

SYNTHESIS OF CE-DOPED YTTRIUM ALUMINUM GARNET IN SUPERCRITICAL WATER FLUID AND INVESTIGATION ITS OPTICAL PROPERTIES

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In this report the method of a producing of fine crystalline Yttrium Aluminum Garnet doped with Cerium (YAG:Ce³⁺) in supercritical water fluid (SCWF) are represented. This way allows obtaining high-pure fine crystalline materials. The YAG:Ce³⁺ was synthesized by way thermotreatment of mechanical stoichiometric mixture from yttrium oxide and aluminum hydroxide in water vapor in two stages: at 280 °C (P_{H2O}=6.3 MPa) and then at 400 °C (P_{H2O}=22 MPa). A cerium nitrate was added to starting mixture. The concentration of cerium ions in reaction medium was changed in an interval 0.012 - 0.706 % concerning a final product. The products of a synthesis were investigated by methods of X-ray diffractometry, FTIR-spectroscopy, electron microscopy and diffuse reflectance. It was found that the formation of crystals of YAG:Ce³⁺ is preceded by an induction period, which is the time required for formation of intermediates (yttrium hydroxide and oxyhydroxide crystals). The induction period can be changed by the addition of dopant into reaction medium. During this period the aluminum component is amorphous. During the induction period the diffusion of aluminum ions and cerium in the structure of yttrium hydroxide is begun and at the end of the induction period the formation of the garnet structure occurs. The role of the water fluid consists in the increase of the mobility of reagents lattice and in the facilitation of the components diffusion to form the final product – YAG:Ce³⁺. The crystals size of as-prepared YAG:Ce³⁺ was in the 0.5 – 3.0 μm range. The crystals have rhombododecahedral habitus. These samples showed the intensive yellow photoluminescence at 530 nm.

INTRODUCTION

In connection with development of manufacture of new light sources, for example light emitting diodes (LED), the technologies of the luminophors, emissive white light, have the special importance. There are several methods to produce a white light emitting diode (LED). The most common commercially available white LED is made by mixing the yellow light from the emission of a yttrium aluminum garnet doped with cerium (YAG:Ce³⁺) and the blue light from a GaN [1]. Trivalent cerium-activated YAG (Y₃Al₅O₁₂:Ce³⁺) is suitable for converting the blue light emitting diodes (LEDs) radiation into a very broad band yellow emission, which provides a basis to use YAG:Ce³⁺ phosphor along with GaN LEDs to produce white light emitting diodes [2].

Cerium-doped yttrium aluminum garnet is a well-known luminescent material with intense broadband emission centered at approximately 530 nm [1]. Therefore development of an effective method of obtaining of YAG:Ce³⁺ is a urgent task. Earlier the method of high-temperature solid-phase synthesis was widely used. In this case, the synthesis of yttrium

aluminum garnet (YAG) proceeds at the temperature in range of 1250 - 1750 °C [3, 4]. This method was superseded by others, modern, more economic ways, which allow modifying of property of synthesized products.

Now there are some methods of synthesis of powder phosphor yttrium aluminum garnet (YAG), doped with trivalent cerium (Ce^{3+}). One of most widely used methods is sol-gel method. Powder phosphor $\text{YAG}:\text{Ce}^{3+}$ is synthesized by sol-gel method with subsequent annealing at $T > 1000$ °C. The fine crystalline $\text{YAG}:\text{Ce}^{3+}$ emission shows one peak in the range 480–535 nm with the maximum near 520 nm [5].

The precipitation technique of synthesis allowed producing of $\text{YAG}:\text{Ce}^{3+}$ nano-sized particles. As starting materials were used metal nitrates. The phase-pure phosphor $\text{YAG}:\text{Ce}^{3+}$, after heating of the product of coprecipitation at temperature ~ 800 °C, can be obtained. The photoluminescence (PL) intensity increased with increasing annealing temperature and decreases with increasing Ce^{3+} doping concentration greater by 0.1 mol % [6].

