Synthesis of luminophores – powders in supercritical water fluid

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Under treatment of oxides or hydroxides of metals in supercritical water fluid occurs a solid-phase reorganization and ordering of oxides structure with formation of fine crystalline product that represent a powder of well-formed single crystals. The adding into reaction medium of dopant as salt or oxide leads to introduction into structure of forming crystals about half of dopant ions. Thermovaporous treatment (TVT) of aluminum hydroxide along with dopant at 400ºC and $P(H_2O) = 26$ MPa results in formation of corundum (α-Al_2O_3) with intensive luminescence bands at 694 nm (Cr), 678 nm (Mn), 614 nm (Eu). The synthesis of gahnite ($ZnAl_2O_4$) doped by Cr or Eu results in occurrence of luminescence bands at 687 and 612 nm. The synthesized $LaAlO_3$:Eu has intensive narrow luminescence bands at 591, 616 and 618 nm. The doping of yttrium - aluminum garnet by Cr ($Y_3Al_5O_{12}$:Cr) results in appearance of luminescence centers of two types with bands at 688 and 694 nm. The formation of oxide structure proceeds in conditions of quasi-equilibrium with water vapor according to a solid-phase mechanism. The formation kinetics of doped corundum is described by the Erofeev equation for a case of ramified chain nucleation, and formation of the complicated oxide by this equation with constant nucleation rate. The formation of oxides in medium of water vapor and water is accompanied by appearance of oxygen vacancies and hydroxyl groups in structure. The annealing of obtained oxides at high temperatures results in removal of residual hydroxyl groups and change of a state of point defects of structure with rise of luminescence intensity.

INTRODUCTION

The transformation of solid-phase oxides and hydroxides in water vapor (Lazarev V. B. 1996, Danchevskaya M. N., 2001) at temperatures about 400°C proceed on the solid-phase mechanism due to intensive processes of hydroxylation - dehydroxylation (Lazarev V. B. 1996, Ivakin Yu. D., 2000, 2001). The introduction into reaction medium of the additives of the suitable salts or oxides allows obtaining the doped products. The transformation product represents a fine crystalline powder of complicated or simple oxides. Sizes of the particles depend on the process conditions and can be varied within an interval of 0.3-400 microns for simple oxides and 0.2-3 microns for complicated oxides (Danchevskaya M. N., 2001, 2005). In the present paper the hydrothermal and thermovaporous synthesis and the structure peculiarity of luminophors based on doped corundum and doped complicated oxides: gahnite ($ZnAl_2O_4$), yttrium - aluminum garnet ($Y_3Al_5O_{12}$), and lanthanum aluminate ($LaAlO_3$) is described.

MATERIALS AND METHODS

The starting materials, such as aluminum hydroxide (hydrargillite), or the stoichiometric mixture hydrargillite with zinc oxide or yttrium oxide were placed into steel stainless container, which was put into autoclave (volume 16 cm^3) on support. The water was added into the container or into the autoclave bottom outside of the container. The degree of autoclave filling with water was equal to 0.2. Doping element (chromium, manganese, neodymium or europium) was added into reaction medium as salt solution or oxide. The hermetically closed autoclave was positioned in the hot furnace (200-420°C). The autoclave was retained under certain temperatures over a specified period of time and was rapidly cooled. The synthesized products was studied by X-ray analysis (diffractometer DRON-3M in filtered Co or Cu-Kα radiation), mass-spectral analysis of volatile impurity (mass spectrometer MI-1311), EPR-spectroscopy (Varian E-109 RS X-band radiospectrometer), diffuse reflectance spectroscopy (spectrometer Specord M40 in the region of 220-800 nm) and photoluminescence (SDL-2M at room temperature in the interval 260-800 nm by exciting light with wavelength 254 nm). Size and habit of crystals were determined by optical and electron microcopy (Cam Scan Series 2). Impurity content in transformation products was determined by chemical and spectrum analysis. The dopant content (wt. %) in reaction medium is indicated in calculating upon final product.

