

Crystals Growth of Complex Oxides in Supercritical Water Fluid

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The report presents the results of the formation mechanism investigation and growth of crystals of barium titanate and yttrium aluminum garnet, synthesized and doped with cerium in sub- and supercritical water vapor. The synthesis was carried out in laboratory autoclaves. The products of reaction were investigated by methods of X-ray diffractometry, SEM and TEM microscopy. It was found, that the synthesis of these compounds crystals in subcritical condition proceeds by way of formation of the spherical aggregates of weak-crystallized nano-particles of YAG:Ce as well as BaTiO₃:Ce. At this stage, the diffusion of cerium ions into intermediate products takes place. During the second step of synthesis, in supercritical conditions, the cocrystallization of particles in these aggregates occurs with appearing of a common crystal lattice. As a result of co-crystallization the well-formed micron-size monocrystals of garnet or barium titanate were produced.

INTRODUCTION

The problem of environmentally friendly and economical method for production of functional powder materials is relevant in connection with the rapid development of electronic industry. Complex metal oxides have a variety of useful properties, and they are widely used when creating a new generation of devices. Such materials include barium titanate and yttrium-aluminum garnet. The barium titanate, ferroelectric with high dielectric permittivity, is used to produce microcapacitors with large capacity. Besides, fine crystalline barium titanate is material absorbing different types of electromagnetic radiation. The use in modern quantum electronics of the pure and doped yttrium aluminum garnet, (Y₃Al₅O₁₂), is based on successful combination of optical, thermal and mechanical properties. YAG is known as luminescent material, widely used in the manufacture of lasers. Yttrium aluminum garnet (Y₃Al₅O₁₂:Ce³⁺) doped with trivalent cerium used by manufacturers of LEDs as a yellow phosphor with intense broadband emission centered at 530 nm [1, 2]. Earlier it was found that fine crystalline complex oxides can be prepared in a medium of water vapor in sub- and supercritical conditions [3]. The best properties possess the complex oxides, synthesized sequentially in subcritical water vapor and then in supercritical fluid [4].

In this report the researches have been devoted to the study of pure barium titanate and yttrium aluminum garnet, as well as doped with cerium ions during their formation in sub- and supercritical water fluid.

MATERIALS AND METHODS

For producing of YAG:Ce was used mechanical mixture of yttrium oxide Y₂O₃ (the main substance 99.999%) and aluminum hydroxide Al(OH)₃ mark "GD-00" (99.6%), for barium titanate – titanium oxide TiO₂ (anatase 99.0 %) and barium oxide BaO (98%). As doping agent was hydrated cerium nitrate Ce(NO₃)₃·6H₂O (99%). The synthesis was carried out in laboratory autoclaves. Stoichiometric mixture of reagents was placed in a stainless steel

container in autoclave of 14 - 18 cm³. The pressure of water vapor carries out by evaporation of water, placed into the space between the walls of autoclave and containers with the starting material. The synthesized products were investigated by physical - chemical methods. The scanning electron microscope SEM “Jeol JSM 6390 LA” and Transmission Electron Microscope TEM Jeol JEM-1011 were used to obtain SEM images of produced materials. X-ray analysis of the synthesized products was performed using X-ray powder diffractometer “STADI P STOE” with a CuK α .

RESULTS

In water vapor the formation of complicated oxides runs through a stage of the existence of an intermediate crystalline substances with Me(OH)_n structure [3]. The formation of Me(OH)_n occurs by way hydroxylation of initial solid oxides. The hydroxylation of reagent with smaller solubility in these conditions is carried out by reorganization of its structure by the solid-phase mechanism. As a rule, one of reagents is coming amorphous and partially dissolved. Diffusion of ions of this component into the structure of solid hydroxide concurrently with the dehydroxylation leads to the formation of complex oxide.

Earlier, authors have obtained by this method some kinds of pure and doped solid oxides [5, 6].

Barium titanate

The barium titanate was synthesized from a powder mixture of anatase (TiO₂) and barium oxide (BaO) in the medium of water vapor in the subcritical conditions (synthesized at T = 200 °C or 280 °C, respectively under P_{H₂O} = 2 MPa and 6.2 MPa) or in supercritical conditions (T = 400 °C, P_{H₂O} = 27 MPa). Also the stepwise synthesis performed: at first in the subcritical and then in supercritical conditions (200 °C, or 280 °C, then 400 °C). Already in the subcritical conditions in short time barium titanate is formed. When heating the initial mixture in water vapor up to 150 °C in the reaction products are detected barium titanate, titanium oxide (in the form of rutile) and barium carbonate. With increasing temperature to 200 °C and reaction time to 24 hours X-ray method fixes barium titanate and traces of titanium oxide and barium carbonate (Fig. 1b). Formed barium titanate represents spherical aggregates of nano-size particles (Fig. 1a).