Recently a synthesis of $\text{YAG}:\text{Ce}^{3+}$ by combustion method has arisen. Synthesis of $\text{YAG}:\text{Ce}^{3+}$ by combustion method with urea ($\text{CO}(\text{NH}_2)_2$) at 1000 °C allows to produce a powder of luminophor with intensive band of emission at 554 nm [7].

Cerium-doped yttrium aluminum garnet ($\text{YAG}:\text{Ce}^{3+}$) powder was synthesized also by a solvo-thermal method under soft conditions from aluminum and yttrium nitrates as the starting materials and the ethylenediamine solution as the solvent. By this method the spherical and well dispersed phase-pure particles of $\text{YAG}:\text{Ce}^{3+}$ in the size range of 200–260 nm were produced. The photoluminescence spectrum of the fine crystalline $\text{YAG}:\text{Ce}^{3+}$ phosphors showed the green-yellow emission with $5d \rightarrow 4f$ transition in Ce^{3+} [8].

YAG synthesis from oxides under hydrothermal conditions at temperatures of 500 – 600 °C and pressures of 70 - 170 MPa in $6 \pm 10\%$ carbonate solutions of K and Na are known [8 - 10]. Under such hydrothermal conditions, the processes of dissolution the oxides and formation crystals of YAG proceed in supercritical water fluid.

Pure YAG and rare earth-doped YAG ultra-fine particles with suitable morphology were obtained by a novel synthesis process employing supercritical water [11]. The synthesis process consisted of two steps including precursor precipitation and hydrothermal treatment in supercritical water. The precursor was prepared by using yttrium nitrate, aluminum nitrate, rare earth nitrate and ammonium hydrogen carbonate aqueous solution as the starting materials. The precursor was collected and dispersed in water. Finally, such water suspension was put into the high temperature and high pressure autoclave. Hydrothermal treatment of precursor was carried out from 300 °C to 420 °C and pressures ranging from 8 MPa to 30 MPa. The YAG particles synthesized were mono-dispersed, featuring spherical or polyhedron shape with the size ranging from 100 nm to 500 nm.

Many considerable papers consecrated to hydrothermal synthesis and synthesis of powders in a supercritical water fluid (SCWF) recently have appeared [12].

In this report the method of a obtaining of fine crystalline $\text{YAG}:\text{Ce}^{3+}$ in supercritical water fluid (SCWF) is represented. This way allows obtaining high-pure fine crystalline materials [13]. Use of SCWF as reaction medium enables to exclude impurity in a synthesis product and to expand opportunities of process control [14, 15]. In [16] the kinetics and mechanism of fine crystalline YAG formation under hydrothermal and supercritical conditions were investigated. It was synthesized from stoichiometric mixture solid oxides at 400 °C and pressure 26 MPa.

In this report our research has been devoted to the study of the doping of yttrium aluminum garnet with cerium ions during the formation of garnet in sub- and supercritical water fluid.

MATERIALS AND METHODS

All samples of yttrium aluminum garnet doped with cerium were synthesized in the same mode: a mixture of initial reagents in a hermetical reactor (autoclave) was heated in two stages: at the first within 24 hours at temperature 280 °C and pressure of water vapor 6.2 MPa, then within 24 hours at temperature 400 °C and $P_{\text{H}_2\text{O}} = 27$ MPa. The raw material:

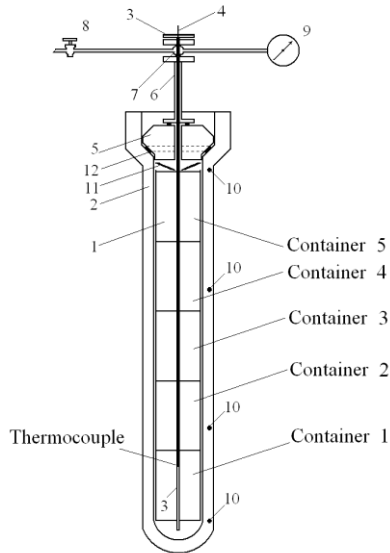


Figure 1. Reactor for synthesis fine crystalline YAG:Ce.