RESULTS AND DISCUSSION

In Fig. 1 the kinetic curve (a) formation of corundum doped by Mn under TVT of hydrargillite at 417ºC is shown. The hydrargillite is transformed into boehmite already during heating of autoclave. The phase of boehmite is persisted during an induction period. And then the formation of corundum begins. The kinetics of boehmite into corundum transformation is described by the Erofeev equation for a case of ramified chain nucleation (Ivakin Yu. D., 2001). The slope ratio of the kinetic curve straightened in coordinates ln[-ln(1-α)] - τ gives value of corundum nucleation constant. In Fig. 1 also the kinetic curves (c, d) of formation of the undoped corundum at 412°C and 422°C in coordinates ln[-ln(1-α)] - τ are shown for comparison. It is seen that in the presence of manganese in reaction medium the duration of induction period increases relative to the formation of undoped corundum. However the greatest slope of a line (a) testifies to acceleration of a nucleation by manganese ions. Previous mechanical activation of hydrargillite (Ivakin Yu. D., 2001) and also change of water vapor pressure (Danchevskaya M. N., 2001) during transformation influence the value of nucleation constant. The size of corundum crystals, character and amount of structure defects depend on nucleation rate (Danchevskaya M. N., 2001). In fig. 2 the morphology of initial hydrargillite, boehmite and corundum particles doped by manganese is shown.

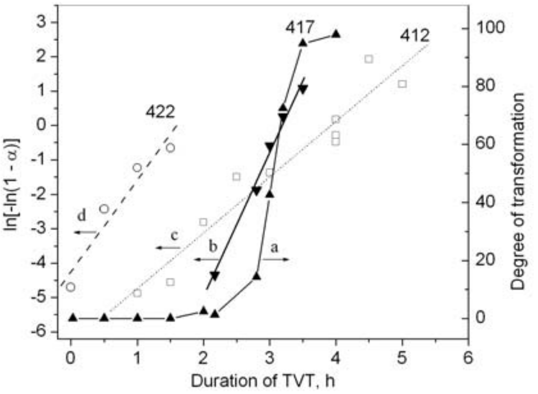
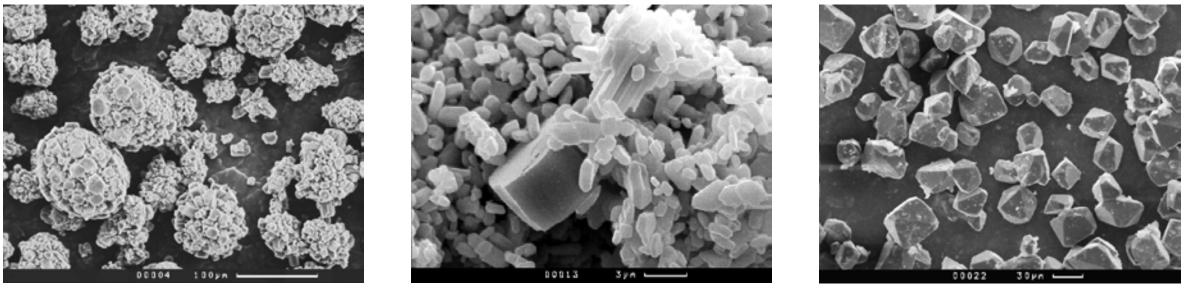


Figure 1. The formation kinetics of Mn doped corundum during TVT of hydrargillite at 417ºC (a, b) and undoped corundum at 412ºC (c), 422ºC (d). The Mn content in reaction medium is $4 \cdot 10^{-2}$ wt%.



a b c

Figure 2. The morphology of hydrargillite, boehmite and corundum particles:

a – aggregate of prismatic crystals of hydrargillite;
b - the occurrence of corundum crystal after TVT of boehmite at 417°C during 2 h;
c - crystals of corundum obtained after TVT of boehmite at 417°C during 4 h.

The nucleating and growth of corundum crystals under TVT conditions occurs due to appearance of solid-phase mobility. It happens at breakage and formation of metal-oxygen bonds in the quasi-equilibrium processes of hydroxylation - dehydroxylation of solid phase under conditions of increased temperature and water vapour pressure (Ivakin Yu. D., 2001). The dopant ions are adsorbed by crystals and involved in these processes along with aluminium ions. As a result the doping ions are incorporated into growing corundum crystals.

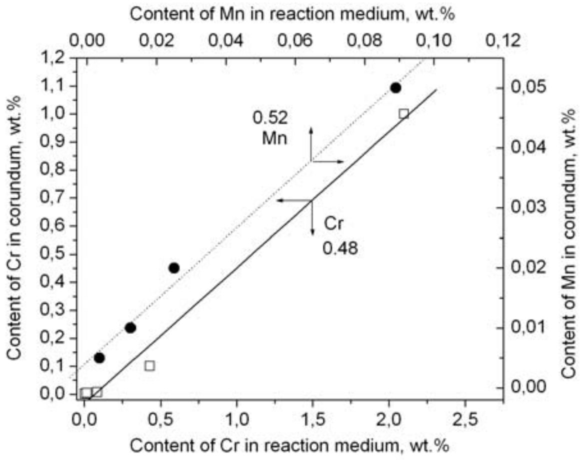


Figure 3. The dependence of manganese or chromium ions content in corundum on content in reaction medium. The conditions of synthesis in SCW are: T= 412°C, P=29 MPa; doping agent is $MnCl_2 \cdot 4H_2O$, or $(NH_4)_2Cr_2O_7$. The numbers indicate partition coefficient of dopant.