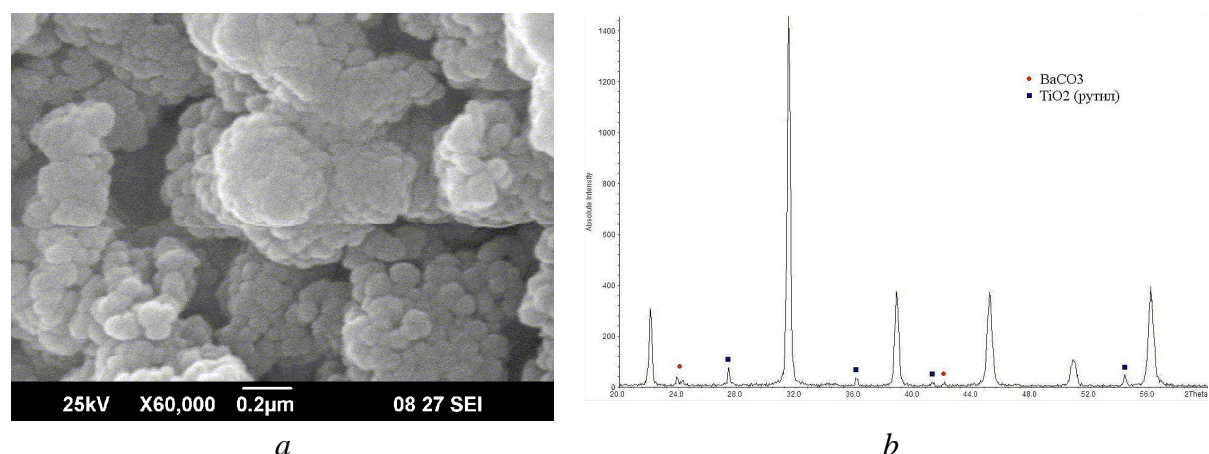


Figure 1. SEM– image and the diffraction pattern of barium titanate synthesized at T= 200 °C and P_{H₂O} = 2 MPa during 24 h in water vapor.

As may be seen from the TEM - image (Fig. 2), each particle from aggregate has a regular crystalline lattice. During realization of synthesis in supercritical condition, under the action of supercritical water fluid ($T= 400\text{ }^{\circ}\text{C}$, $P_{\text{H}_2\text{O}}= 27\text{ MPa}$), an intergrowth of these nanoparticles happens, that leads to formation of fine crystals of barium titanate with mild facet (Fig. 3). Formation of these crystals occurs by means of orientated co-crystallization of contacting particles.

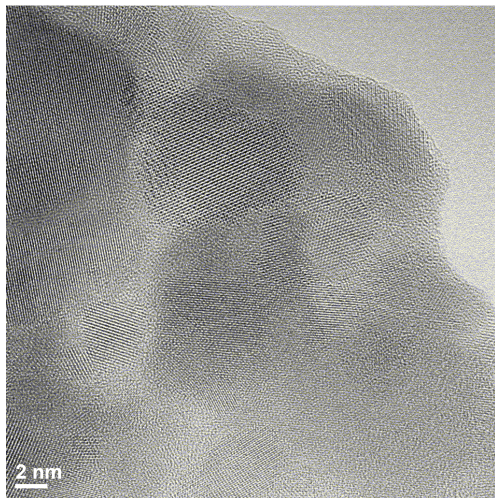


Figure 2. TEM – images of barium titanate synthesized at $T= 200\text{ }^{\circ}\text{C}$ and $P_{\text{H}_2\text{O}}= 2\text{ MPa}$ during 24 h.

