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LUMINESCENCE OF ZnGa₂O₄ AND ZnAl₂O₄ SPINELS DOPED WITH Eu³⁺ AND Tb³⁺ IONS

Spinel type mono-phase the ZnGa₂O₄ and ZnAl₂O₄ compounds doped with Eu³⁺ and Tb³⁺ ions were obtained using two methods: solid phase reactions and deposition from chemical solutions. The luminescent analysis of the materials shows that the rare earth ions are localised at the defect sites (regions) of the crystallite (grain) boundaries. The emission spectra of the samples with europium are characterized by an intense emission in red region due to the ⁵D₀ → ⁷F_{1,2} transitions of Eu³⁺ ions, whereas, in the case of terbium, the highest intensity corresponds to the green emission due to the ⁵D₄ → ⁷F₃ transitions of Tb³⁺ ions. The intensities of the intra-shell emission of the Eu³⁺ and Tb³⁺ ions in comparison with luminescence intensity of the chromium impurity traces (residual small amount of the Cr³⁺ ions) show that the materials doped with transition metals are more promising for development of phosphors based on oxide spinels than the materials doped with rare-earth elements.

INTRODUCTION

Semiconductors, doped with rare earth elements, are considered to be perspective materials for optoelectronics and photonics due to the presence of narrow emission spectral lines. Wide band gap semiconductors and dielectrics are more preferable for doping, because the effects of thermal quenching of the radiation are inversely proportional to the band gap value [1]. Another advantage of the wide band gap materials is their chemical stability and stability of the physical characteristics in a large temperature interval. Actually, the most widely used phosphors for planar displays are sulfides. However, the chemical reactions stimulated by the electronic beam leading to the formation of a non-luminescent layer with the deficiency of sulfur at the surface of the phosphor are the important shortcomings of the sulfide phosphors. These reactions considerably reduce the efficiency of phosphors [2].

Besides, the reaction products, stimulated by electron beam, pollute electronic emitters. Many problems related to the degradation are avoided by using of the oxide phosphors. Among them, the ZnGa₂O₄ compound is one of the best studied low voltage cathodoluminescent phosphors [3]. ZnAl₂O₄ is another compound, which recently has attracted considerable interest for electroluminescent thin film displays and opto-mechanical sensors [4-6]. It was reported about the synthesis of bulk and nano-structured ZnAl₂O₄ using solid phase reactions of zinc and aluminium oxides at temperatures higher than 800°C [7], or by means of chemical reactions in solutions [8-10]. Several papers have been dedicated to the investigations of luminescence properties of ZnAl₂O₄ [4, 11-14] and ZnGa₂O₄ doped with rare earth elements [3, 16]. However, the quantitative analysis of the emitted intensity, or a comparative analysis with the luminescence intensity of other radiative centers are not presented in these works.

In this paper the luminescence caused by intra-shell radiative transitions of Eu³⁺ и Tb³⁺ ions intro-

duced in ZnGa₂O₄ and ZnAl₂O₄ hosts is investigated. The comparison of this luminescence intensity with the emission intensity of the Cr³⁺ ions existing in the host lattices as traces of residual impurity is carried out. The difficulties concerning the incorporation of the big radius rare earth ions in the octahedral sites of the oxide spinel hosts, that are not inherent in the case of small radius transition metal impurities, are revealed.

PREPARATION OF SAMPLES AND EXPERIMENTAL TECHNIQUES

Undoped ZnGa₂O₄ and ZnAl₂O₄ compounds as well as the ones, doped with Eu and Tb, were prepared by means of two technological methods.

In the first process, the material has been obtained using solid phase reactions method by mixing ZnO (99.99%) and Ga₂O₃ (99.99%), or ZnO (99.99%) and Al₂O₃ (99.99%) powders in 1:1 ratio, followed by forming pellets under a press and sintering at 1200°C during 16-18 hours. Doping with rare earth elements was carried out by adding Eu₂O₃ and Tb₂O₃ powders with concentration of (0.1–2) %.