In fig. 3 the dependence of doping ions content in corundum on their content in reaction medium during treatment of hydrargillite in SCW is shown. Both ions change a charge at incorporation into corundum structure. The dates of photoluminescence and ESR testify to it. In fig. 4, 5 are shown spectra luminescence of corundum doped by chromium and manganese. The photoluminescence (PL) spectrum of Cr^{3+} ions in corundum (fig. 5) is well-known. The intensity increase of long-wave luminescence bands (700-800 nm) of Cr^{3+} ions with an increase of the chromium content in corundum more than 0.1 wt.% is determined by formation of the associates of interactive Cr^{3+} ions (pair, triples ets.) (Danchevskaya M. N., 2003). The corundum doped by manganese has red luminescence band with basic maximum at 678 nm (fig. 6). This luminescence is identified (Geschwind S., 1962, Jovanic, B. R., 1997) with an emission transitions in Mn^{4+} ions, which substitute Al^{3+} ions into the octahedral site in structure of corundum.

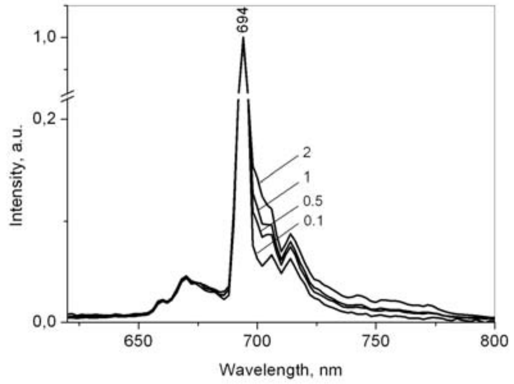


Figure 4. Normalized to the intensity maximum of basic band (694 nm) of luminescence corundum doped by Cr (exciting wavelength is 254 nm). The numbers indicate the chromium content (wt.%) in reaction medium during corundum synthesis.

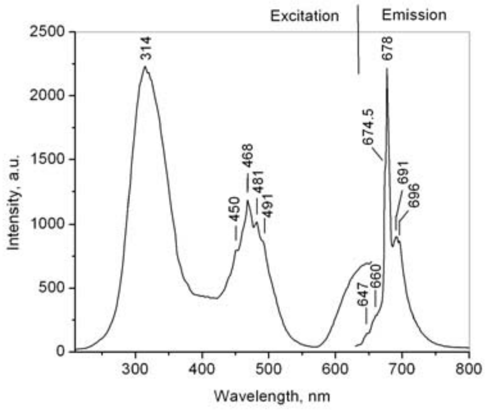


Figure 5. Composite luminescence band (with basic maximum at 678 nm) of manganese ions in corundum and its excitation spectrum.

ESR spectroscopic study of corundum doped by manganese reveals that in ESR-spectra three types of signals of paramagnetic ions manganese are presented. The multicomponent signal at $g_{exp.} = 2.00$ with pronounced hyperfine structure induced by the ^{55}Mn nucleus (A_{ev} = 84 G) and signal with traces of hyperfine structure at $g_{exp.} = 3.75 – 3.8$ are in accord with $Mn^{2+}(d^5)$ ions occupied in corundum structure positions with local symmetry differing from D_3 symmetry nodal position in corundum lattice. The third signal (singlet at $g_{exp.} = 2.00$) accords with exchange-bonded ions Mn^{4+} and Mn^{2+}. We suppose that the exchange interaction between Mn^{4+} and Mn^{2+} ions is realized in consequence of the occurrence $[Mn^{4+}\text{-}V_O\text{-}Mn^{2+}]$ pairs in corundum structure. The Mn^{2+} ions are one of a series of the compensators of charge difference of Mn^{4+} and Al^{3+} ions. The residual hydroxyl groups and oxygen vacancies

(V_O, in form of F-centers) are characteristic defects nascent during formation of simple and complicated oxides in conditions of a reversible dehydroxylation (Ivakin Yu. D., 1997). The oxygen vacancies and OH-groups also enter into the structure of luminescence center on the basis of Mn^{4+} ions. In fig. 6 a typical luminescent spectrum change of corundum after annealing in vacuum or air up to 1400° C is shown.
The water is the basic volatile impurity removed at heating up of corundum in vacuum (fig. 8).