yttrium oxide and aluminum hydroxide with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, placed into the containers, which were located on a special support in an autoclave (**Figure 1**). 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. After synthesis completed the water vapor is released from autoclave and the dry product is unloaded. The synthesized products were investigated by physical-chemical methods. The “Jeol JSM 6390 LA” microscope and Transmission Electron Microscope 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 $\text{CuK}\alpha$ and diffractometer DRON-3M. Diffuse reflection (DR) spectra were recorded with M-40 spectrometer. Water included in garnet structure was defined by Fourier – Transform absorption spectrometry using FTIR-spectroscop (EQUINOX 55/S in a region of

$4000\text{-}400\text{ cm}^{-1}$). The spectrum of photoluminescence was measured with the SDL-2M device at room temperature with DKsSh-150 lamp as excitation source.

RESULTS

As was shown earlier [17], the processes of formation of complicated oxides in water fluid proceed through a stage of the existence of an intermediate crystalline substance with $\text{Me}(\text{OH})_n$ structure. In case of the YAG formation under water vapor, the intermediates are $\text{Y}(\text{OH})_3$ and YOOH . Aluminum component is presented in the form of boehmite and an amorphous hydrated aluminum oxide [18]. Intermediates appear at temperatures above 250 °C. In the first stage of isothermal process at 280 °C the formation of intermediate compounds, yttrium hydroxide, oxyhydroxide and some amount of garnet, happened [16]. During the second stage at temperature 400 °C in isothermal conditions, in medium of supercritical water fluid ($P_{\text{H}_2\text{O}} = 27$ MPa), the transformation process of intermediates into thermodynamic stable product ($\text{YAG}:\text{Ce}^{3+}$) occurs. Prolonged exposure in SCWF leads to dehydration of YAG and the improving its structure. Our research showed that the adding to the reaction medium of cerium ions initiates a retardation process of the garnet formation in SCWF.

As can be seen from the X-ray diffraction patterns of the synthesis products of YAG:Ce (**Figure 2**), under the same synthesis parameters, but with different contents of cerium, complete transformation of precursors to $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ occurs in the absence of cerium in the reaction medium or at low concentrations of cerium (<0.2%). When the content of cerium in the reaction medium reaches 0.7%, to the final product - $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, in the

reaction products, except for garnet, recorded slight reflexes of intermediate compounds: $Y(OH)_3$, $YOOH$, $AlOOH$ (**Figure 2**).