In the second process, the powders were obtained using the chemical deposition method, that allows the formation of ZnGa₂O₄ and ZnAl₂O₄ precipitates with spinel structure at temperature less than 300°C. For comparison, several samples simultaneously doped with phosphor and rare earth elements were prepared. The phase composition of the compounds was analyzed by EDX and XRD methods.

The luminescent properties of the obtained materials were studied at room temperature using different spectral lines of a Spectra Physics 2017 Ar⁺ laser for optical excitation, SDL-1 double spectrometer (resolution better than 1meV), PEU-106 photomultiplier and a photon counting system.

RESULTS AND DISCUSSION

The ZnGa_2O_4 and ZnAl_2O_4 materials with spinel structure, belong to the space group O_h^7 with eight formula units in the unit cell. Thirty two oxygen atoms occupy sites with C_{3v} symmetry forming a closely packed cubic lattice with 64 tetrahedral (T_d) and 32 octahedral (D_{3d}) cation sites, only 8 tetrahedral (8A) and 16 octahedral (16B) of them being occupied by cations. Both compounds under study, belong to normal spinels, where all Zn atoms occupy the tetrahedral A sites, and atoms of Ga or Al occupy the octahedral sites. At the same time, insignificant inversion of the spinel structure, where a part of Ga or Al atoms may occupy the tetrahedral A sites, is possible.

Thus, rare-earth ions, potentially, may occupy both the tetrahedral and octahedral lattice sites. However, it is known that in the III–V and II–VI materials, due to a large ion radius, the rare-earth elements hardly occupy lattice sites with the tetrahedral coordination [15], preferring the sites with a coordination number greater than 6. Efficiency of the rare-earth ion occupation of sites with the octahedral coordination in $A^{II}B^{III}O_4$ compounds with the spinel structure is studied insufficiently.

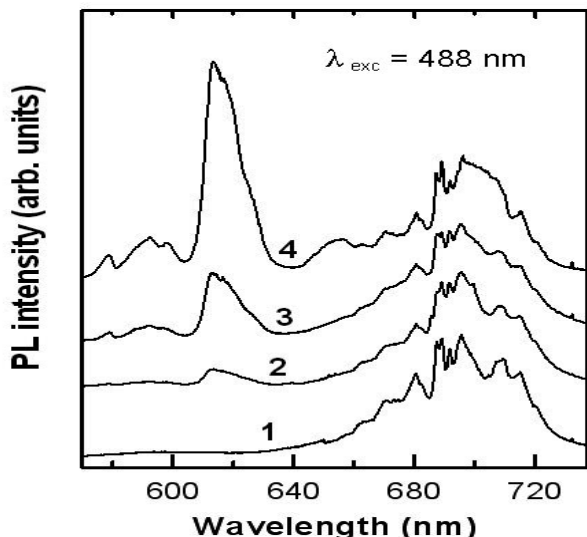


Fig. 1. PL spectra of ZnGa_2O_4 powders doped with Eu concentrations: 1 – 0%; 2 – 1%; 3 – 0.5%; 4 – 2%

Figure 1 shows the luminescence spectra of ZnGa_2O_4 with various concentrations of Eu doping impurity prepared from initial materials of high purity. Let us note that the form of the samples spectra, obtained by the method of solid phase reactions and by the chemical method is practically identical.

The luminescence spectrum consists of emission lines related to the ${}^5D_0 \rightarrow {}^7F_1$ intra-shell transitions (in the range of 570–600 nm) and ${}^5D_0 \rightarrow {}^7F_2$ (in the range of 600–630 nm) of Eu^{3+} ions as well as of the structured band in the range of 650–730 nm, corresponding to emission, induced by residual chromium impurity. The highest intensity of the luminescence, due to Eu ions presence, is obtained at excitation by the 465.8 nm laser line (see Fig. 2, curve 1), which quantum energy coincides with the energy of the ${}^7F_0 \rightarrow {}^5D_2$ intra-shell transitions of Eu^{3+} ions, allowing their resonance excitation. Appearance of the band, induced by

the residual chromium impurity in the luminescence spectra, makes it possible to compare the efficiency of the incorporation of Eu^{3+} ions into the spinel structure with the respective efficiency of Cr^{3+} ions. Chromium concentration in ZnGa_2O_4 powders, prepared from high purity materials is ~ 10 ppm.