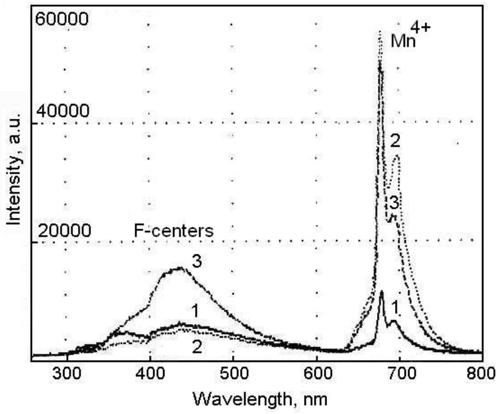


Figure 6. The luminescence spectra of Mn doped corundum: before heating (1), after heating up to 1200°C (2) and 1400°C (3). (Exciting wavelength is 254 nm).

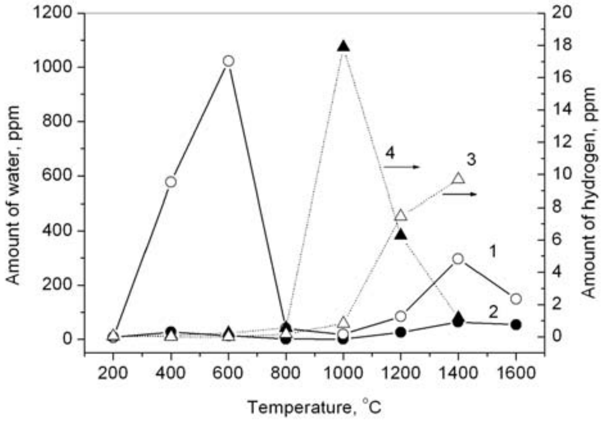


Figure 7. Amounts of water (1, 2) and hydrogen (3, 4) removed at stepwise vacuum annealing of undoped (1, 3) and Mn doped (2, 4) corundum. (According to mass spectral analysis). Content of manganese is 0.001 wt%.

The corundum doping by manganese results in a multiple decrease of content of surface water (up to 600°C) as well as structural water (more 600°C). The character of removing hydrogen at the annealing in vacuum of undoped and doped corundum (fig. 8) is also noticeably changed. The removing of hydrogen from structure of doped corundum may be attributed to reaction $Mn^{2+} + 2OH^{-} \rightarrow Mn^{4+} + H_2 + 2O^{2-}$ because the increase of luminescence band intensity at 678 nm in 4 times after annealing (fig.7) testifies to formation of additional Mn^{4+} ions. The intensity magnification of F-centers luminescence band (broad band about 440 nm, fig. 7) testifies to formation of oxygen vacancies:

$$2OH^{-} \rightleftarrows O^{2-} + V_O + H_2O.$$

The annealing of Mn-doped corundum results in multiple intensity increase of luminescence excitation bands at 314 and 470 nm (fig. 6). The luminescence excitation band with fine structure around the 470 nm is determined by the light absorption by Mn^{4+} ions (Geschwind, S., 1962). The luminescence excitation band of the Mn^{4+} ions at 314 nm is determined by oxygen vacancies, which enter into the structure of luminescence center. At incorporating into corundum lattice the manganese ion can have an oxidation level of 4+ or 2+. The change of water vapour pressure at formation of corundum structure influences a relation of Mn^{4+}/Mn^{2+}:

$$Mn^{4+} + O^{2-} + H_2O \underset{-P}{\overset{+P}{\rightleftarrows}} Mn^{2+} + 2HO^{-}$$

In Fig. 8 it is visible that with increase of water vapour pressure the equilibrium is displaced to the right and the band intensity at 678 nm is diminished. The amount of structural water makes up 145 ppm in Mn-doped corundum and 550 ppm in undoped corundum. The removing temperature of water from corundum structure makes up 1400°C (Fig. 7).