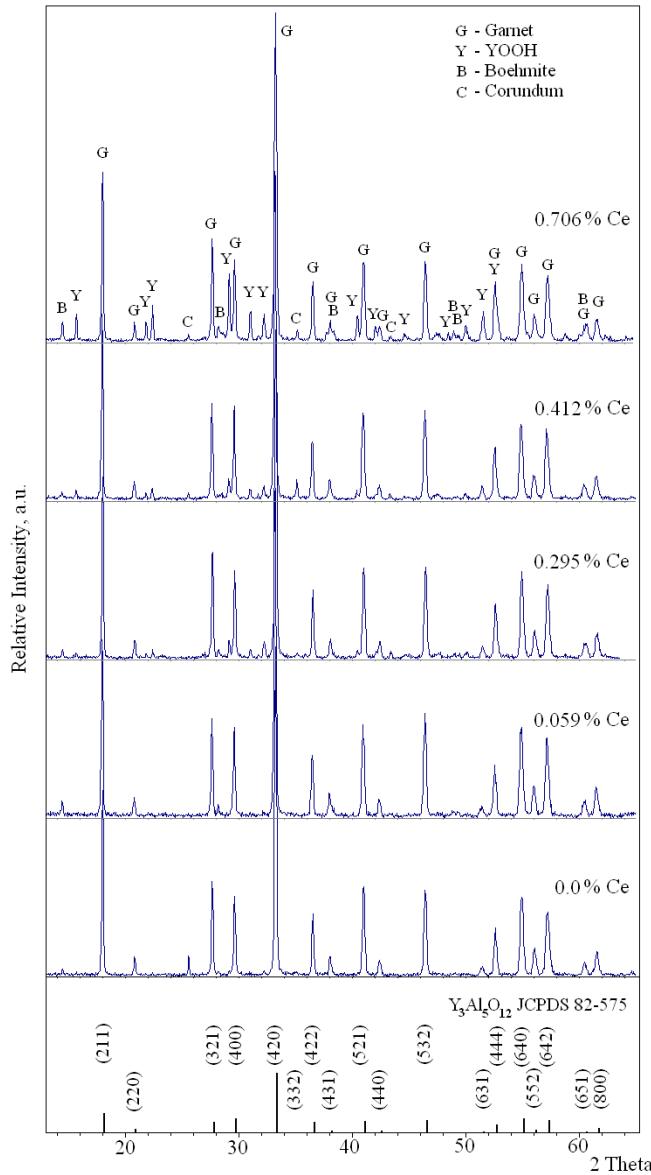


Figure 2. The XRD patterns of YAG:Ce samples prepared at 280 °C and then at 400 °C in water fluid with different amount of cerium (mass.%) in reaction medium, concerning final product: $Y_3Al_5O_{12} \cdot Ce$.

It should be noted, that even with incomplete transformation of intermediate compounds into garnet, in the reaction medium were not determined compounds of cerium. This indicates that cerium is included into the structure of intermediate compounds at the stage of their formation. During the formation of crystals of $YAG:Ce^{3+}$ from the intermediates the cerium ion occupies the site of the strong crystal field of O^{2-} . The D_2 site symmetry of the Ce^{3+} ion, which substitutes for Y^{3+} in the YAG crystal, splits the 5d excited state into five crystal-field levels. The location of three of the 4f–5d bands at about 460, 340 and 220 nm were well studied, although there are differences in the assignments of the remaining two bands. The excitation and absorption spectra of $YAG:Ce^{3+}$ depend to some extent upon temperature and the concentration of Ce^{3+} , as well as the preparation method. In our case two broad bands with maxima at 340 and 460 nm are characterized the photoluminescence excitation of synthesized $YAG:Ce^{3+}$ (**Figure 3**). They are caused by the splitting of the ground 4f state of the Ce^{3+} , because in the YAG host, Ce^{3+} occupies a distorted cube [7, 19]. The absorbance broad peaks at 400–510 nm corresponds to the absorption of Ce^{3+} from the 4f ground state to 5d excited state. The broadband emission peak of Ce^{3+} at 490 – 650 nm with maximum at 530 nm as exciting by light at 460 nm (**Figure 3**) is caused by 4f - 5d transitions of electrons with subsequent reverse

transition and emission of light. This kind of spectra indicates the inclusion of cerium ions into the lattice of YAG with the substitution of yttrium ions. In **Figure 4** the luminescence spectra of samples $YAG:Ce^{3+}$ obtained with the different cerium contents are shown. As will be seen from the **Figure 4**, the luminescence intensity of $YAG:Ce^{3+}$ at the doping of YAG sharply grows and is increased with the rise of a cerium concentration. However at the cerium concentration in reaction medium 0.706 % synthesized $YAG:Ce^{3+}$ shows lower intensity of luminescence. This sample is ill-formed and contains not reacted precursors (**Figure 2**). At

small cerium concentration the shift of a maximum of the luminescence peak in spectrum is not observed.

Diffuse reflections (DR) of the YAG:Ce³⁺ samples with different contents cerium (mass.%) in reaction medium were presented in **Figure 5**. From these curves it will be obvious three broad bands of absorption with maxima in the range from 426 to 453 nm, 256 - 293 nm and 200 - 230 nm. As was shown in [19, 20] and in [7] the absorption peaks at 460, 340 and 230 nm concern to ions Ce³⁺ isomorphically included in a crystal YAG, and peak at 270 nm to defects of structure: F⁺-centers. It should be noted that the presence charged vacancies defects in structure is typical for fine crystalline materials synthesized in water fluid [14, 15].

The increase of a cerium concentration in reaction medium at synthesis of garnet in water fluid is leads to a rise of content of ions Ce³⁺ and F⁺-centers in its structure.