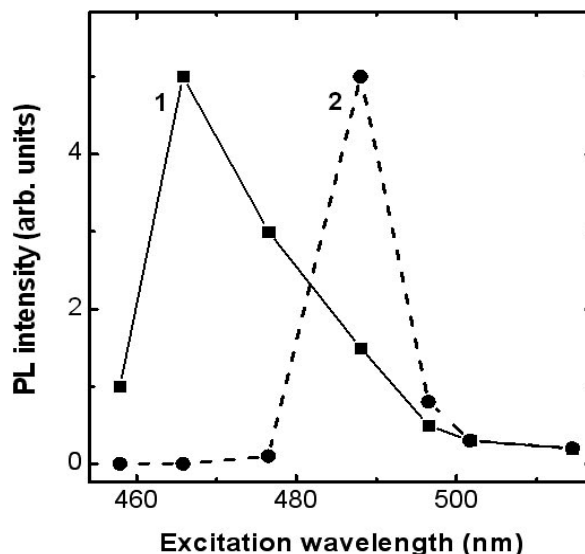


Fig. 2. PL intensity dependence in the spectral region of 600–630 nm for ZnGa_2O_4 powders doped with Eu (curve 1, squares) and in the spectral region of 540–560 nm for ZnGa_2O_4 powders doped with Tb (curve 2, circles) upon the excitation laser wavelength

As one could see from Fig. 1, the intensity of the luminescence due to the Eu doping impurity becomes comparable with the intensity of the luminescence of chromium impurity only at europium concentration of 1 %, i.e., by three orders of magnitude higher than the chromium concentration. This observation is a direct evidence of inefficiency of Eu^{3+} ion incorporation into the spinel lattice sites with a coordination number equal to 6.

Let us note that the Eu^{3+} ion radius is equal to 0.95 E and it is obviously greater than the radius of Ga^{3+} ions (0.62 E) practically coinciding with the radius of trivalent Cr^{3+} ions (0.615 E). The assumption of low efficiency of the rare-earth element ion incorporation is also confirmed by the form of the luminescence spectra in the region of the Eu^{3+} intra-shell transitions. Broad overlapping lines are observed instead of narrow lines due to the Stark splitting. This form of spectra is characteristic of amorphous materials and glasses.

On the other hand, the form of the X-ray diffraction patterns, shown at Fig. 3 indicates the presence of perfect crystallites with the spinel structure. The average size of the crystallites in powders was determined by the Scherer formula [16]

$$d = \frac{K\lambda}{(\beta^2 - \beta_0^2)^{1/2}} \cos\theta,$$

where β is the half-width of the diffraction peak in radians, β_0 corresponds to the instrumental broadening, $K = 180/\pi$, λ is the X-ray wavelength, θ is the Bragg diffraction angle. The average crystallite size determined by the given formula is 20 nm. Discrepancy between the broad lines of the luminescence spectra and

the X-ray analysis data is explained by the presence on the crystallite boundaries of regions with defect structure close to the amorphous one. The Eu impurity penetrates in these defect boundary regions (being practically not incorporated into the volume of crystallites with perfect spinel structure); this determines the form of the luminescence spectra.