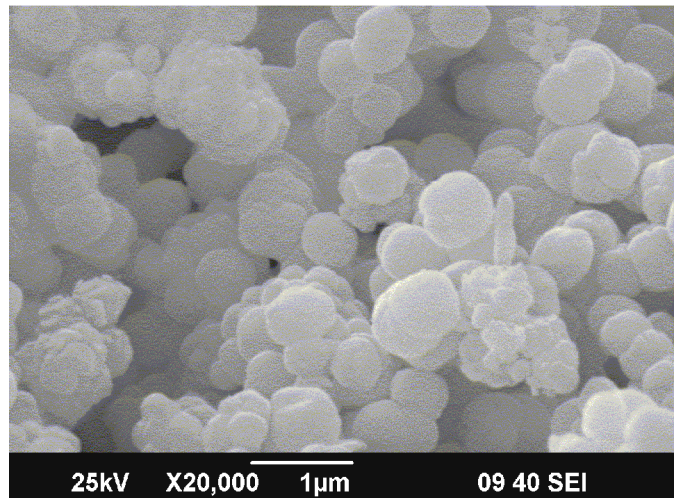


Figure 3. SEM – images of barium titanate synthesized at $T= 400\text{ }^{\circ}\text{C}$ and $P_{\text{H}_2\text{O}}= 27\text{ MPa}$ during 72 h

In TEM –image of particles of barium titanate, synthesized in supercritical condition, one can see as the orientation and intergrowth of nano-size crystals in particles were occurring (Fig. 4). This process is made possible due to the high mobility of the crystal lattice of nanoparticles in aggregates of barium titanate in the medium of supercritical water vapor.

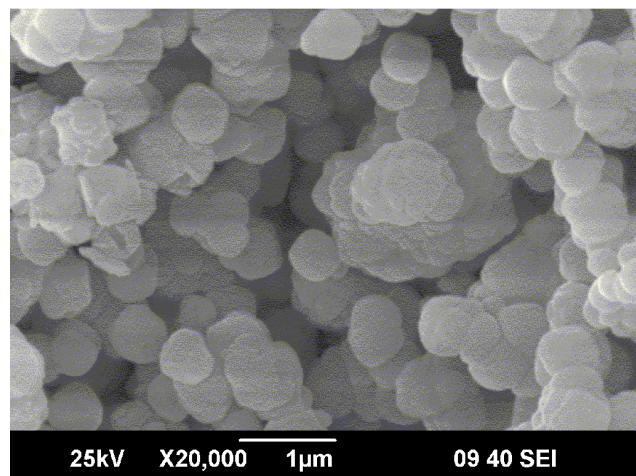
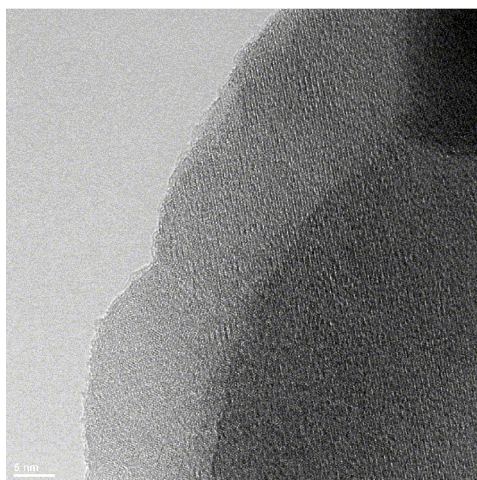


Figure 4. TEM and SEM– images of doped barium titanate (Ce 0.1%) synthesized at $T= 400\text{ }^{\circ}\text{C}$ and $P_{\text{H}_2\text{O}}= 27\text{ MPa}$ during 72 h.

The addition into the reaction medium a doping agent (cerium) accelerates the process of crystals formation of barium titanate and alters its dielectric properties even if process occurs in subcritical area (Fig. 5). In supercritical fluid the isometric crystals of submicron size are formed (Fig. 3, 6). The barium titanate powder, doped with cerium (1.2 %), had the permittivity in three times higher than without cerium, the permittivity respectively equal 26 and 8 at 2GHz.

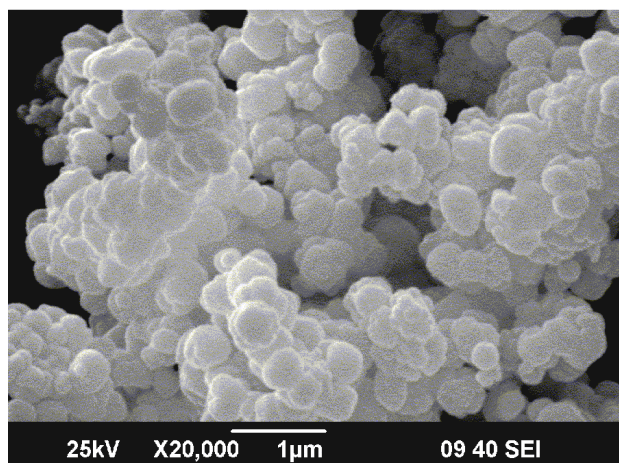


Figure 5. SEM – image of barium titanate doped with cerium (0.1%) and synthesized at $T = 280\text{ }^{\circ}\text{C}$ and $P_{\text{H}_2\text{O}} = 6.2\text{ MPa}$ during 24 h in water vapor.