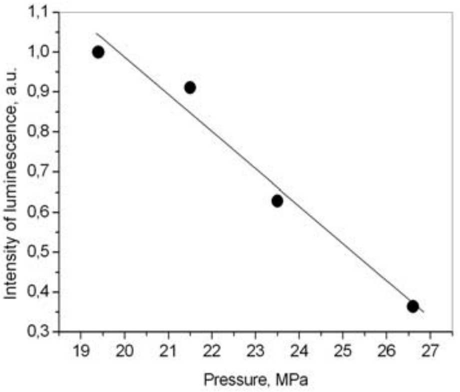


Figure 8. The intensity dependence of luminescence band at 678 nm on water vapour pressure during synthesis of corundum.

The spectra of excitation and luminescence for Eu (0.67 mol%) doped corundum are shown in Fig. 9, 10. The Eu doped corundum has characteristic series of PL bands (Fig. 10) with the basic maximum near 614 nm and maxima of weak intensity at 579, 592, 654 and 704 nm. It should be noted that PL bands have a characteristic broadening. It indicates on disordering of cationic sites which one are occupied by Eu^{3+} ions. In Fig. 9 it is visible that the narrow excitation bands in region 300-500 nm coincide with absorption bands of Eu^{3+} ions (Fig. 9, in inset). The annealing at 1400ºC does not influence intensity of these excitation bands. However the relation of intensities of some luminescence bands is changed (Fig. 10). It testifies (Kurokawa Y., 1998) to change of the crystal environment around Eu^{3+} ions. The increasing of excitation band at 270 nm (Fig. 9) testifies that it can be by result of oxygen vacancies formation during removal of hydroxyl groups alongside of Eu^{3+} ions. The similar effect is observed for a luminescence center on the basis of Eu^{3+} ions incorporated in structure of gahnite (zinc aluminate, $ZnAl_2O_4$).

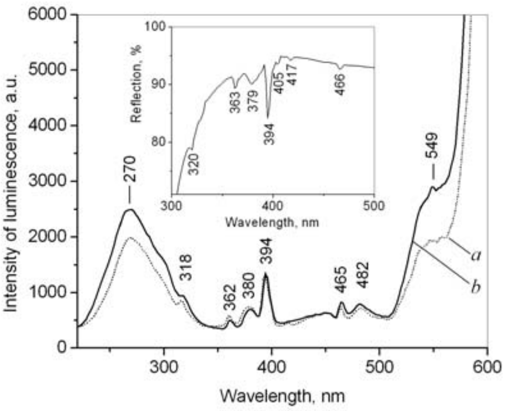


Figure 9. Excitation spectra of Eu (0.67 mol%) doped corundum *a* – before and *b* – after annealing at 1400ºC, λ_{em} = 614 nm. In the inset the reflectance spectra section is shown.

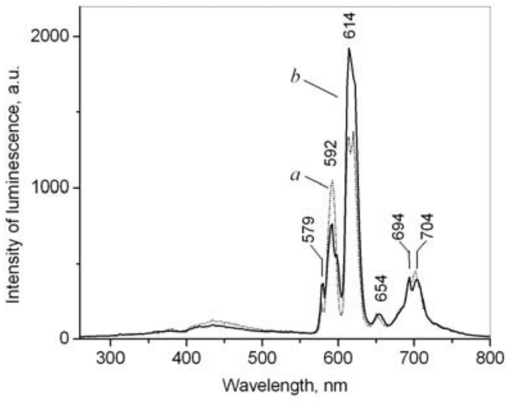


Figure 10. Luminescence spectra of Eu (0.67 mol%) doped corundum *a* – before and *b* – after annealing at 1400ºC. (Exciting wavelength is 254 nm).

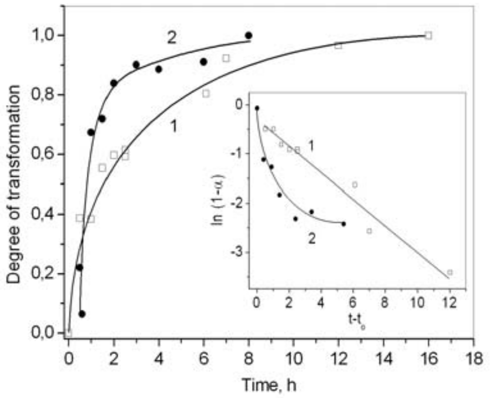
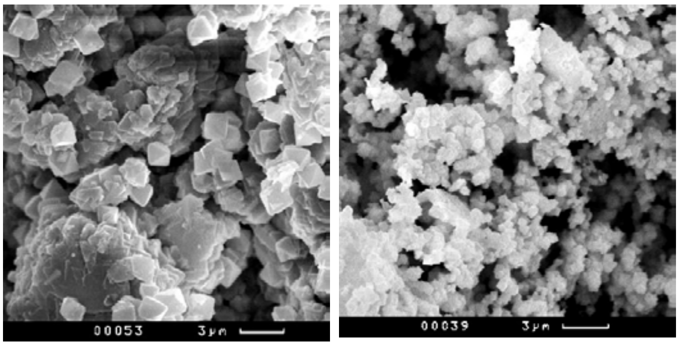