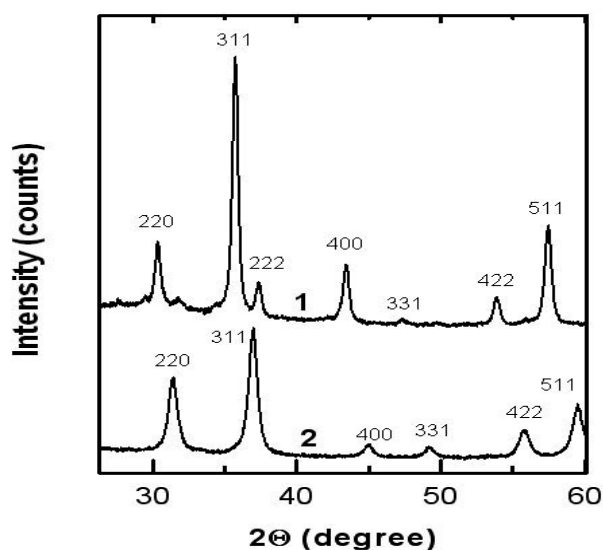


Fig. 3. XRD patterns for ZnGa_2O_4 (1) and ZnAl_2O_4 (2) compounds

As it was mentioned above, big rare-earth ions are incorporated more easily into places with high coordination number. Such a compound is EuPO_4 , as it easily crystallizes in a monazite structure at the synthesis temperatures above 600°C . In the monoclinic monazite structure $\text{P2}_1/\text{n}$ the coordination number for Eu ions is equal to 9. Taking this into account, we have prepared ZnGa_2O_4 samples with Eu concentration of 1% being simultaneously doped with various phosphor concentrations and we have measured the luminescence spectra depending on phosphor concentration.

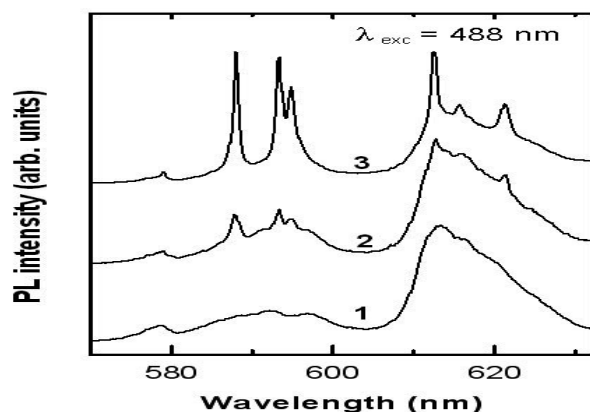


Fig. 4. PL spectra of ZnGa_2O_4 powders doped with 1% wt concentration of Eu (1) and with addition of 0.3% wt (2) and 2% wt (3) phosphor impurity

As one could see from Fig. 4, additional narrow peaks appear in the luminescence spectrum instead of broad bands when concentrations of phosphorus and europium are comparable. The luminescence spectrum completely coincides with the known spectrum of EuPO_4 compound when the phosphor concentration is equal to or is higher than the europium

concentration [17]. This experiment is an additional confirmation of the fact that for big Eu^{3+} ions it is easier to be incorporated into the lattice sites with a high coordination number forming a new EuPO_4 compound, than to penetrate into amorphous regions on the boundaries of ZnGa_2O_4 crystallite grains. The probability of their implantation directly into the spinel structure of the crystalline grains is even lower.

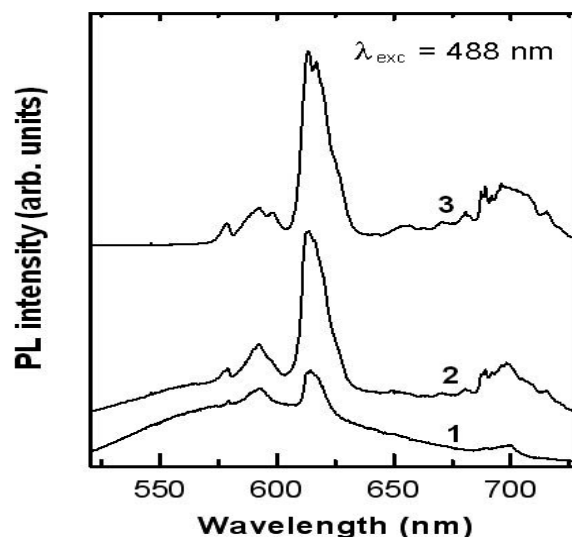


Fig. 5. PL spectra of ZnGa_2O_4 powders doped with 1% wt Eu concentration prepared from high purity components before (1) and after annealing at 500°C (2) and 700°C (3)

Figure 5 shows the annealing influence on spectra of ZnGa_2O_4 samples doped with Eu^{3+} ions prepared of high purity materials. The luminescence spectrum of the non-annealed sample consists of a broad band determined, apparently, by the crystal structure defects, whereupon narrow bands corresponding to the intra-shell transitions of Eu^{3+} ions impose.