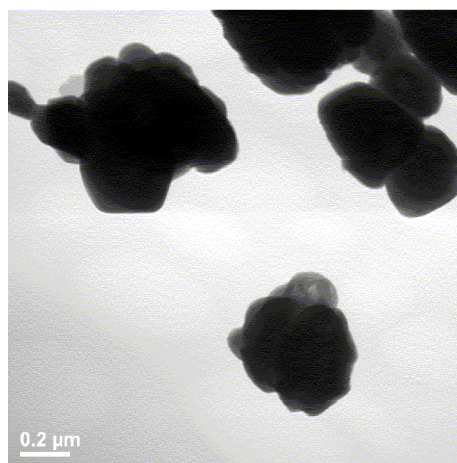


Figure 6. TEM – images of barium titanate with Ce (0.1%) synthesized at $T = 400\text{ }^{\circ}\text{C}$ and $P_{\text{H}_2\text{O}} = 27\text{ MPa}$ during 72 h.

Yttrium-aluminum garnet

The fine crystalline yttrium-aluminum garnet pure ($\text{Y}_3\text{Al}_5\text{O}_{12}$) and doped with cerium ($\text{Y}_{3-x}\text{Ce}_x\text{Al}_5\text{O}_{12}$) was produced in sub- and supercritical water fluid (SCWF) as well as the barium titanate. For example, the stoichiometric mixture of yttrium oxide and aluminum hydroxide (dry or with a water solution of cerium nitrate) was maintained the certain time at $280\text{ }^{\circ}\text{C}$ under vapor water pressure 6.3 MPa. Besides, the garnet synthesis was carried out in supercritical conditions at $T > 400\text{ }^{\circ}\text{C}$ and pressures above 22 MPa. In some cases the producing of garnet was including a treatment of raw material (the starting mixture of reagents) sequentially in the subcritical, and then, in supercritical conditions, for that the temperature and pressure were risen up to $T = 392 - 400\text{ }^{\circ}\text{C}$ and $P_{\text{H}_2\text{O}} = 22 - 27\text{ MPa}$.

At the beginning of treatment of the initial mixture of reagents by water vapor in subcritical conditions yttrium hydroxide (oblong prisms), yttrium-aluminum garnet ($\text{YAG}:\text{Ce}^{3+}$) and aluminum oxyhydroxide (AlOOH) are formed (Fig. 7a). In 11 hours a mixture of yttrium hydroxide, AlOOH and spherical aggregates of nanoparticles of garnet are shown (Fig. 7b). After 60 hours, only garnet with traces of aluminum oxyhydroxide is fixed. The synthesized $\text{YAG}:\text{Ce}^{3+}$ represents aggregates of nano-size crystals (Fig. 7c).

