficheskoe izuchenie kristallicheskih gidrookisei redkozemelnyh elementov i ittriya, *Izv. Akad. Nauk SSSR. Neorg. Materialy*, **1**, 2219.

[13] Schröpfer, L. and Bartl, H. (1993). Oriented decomposition and reconstruction of hydrogarnet $Ca_3Al_2(OH)_{12}$, *Eur. J. Miner.*, **5**, 1133.

[14] Lager, G. A., Armbruster, Th. and Faber, J. (1987). Neutron and X-ray study of hydrogarnet $Ca_3Al_2(OH)_{12}$, *American Mineralogist*, **72**, 756.

[15] Mill, B. V., Isomorphism in a structural type of garnet. In: *Magnetic and crystalochemistry researches of ferrite* [Moscow, MSU, 1971], p. 56.

[16] Wall, W. A., Karpick, J. T. and Di Bartolo , B. (1971). Temperature dependence of the vibronic spectrum and fluorescence lifetime of $YAG:Cr^{3+}$, *J. Phys. C: Solid St. Phys.*, **4**, 3258.

[17] Graver, V. E. and Kruminsh, I. Ya., Zentry F-tipa v termohimicheski obrabotannyh ittrii-aluminievyh granatah, *Thermoactivation spectroscopy defects in ionic crystals* [Riga, 1983], p. 145.

[18] Godovikov, A. A., *Mineralogiya* [Moscow, Nedra, 1983], p. 290.

[19] Ivakin, Yu. D., Danchevskaya, M. N., Muravieva, G. P. and Torbin, S. N. (1997). Photolumineszentnoe issledovanie defektoobrazovaniya pri tverdofaznom prevraschenii kremnezema v usloviyah termoparovoi obrabotki, *Vestnik MGU, seriya 2, Khimiya*, **38**, 312.