Let us note, that in the given case, in the wavelength range of 650–730 nm, only a weak band due to the transitions ${}^3\text{D}_0 \rightarrow {}^7\text{F}_4$ of Eu^{3+} ions is observed and the band due to presence of Cr^{3+} ions is not found because of extremely low concentration of residual chromium (1 ppm). As the annealing temperature increases above 500°C the broad band luminescence is quenched. This may be explained by annealing of the defects.

At the same time, the activation of Eu impurity takes place and spectral lines inherent to Cr^{3+} ions appear due to diffusion of the chromium impurity during annealing.

Similar behavior of the rare-earth ions is observed in the case of ZnGa_2O_4 doped with terbium.

As one could see from Fig 6, where the luminescence spectra of ZnGa_2O_4 doped with Eu and Tb are compared, in the sample with terbium, the overlapping of Stark lines takes place, and the luminescence from Tb^{3+} ions is comparable to the intensity of the luminescence due to the residual Cr impurity, while its concentration being less by three orders of magnitude.

The highest intensity of the luminescence due to Tb is obtained at excitation by 488 nm line (see Fig. 2, curve 2), its quantum energy coinciding with the energy of the intra-shell transitions ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$ of Tb^{3+}

ions allowing resonance excitation of these ions. The emission is due to the transitions ${}^3D_4 \rightarrow {}^7F_{2,3,4,5}$.

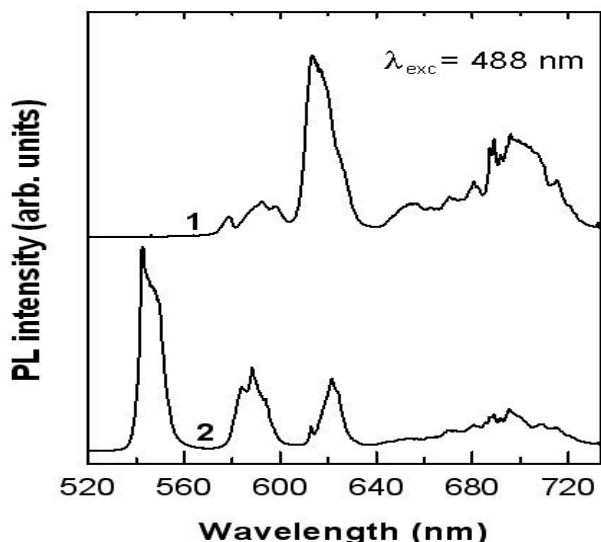


Fig. 6. PL spectra of $ZnGa_2O_4$ powders doped with 2% wt Eu (1) and Tb (2)

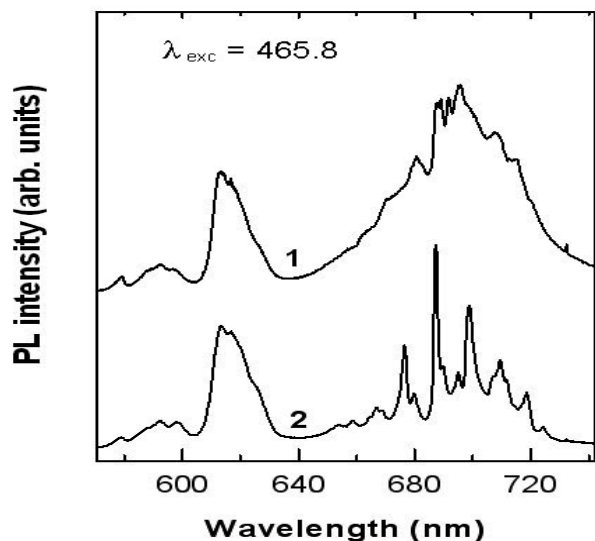


Fig. 7. PL spectra of $ZnGa_2O_4$ (1) and $ZnAl_2O_4$ (2) powders doped with 0.5% wt Eu

Let us note that the behavior of the rare-earth ions in $ZnAl_2O_4$ is analogous to their behavior in $ZnGa_2O_4$. As it follows from Fig. 7, the bands of the intra-shell luminescence of rare-earth ions are identical for $ZnAl_2O_4:Eu$ and $ZnGa_2O_4:Eu$ compounds. This confirms that ions of Eu and Tb penetrate into amorphous regions on the grain boundaries.