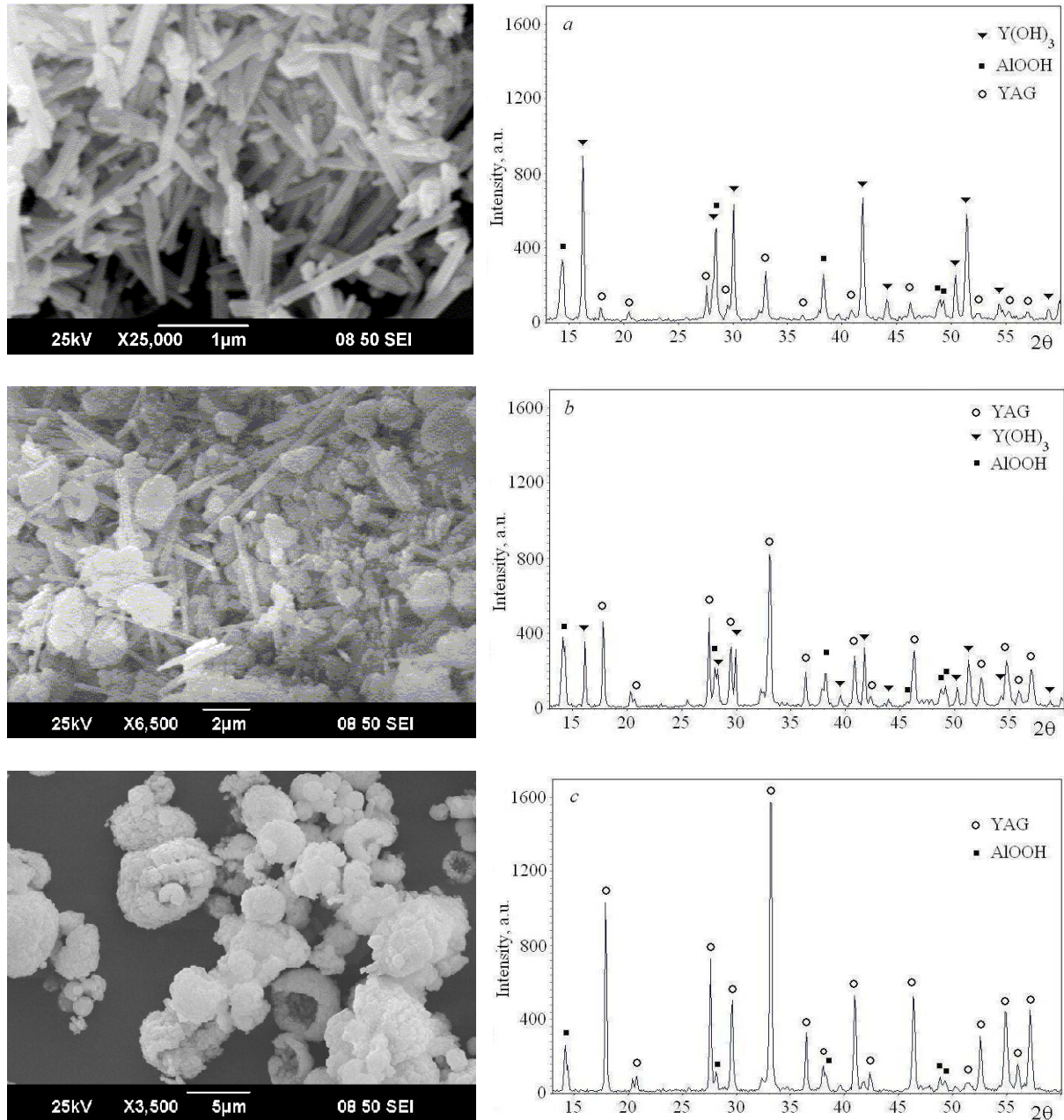


Figure 7. XRD pattern and SEM image of products of $Y_{3-0.01}Ce_{0.01}Al_5O_{12}$ synthesis at 280 °C under pressures of 6.3 MPa. Time of synthesis at 280 °C: *a* – 1 h; *b* – 11 h; *c* – 60 h.

In supercritical water fluid the cocrystallization of nanocrystals in aggregates with formation of microcrystals of garnet occurs. In Fig. 8 and 9 is shown SEM-images of particle of doped YAG:Ce³⁺ ($Y_{3-0.01}Ce_{0.01}Al_5O_{12}$), synthesized in subcritical ($T= 280\text{ °C}$, $P_{H_2O}= 6.3\text{ MPa}$) and then in supercritical ($T= 392\text{ °C}$, $P_{H_2O}= 22\text{ MPa}$) conditions at different exposure time in the supercritical water fluid.

Under short-term influence of supercritical water fluid on aggregates of nanoparticles garnet, formed at 280 °C, they transform into spherical ill-formed microparticles (Fig. 8). With the increase in treatment time of garnet by fluid, the structure of the micron particles is improved and they get rhombododecahedral habitus (Fig. 9).