Figure 11. Kinetics of gahnite synthesis at 200°C during treatment of hydrargillite with zinc oxide mixture in aqua ammonia (1), in solution of $(NH_4)_2Cr_2O_7$ (2) and kinetic curves in coordinates ln(1-α) – τ. Chromium content in reaction medium is 1 mol%.

The synthesis of gahnite occurs under mixture treatment of hydrargillite, boehmite or aluminium oxide with zinc oxide in thermovaporous or hydrothermal conditions within temperature region of 200-400°C and water vapour pressure of 2-26 MPa (IVAKIN YU.D., 2004). The gahnite formation rate essentially depends on the different additives into reaction medium. In water vapour or in water the gahnite formation occurs slowly. Under intermixture treatment of hydrargillite with zinc oxide the transformation occurs at 200°C for 144 hours on 50%, and at 400°C is completed for 24 hours. However the gahnite formation at 200°C in medium of aqua ammonia is completed for 16 hours (Fig. 11, the curve 1) and in solution medium of $(NH_4)_2Cr_2O_7$ it is completed for 8 hours (Fig. 11, the curve 2). The curve 1 satisfactorily is straightened in coordinates ln(1-α) – τ of the equation of solid-phase transformation with a rate-determining step of nucleation with constant rate (Brown M. E., 1980). The constant nucleation rate suggests that the diffusion of zinc ions in an aluminous matrix occurs rapidly [Ivakin Yu.D., 2005]. On reaching certain concentration of zinc ions, the nucleation of a gahnite phase starts. The formation of gahnite in medium of $(NH_4)_2Cr_2O_7$ solution has other rate-determining step. In coordinates of the Avrami-Erofeev equation $\ln[-\ln(1-\alpha)] - \ln(t-t_o)$ this kinetic curve has slope angle 0.43, that considerably differs from 1. By this is meant that the chromium ions accelerate the nucleation step and the diffusion of zinc ions becomes a rate-determining step. The size diminution of forming crystals (Fig. 12) confirms a conclusion about acceleration of nucleation. In fig. 12 (a) it is visible that in medium of aqua ammonia the octahedral crystals of gahnite are obtained with the size about 2 microns. However in the presence of chromium ions the gahnite crystals have the size less than 1 micron (fig. 12, b).



a b

Figure 12. SEM images of gahnite obtained at 200°C in medium: a – aqua ammonia during 12 h, b – solution of $(NH_4)_2Cr_2O_7$ during 8 h.

The Cr-doped gahnite has a red luminescence band with basic maximum at 688 nm. The gahnite synthesized in presence (1 mol%) of europium oxide has characteristic series of PL bands (Fig. 14, a) with the basic maximum near 612 nm and maxima of weak intensity at 590, 626, 654 and 706 nm. The appearance of luminescence bands at 382 and 550 nm may be attributed to formation of oxygen vacancies in the reducing conditions of gahnite synthesis (Ivakin Yu.D., 2005). Both PL bands are excited in band at 267 nm. After annealing this sample in air at 1400°C for 2 hours the PL spectrum (Fig. 14, b) contains only bands of europium. However, position of the most intensive band shifts to 616 nm. The relation of intensities and position of some other bands also change. The high-temperature annealing of gahnite produces also magnification and broadening of excitation band at 271 nm (Fig. 14, a, b). The maximum of band shifts to 285 nm (Fig. 14, b). As is the case with corundum, these luminescence changes may be due to the same oxygen vacancies formation in environment around Eu^{3+} ions.

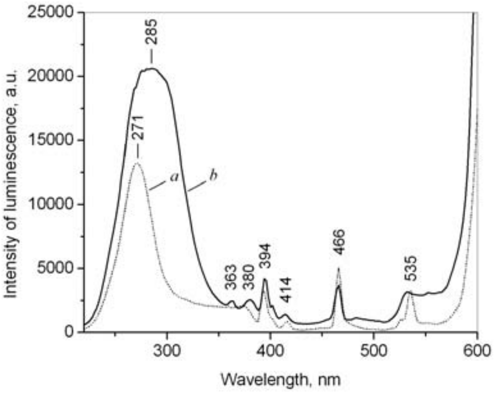


Figure 13. Excitation spectra of Eu doped gahnite *a* – before and *b* – after annealing at 1400ºC.