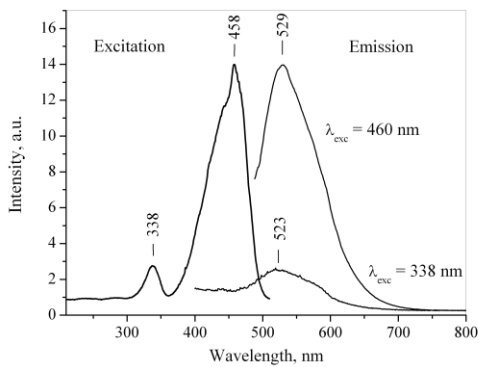


Figure 3. Excitation spectrum of YAG:(0.12%)Ce³⁺ for the band 530 nm and emission specter under lighting with $\lambda = 460$ nm and $\lambda = 338$ nm.

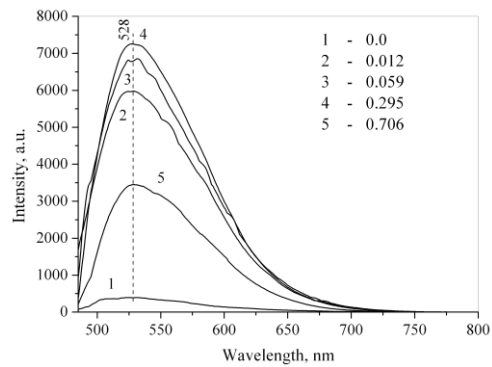


Figure 4. Emission spectra of cerium ions in YAG:Ce³⁺ with different contents of cerium (mass.%) $\lambda_{ex} = 460$ nm, concerning final product: Y₃Al₅O₁₂:Ce³⁺.

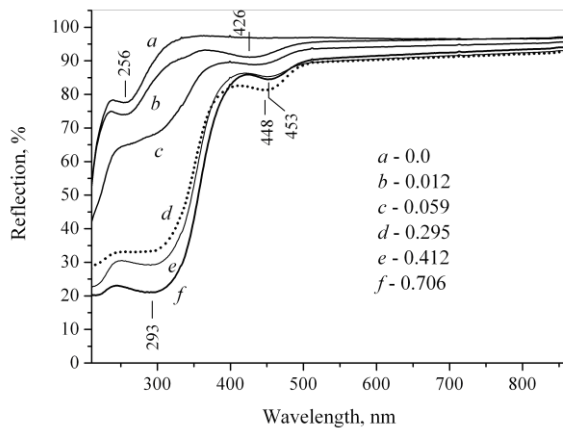


Figure 5. DR spectra of the YAG:Ce³⁺ samples with different contents cerium (mass.%) in reaction medium, concerning final product: Y₃Al₅O₁₂:Ce³⁺.

and X-ray pattern shows the traces of intermediates: YOOH, and AlOOH, but the basic product is YAG:Ce³⁺.

Figure 6 shows SEM images of the YAG:Ce³⁺ samples synthesized under the same conditions, but with the various contents cerium in reaction medium. YAG synthesized without cerium represents as well formed crystals with rhombododecahedral habitus. In this case the average size of crystals is at 1.5 μ m. Addition into reaction medium of small amount (0.0236 %) of cerium results in little increase of the size of crystals synthesized YAG:Ce³⁺ with preservation of perfect cut crystals. However at the increase of cerium concentration up to 0.4% the process of formation of crystals is slowed down