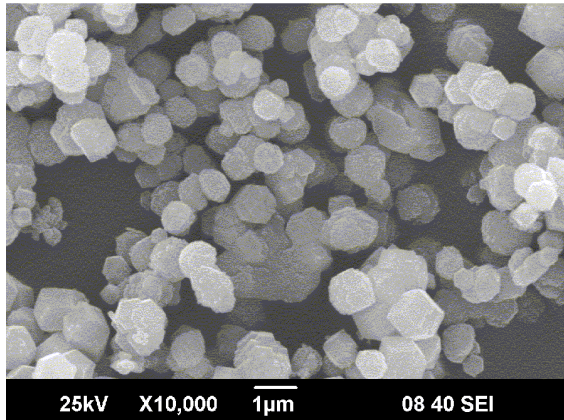


Figure 8. SEM image of $Y_{3-0.01}Ce_{0.01}Al_5O_{12}$ synthesized at $T= 280\text{ }^\circ\text{C}$, $P_{H_2O}= 6.3\text{ MPa}$, $t= 24\text{ h}$ and then under $T= 392\text{ }^\circ\text{C}$, $P_{H_2O}= 22\text{ MPa}$, $t= 1\text{ h}$.

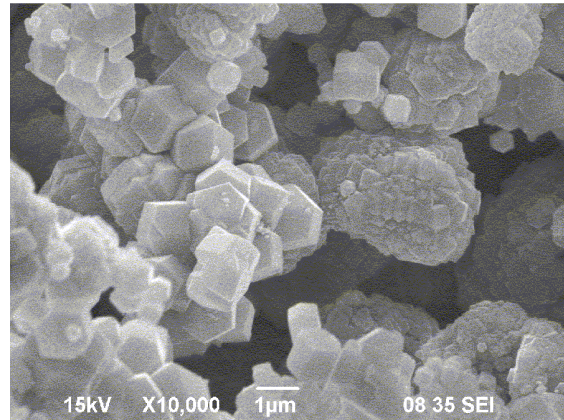


Figure 9. SEM image of $Y_{3-0.01}Ce_{0.01}Al_5O_{12}$ synthesized at $T= 280\text{ }^\circ\text{C}$, $P_{H_2O}= 6.3\text{ MPa}$, $t= 24\text{ h}$ and then under $T= 392\text{ }^\circ\text{C}$, $P_{H_2O}= 22\text{ MPa}$, $t= 24\text{ h}$.

At the same time the intensity of the luminescence of the synthesized garnet greatly increases (Fig. 10). In Fig. 11 presents the luminescence spectra of garnets synthesized in subcritical conditions (Fig. 11a) in supercritical water fluid (Fig. 11b) and by the two-step method (Fig. 11c). The garnet synthesized sequentially in subcritical and supercritical conditions showed highest intensity of luminescence at 530 nm (Fig. 5c).

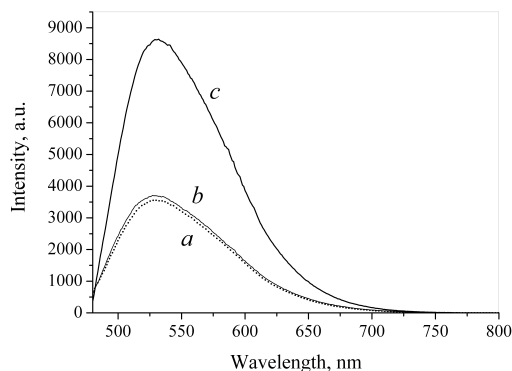


Figure 10. Luminescence spectra of products of $Y_{3-0.01}Ce_{0.01}Al_5O_{12}$ synthesized first at $280\text{ }^\circ\text{C}$ under 6 MPa , 24 hours , then in SCWF at $392\text{ }^\circ\text{C}$ under 25 MPa during times: a) 1 h ; b) 2 h ; c) 24 h . The excitation by light 458 nm .

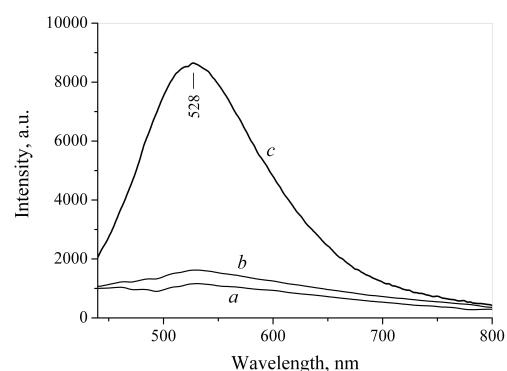


Figure 11. Luminescence spectra of $Y_{3-0.01}Ce_{0.01}Al_5O_{12}$ synthesized: a- at $280\text{ }^\circ\text{C}$ under 6 MPa during 24 h ; b- at $392\text{ }^\circ\text{C}$ under 25 MPa , 80 h ; c- at $280\text{ }^\circ\text{C}$, 24 h and then in SCWF at $392\text{ }^\circ\text{C}$ under 25 MPa , 24 h . The excitation by light 458 nm .