Otherwise, the spectra must differ, since crystal fields are different for different materials. The latter statement is well illustrated by analysis of the luminescence due to Cr impurity. As one could see from Fig. 7, in the range of 650–730 nm, the forms of the luminescence spectra of $ZnAl_2O_4$ and $ZnGa_2O_4$ compounds are completely different.

Thus, in contrast to Eu ions, Cr ions are easily incorporated into the spinel crystal structure of the grains due to nearly the same value of ion radii of Ga and Cr, determining the luminescence intensity being incomparably higher than in the case of the intra-shell luminescence of Eu ions.

CONCLUSIONS

1. The results of this work reveal the difficulties of the incorporation of the rare earth ions in the octahedral sites of the oxide spinel crystalline lattices. These difficulties are caused by the large radius of the RE ions, that prefer to be located in the sites with coordination number bigger than six.

2. The luminescent spectra analysis registered for $ZnAl_2O_4$ and $ZnGa_2O_4$, doped with europium and terbium from the one side and containing a residual Cr impurity on the other side has shown that in comparison with rare earth elements the transition metal ions are much more efficient for using as activating impurity of phosphors based on spinel type materials.

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ЛЮМИНЕСЦЕНЦИЯ ШПИНЕЛЕЙ ZnGa_2O_4 AND ZnAl_2O_4 ЛЕГИРОВАННЫХ ИОНАМИ Eu^{3+} И Tb^{3+}

Методом твердофазных реакций и осаждением из химических растворов изготовлены порошки однофазных соединений со структурой шпинели легированные ионами Eu^{3+} и Tb^{3+} . На основе люминесцентного анализа материалов сделан вывод о преобладающем внедрении ионов редкоземельных элементов в дефектные области, образованные на границах кристаллических зерен. Спектры люминесценции образцов с примесью европия характеризуются наибольшей интенсивностью в красной области за счет переходов ${}^3\text{D}_0 \rightarrow {}^7\text{F}_{1,2}$ ионов Eu^{3+} , тогда как в случае примеси тербия наибольшая интенсивность соответствует зеленому свечению, за счет переходов ${}^3\text{D}_4 \rightarrow {}^7\text{F}_5$ ионов Tb^{3+} . Результаты анализа интенсивности внутрицентральной люминесценции ионов Eu^{3+} и Tb^{3+} в сравнении с интенсивностью люминесценции, вызванной остаточной примесью хрома (ионов Cr^{3+}), свидетельствует о том, что большую перспективность для разработки люминофоров на основе оксидных шпинелей имеют материалы, легированные переходными металлами, по сравнению с редкоземельными элементами.

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ЛЮМИНЕСЦЕНЦИЯ ШПИНЕЛЕЙ ZnGa_2O_4 I ZnAl_2O_4 , ЛЕГОВАНІХ ІОНАМИ Eu^{3+} I Tb^{3+}

Методом твердофазних реакцій і осаджуванням хімічних розчинів виготовлені порошки однофазних сполучень ZnGa_2O_4 and ZnAl_2O_4 з структурою шпінелі, легованих іонами Eu^{3+} и Tb^{3+} . На основі люмінесцентного аналізу матеріалів зроблено висновок про переважне впровадження іонів рідкоземельних елементів в дефектні області, створені на кордонах кристалічних зерен. Спектри люмінесценції зразків з домішками европія відзначаються найбільшою інтенсивністю у червоній області за рахунок переходів ${}^3\text{D}_4 \rightarrow {}^7\text{F}_5$ іонів Tb^{3+} . Висновки аналізу інтенсивності внутріцентральної люмінесценції іонів Eu^{3+} і Tb^{3+} у порівнянні з інтенсивністю люмінесценції, викликаний остаточними домішками хрому (іонів Cr^{3+}), свідчать про те, що велику перспективність для розробки люмінофорів на основі оксидних шпінелей мають матеріали, леговані перехідними матеріалами, по зрівнянню з рідкоземельними елементами.