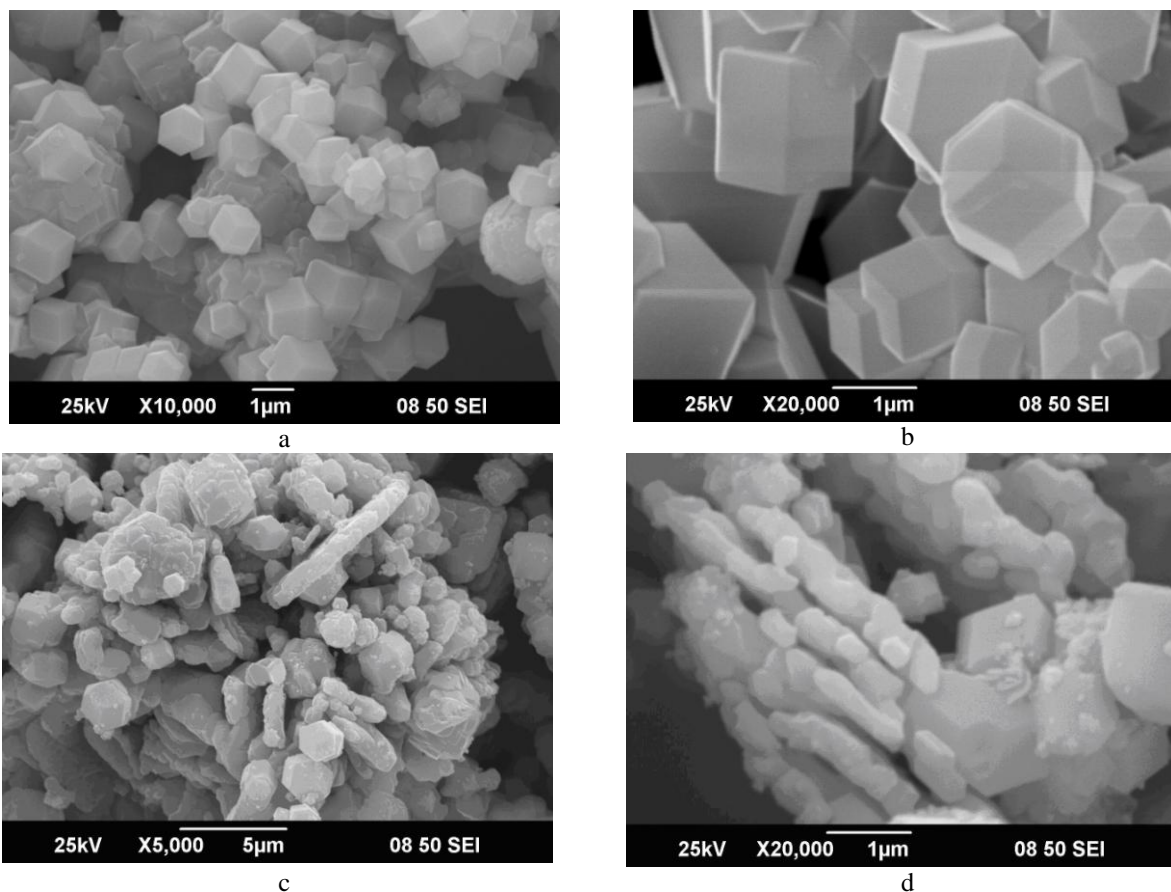


Figure 6. SEM images of the YAG:Ce^{3+} samples with different contents cerium in reaction medium: a) without cerium; b) $C_{\text{ce}} = 0.0236\%$; c) $C_{\text{ce}} = 0.470\%$; d) $C_{\text{ce}} = 0.7063\%$.

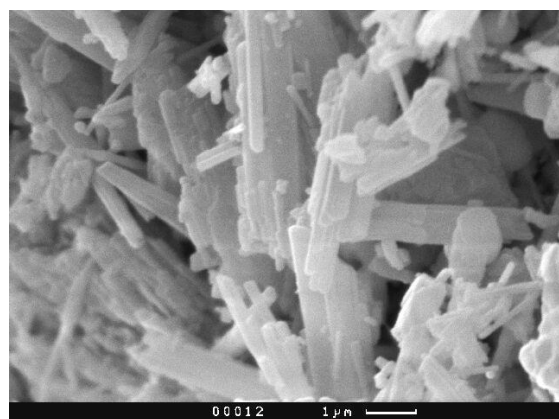


Figure 7. SEM image of Y(OH)_3 - synthesis product of YAG without cerium then treatment starting raw at $280\text{ }^\circ\text{C}$ (at the first isothermal stage of a synthesis).