In Fig. 12 is shown TEM-image of particle of $YAG:Ce^{3+}$ ($Y_{3-0.01}Ce_{0.01}Al_5O_{12}$), synthesized in subcritical condition. In this photo the nanocrystals, which make up the aggregated particles of garnet, are clearly visible. The corresponding SEM - image of this sample of garnet is presented in Fig. 13. In supercritical water fluid the cocrystallization nanocrystals in aggregates with formation of microcrystals of garnet occurs (Fig. 14, 15).

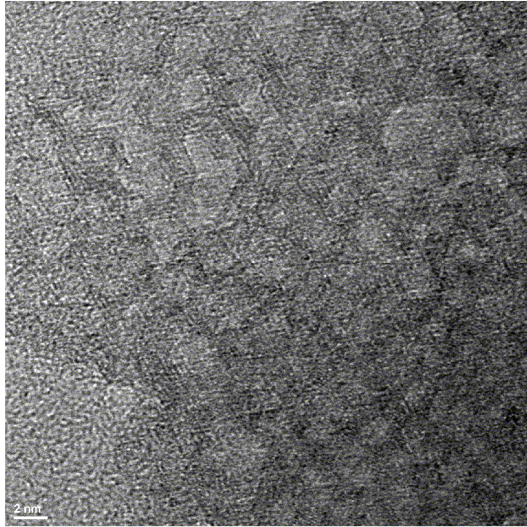


Figure 12. TEM – image of $Y_{3-0.01}Ce_{0.01}Al_5O_{12}$ synthesized at 280 °C, $P_{H_2O}= 6$ MPa, 24 hours.

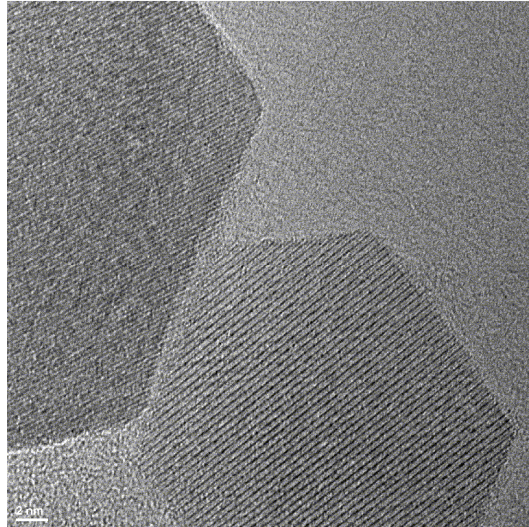


Figure 14. TEM – image of $Y_{3-0.03}Ce_{0.03}Al_5O_{12}$ synthesized at 280 °C, $P_{H_2O}= 6$ MPa, 24 hours, then at 400 °C, $P_{H_2O}= 27$ MPa, 24h.

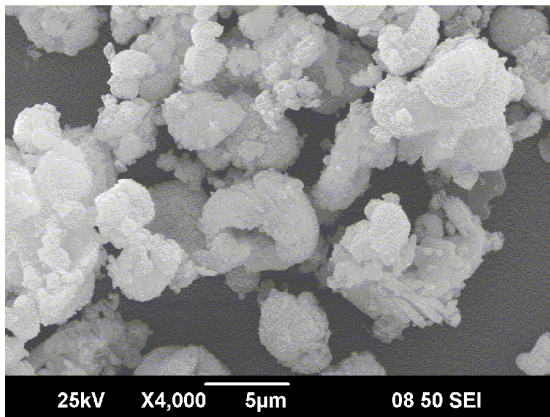


Figure 13. SEM – image of $Y_{3-0.01}Ce_{0.01}Al_5O_{12}$ synthesized at 280 °C, $P_{H_2O}= 6$ MPa, 24 hours.

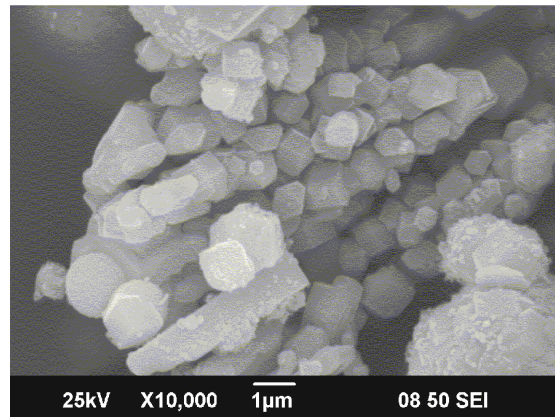


Figure 15. SEM– image of $Y_{3-0.03}Ce_{0.03}Al_5O_{12}$ synthesized at 280 °C, $P_{H_2O}= 6$ MPa, 24 hours, then at 400 °C, $P_{H_2O}= 27$ MPa, 24h.