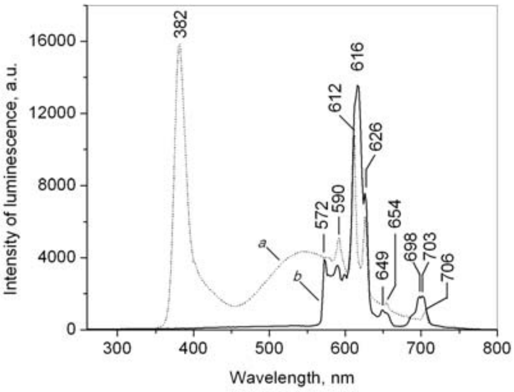


Figure 14. Luminescence spectra of Eu doped gahnite *a* – before and *b* – after annealing at 1400ºC.

In contrast to Eu doped corundum and gahnite, the Eu doped lanthanum aluminate has the narrowed luminescence bands (Fig. 16). The $LaAlO_3$:Eu was synthesized under TVT of stoichiometric mixture of hydrargillite and lanthanum oxide with addition of europium oxide at 400°C and water vapour pressure of 26 MPa. The narrowed luminescence bands testify that the Eu^{3+} ions occupy homogeneous sites with narrow energy distribution. Therefore cationic sublattice of synthesized $LaAlO_3$:Eu is well ordered. Also notice that as contrasted to by luminescent spectra of Eu^{3+} in gahnite (Fig. 14) and corundum (Fig. 10) the relation of bands intensities has changed sharply.

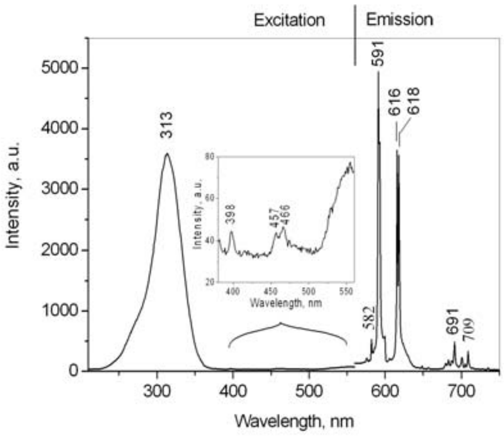


Figure 15. Excitation and emission spectra for Eu^{3+} doped $LaAlO_3$ synthesized at 400°C and water vapour pressure of 26 MPa with content of Eu (4.5 mol%) in reaction medium.

This is due to that in lanthanum aluminate the Eu^{3+} ion substitutes La^{3+} ion instead of Al^{3+}. It is interesting that the excitation of Eu^{3+} luminescence in lanthanum aluminate also is most effective in absorption band of oxygen vacancies at 313 nm, whereas the excitation of Eu^{3+} luminescence in absorption bands of europium (Fig.15, in inset) is much weaker. It can be seen (Fig. 9, 13, 15) that with increasing excitation in band of oxygen vacancies (UV-band) concerning excitation in absorption band by europium ions (394 or 466 nm), the position shift of the UV-band to the red region increases. Both of these effects are caused by the strengthening of interaction of oxygen vacancies with Eu^{3+} ions and shift of electron density from vacancy (F-center) unto ions.

As compared with corundum and gahnite in structure of fine crystalline yttrium-aluminum garnet ($Y_3Al_5O_{12}$, YAG) may be contained more hydroxyl groups. The synthesis of fine crystalline yttrium-aluminum garnet at 200-400°C under treatment of the stoichiometric mixture of oxides proceeds in hydrothermal and thermovaporous conditions through a solid-phase mechanism with a rate-determining step of nucleation with constant rate (Ivakin Yu.D., 2001). Synthesized YAG contains 5-7% of water in the form of hydroxyl groups which substitute a part of tetrahedra $[AlO_4]$ onto tetrahedra $[OH]_4$. The basic amount of water is removed out structure of synthesized YAG at heating on air within the temperature region of 510-710°C (Ivakin Yu.D., 2001). At addition into reaction medium of $(NH_4)_2Cr_2O_7$ or neodymium oxide the YAG doped by Cr^{3+} or Nd^{3+} ions is obtained. The Nd^{3+} ions substitute yttrium ions in structure of IAG. It results in appearance of a luminescence with the basic maximum at 1064 nm. The Cr^{3+} ions substitute octahedral aluminium ions. The obtained YAG:Cr (Fig.16) has two types of centers of Cr^{3+} ions with the luminescence bands about