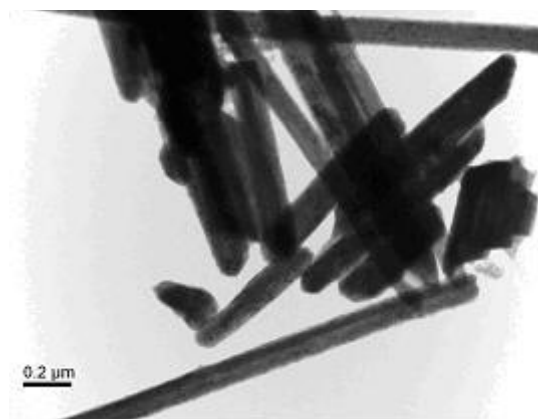


Figure 8. TEM image of Y(OH)_3 - synthesis product of YAG without cerium then treatment starting raw at $280\text{ }^\circ\text{C}$ (at the first isothermal stage of a synthesis).

It should be noted, that at the first isothermal stage ($280\text{ }^\circ\text{C}$) of a synthesis YAG the fine crystals of Y(OH)_3 and YOOH with habits of elongated hexagonal prism were arisen (**Figures 7, 8**). At the second stage at temperature $400\text{ }^\circ\text{C}$ in isothermal conditions, in medium of supercritical water fluid ($P_{\text{H}_2\text{O}} = 27\text{ MPa}$), the transformation process of intermediates into YAG:Ce^{3+} occurs. Addition a cerium in to reaction medium slows down a process of formation of garnet crystals. The appearing crystals of YAG:Ce^{3+} also have habitus elongated

hexagonal prisms as well as intermediate crystals $Y(OH)_3$ (**Figure 6 d**). With increasing time of treatment of garnet by water fluid the hexagonal prisms of $YAG:Ce^{3+}$ break up on fine crystals (0.5 – 3.0 μm) with rhombododecahedral habitus (**Figure 6**).

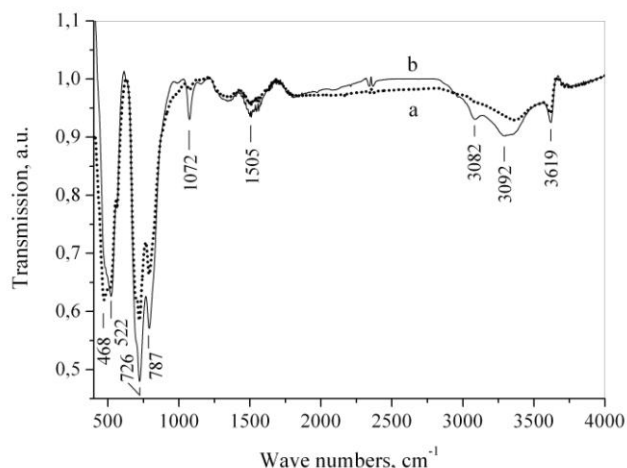


Figure 9. FTIR spectra of YAG (a) and $YAG:(0.059\%)Ce^{3+}$ (b) synthesized at 280 °C and then at 400 °C in water fluid.

the broad bands, caused by stretching and bending vibrations of O-H included into structure of YAG and $YAG:Ce^{3+}$ (3000 – 36500 cm^{-1} and 1500 – 1650 cm^{-1}), are more intensive for garnet doped with cerium. This fact confirms the presence of aforesaid defects, which are optically active centers.

CONCLUSION

Use water fluid as reaction medium allows carrying out the synthesis of complicated oxides in soft conditions. The processes of formation of complicated oxides in water fluid proceed through a stage of the existence of an intermediate crystalline substance with $Me(OH)_n$ structure, which are formed already at temperature of a below a critical point. Therefore, it is profitable to realize the synthesis of complicated oxides in water fluid in a stepwise manner: first at $T < T_{critical}$ and then in supercritical conditions.

In case of the YAG formation under water vapor, the intermediates are $Y(OH)_3$ and $YOOH$. The role of the water fluid consists in the increase of the mobility of lattice sites of reagents during hydration and in the facilitation of the components diffusion to form the final product - garnet doped cerium. Doping component is included into intermediates structure at stage their formation and at formation of garnet it enters into structure of garnet. Obtained in this way a powder $YAG:Ce^{3+}$ consisted of well-faceted small crystals of 0.5 - 3.0 μm with a rhombododecahedral habitus, and showed a high intensity of yellow luminescence at 530 nm.

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