In Fig. 16 can be seen the crystals with the characteristic defects of structure, which are caused by the peculiarities of crystal growth. On the faces of the crystals are clearly visible residuary boundaries between the accrete particles. Such structural defects can occur if the rate of accretion of nanoparticles in SCWF is commensurable to the rate the faceting garnet microcrystals. The formation of microcrystals of undoped garnet through the coalescence of nanoparticles to form a single crystal lattice occurs faster than the faceting. The crystals of undoped garnet, obtained in same conditions, as and the doped garnet (Fig. 16) are presented in Fig. 17. In case of pure garnet, synthesized in SCWF, on faces its crystals the residuary boundaries between the accreted particles are not fixed.

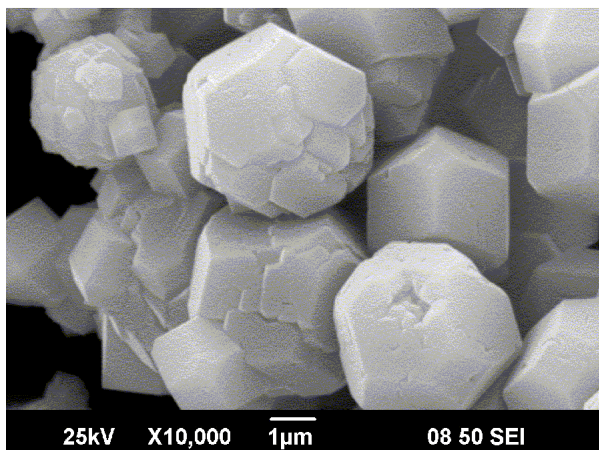


Figure 16. SEM – image of $Y_{3-0.0005}Ce_{0.0005}Al_5O_{12}$ synthesized at 280 °C, $P_{H_2O}= 6$ MPa, 24 hours, then at 400 °C, $P_{H_2O}= 27$ MPa, 24h.

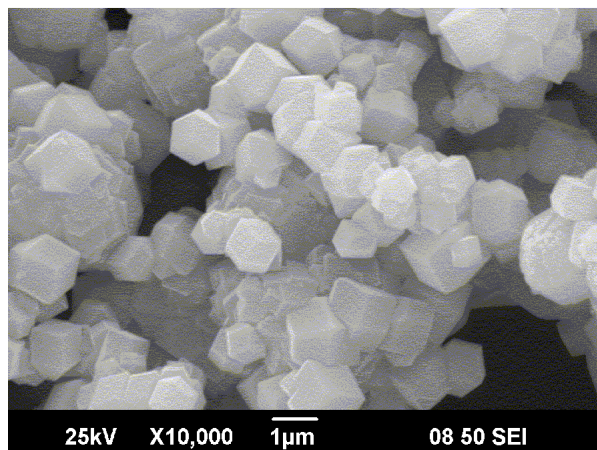


Figure 17. SEM – image of $Y_3Al_5O_{12}$ synthesized at 280 °C, $P_{H_2O}= 6$ MPa, 24 hours, then at 400 °C, $P_{H_2O}= 27$ MPa, 24h.

CONCLUSION

The close similarity of the morphological features of products, formed during the synthesis of complex oxides, barium titanate, and yttrium aluminum garnet, indicates the same type of structural transformations of precursors under treatment by water vapor. In subcritical conditions, at $T < 374$ °C and $P_{H_2O} < 22$ MPa, in either case, under an effect of water vapor the spherical aggregates of nanoparticles of complicate oxides were formed. Under subsequent treatment by supercritical water fluid, the nanoparticles of aggregates were accreted with formation of well-formed microcrystals. These crystals showed significantly better performance characteristics, than the crystals obtained in the subcritical conditions. The same type of the formation stages of barium titanate, and yttrium aluminum garnet is the result of mechanism unity of synthesis in water vapor [7]. Peculiarity of this mechanism is the active participation of water molecules in the restructuring of the precursor in hydration-dehydration quasiequilibrium condition [8].

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