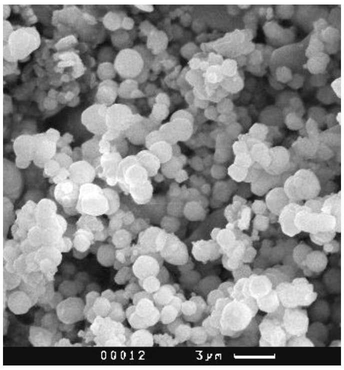


Figure 16. SEM images of YAG:Cr obtained at 300°C in medium water solution of $(NH_4)_2Cr_2O_7$. Chromium content in reaction medium is 8.6 mol%.

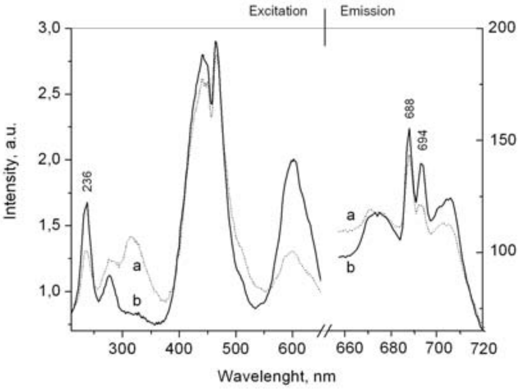


Figure 17. Luminescence of Cr^{3+} doped YAG: a – synthesized sample, b – after annealing at 550°C. Excitation spectra of luminescence band at 688 nm at the left are shown. Luminescence spectra of Cr^{3+} ions at excitation 410 nm at the right are shown.

688 and 694 nm. The first (688 nm) belongs to Cr^{3+} ion in YAG structure (Wall W.A., 1971). The second (694 nm, the ruby band) is similar to Cr^{3+} ion in corundum. The appearance of the ruby band of YAG:Cr luminescence is caused by formation of oxygen vacancies in its structure during synthesis (Ivakin Yu.D., 2001). The annealing of synthesized YAG:Cr on air at 550°C result in removal about 80% of structural water. In fig. 18 are shown the influence of annealing on a luminescence of Cr^{3+} ions. It is seen that the elimination of hydroxyl group leads to formation of additional oxygen vacancies. In luminescence spectrum of Cr^{3+} the ruby band (at 694 nm) increase greatly. The band at 688 nm with vibronic spectrum in sideband about 700 nm belongs to Cr^{3+} ions occupying sites not distorted by oxygen vacancies. After annealing of YAG:Cr the fine structure of vibronic spectrum is better discernible. It testifies to ordering of sites of Cr^{3+} ions. In excitation spectra the formation of additional oxygen vacancies results in the intensity increase of oxygen vacancies band at 236 nm. The efficiency of excitation in this band is much lower than in absorption band of Cr^{3+} ions (in region 400-500 nm), and its location is not shifted to the red region. Therefore oxygen vacancies weakly interact with Cr^{3+} ions. The excitation band about 600 nm can belong to the not bridging oxygen. It also can be formed during dehydroxylation of YAG structure.

The annealing of Nd doped YAG at 1100°C leads to the intensity increase and narrowing of the Nd^{3+} luminescence band at 1064 nm (Ivakin Yu.D., 2001). In excitation spectrum the relation of band intensities is changed.

CONCLUSION

Owing to increased temperature and water vapour pressure the process of dehydroxylation of partial hydrated oxides proceeds in the quasi-equilibrium conditions and is accompanied by appearance high solid-phase mobility and formation of oxygen vacancies and hydroxyl groups. The ions of dopants present in reaction medium are proportioned in forming crystals and influence the nucleation rate. The doping ions interact with a residual hydroxyl groups and oxygen vacancies. Thus the complicated luminescence centers can be formed. The residual hydroxyl groups cause lattice disturbance and result in a broadening of luminescence bands with diminution of their intensity. The interaction of doping ions with oxygen vacancies appears in change of excitation spectrum of luminescence. With increase of interaction the efficiency of luminescence excitation in absorption band of vacancies considerably rises. Such interaction of Eu^{3+} ions with oxygen vacancies appears in structure of complicated oxides (gahnite and lanthanum aluminate) more, than in corundum. The annealing of fine-crystalline oxides at high temperatures results in removal of residual hydroxyl groups, change of a state of point defects of structure and of their spectral properties.

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