Optical properties of Tb and Eu doped cubic YAlO$_3$ phosphors synthesized by sol–gel method

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**Abstract**

In this work, terbium and europium doped YAlO$_3$ phosphors were synthesized by sol–gel method. It has been shown that after annealing at 1000 °C these phosphors crystallize in the cubic garnet phase, similar to Y$_3$Al$_5$O$_{12}$. As evidenced by the time-resolved photoluminescence spectroscopy and Maximum Entropy Method, the photoluminescence decay of both europium $^5D_0$ and terbium $^5D_4$ states has two lifetime components: short and long, both of the order of milliseconds. Moreover, for both phosphors the short photoluminescence lifetime was ascribed to the ions occupying low-symmetry sites in the vicinity of the nanocrystal surface, while the long decay component was related to the ions present in the bulk of YAlO$_3$ nanocrystal. For both dopants, the long lifetime component of Tb$^{3+}$ and Eu$^{3+}$ emission is longer than the equivalent lifetimes in bulk Y$_3$Al$_5$O$_{12}$ crystal.

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1. Introduction

Phosphors containing rare-earth ions have received considerable attention in the recent years due to their technological importance. Particularly, much research has been devoted to these materials which could be used in X- and γ-ray detectors [1,2] or modern cathode-ray tube field emission displays [3]. Considerable attention has been also paid to the transparent, polycrystalline ceramics made on the basis of the rare-earth doped phosphors. This kind of materials is considered to be the alternative for large bulk crystals as they are known to be an efficient lasing material [4,5].

Among various hosts for the lanthanides (Ln$^{3+}$), especially two compounds have been investigated very thoroughly: Y$_3$Al$_5$O$_{12}$ (yttrium alumina garnet) and YAlO$_3$ (yttrium orthoaluminate). The first of the mentioned materials crystallizes in the cubic form having a garnet structure [6]. The second compound has two well-known modifications: orthorhombic and hexagonal [7]. Moreover, as reported first by Keith and Roy [8] and then by Yamaguchi et al. [9], it is also possible to obtain YAlO$_3$ in a cubic garnet structure. This kind of material can be obtained e.g. after annealing of the hexagonal YAlO$_3$ nanopowder at temperature of around 1000 °C [9]. Noteworthy, further annealing at 1100–1200 °C leads to decomposition of the cubic YAlO$_3$ to Y$_3$Al$_5$O$_{12}$ and Y$_2$Al$_2$O$_3$.

While considerable attention has been paid to the orthorhombic and hexagonal Ln$^{3+}$:YAlO$_3$ phosphors [10–14], only little research has been focused on the cubic garnet form of this material [15–17]. Therefore, in the following paper, we describe a sol-gel method of synthesis of Tb and Eu doped cubic YAlO$_3$ phosphors which have the garnet structure. This structure has been evidenced by X-ray Diffraction and infrared (IR) absorption measurements. Moreover, the main goal of this paper is to investigate the emission properties of Eu$^{3+}$ and Tb$^{3+}$ ions in the cubic form of YAlO$_3$ nanopowders by means of photoluminescence and time-resolved photoluminescence spectroscopy. Especially, we focus on the relaxation kinetic of the excited $^3D_0$ and $^3D_4$ levels of Eu$^{3+}$ and Tb$^{3+}$ ions, respectively. Our results show that the photoluminescence decay in both phosphors is double-exponential, with short and long lifetime component. The long-living emission for both phosphors can be attributed to the ions occupying lattice sites inside the YAlO$_3$ nanocrystal. Moreover, for both dopants, the lifetime of Tb$^{3+}$ and Eu$^{3+}$ emission is longer than equivalent lifetimes in bulk Y$_3$Al$_5$O$_{12}$ crystal.

2. Experimental

For preparing Tb and Eu doped phosphors, we used sol-gel synthesis method. In this method, aluminum isopropanoxide Al(O-i-Pr)$_3$, "..."
where i-Pr is the isoproyl group (CH(CH₃)₂), and yttrium nitrate (Y(NO₃)₃·6H₂O) were dissolved in ethylene glycol monomethylene ether (HOCH₂–CH₂–OCH₃). Terbium (europium) nitrate was dissolved in nitric acid. The prepared solutions were mixed according to the chemical formula of Y₂.85Tb₀.15Al₅O₁₂ (Y₂.85Eu₀.15Al₅O₁₂) with 5 at.% of terbium (europium) with respect to yttrium. The molar concentration of all metal ions in the solution was adjusted to 0.2 M. The obtained solutions were stirred for 2 h. In the next step, the produced sols were heated in a bain-marie for 30 min and turned into gels. The obtained gels were then dried at 200 °C, resulting in the formation of dried gel powders. Finally, the dried gels were annealed at 1000 °C for 2 h, forming the investigated xerogel powders (phosphors).

Scanning Electron Microscope (SEM) examination has been carried out using JSM-840 microscope. The X-ray Diffraction (XRD) spectra were collected using Philips diffractometer supported by the parallel beam optic and Cu Ka radiation source (λ = 0.15406 nm). The IR spectra, were measured on Bruker Vertex spectrometer in a rapid scan mode. We used globar as the source of the probing light, DTGS detector, and ATR (attenuated total reflectance) accessory. In the far infrared spectral region (below 600 cm⁻¹), the mercury lamp and silica bolometer were additionally used as a source of light and detector, respectively. All the measurements were performed with the whole optical path under the vacuum (1.5 × 10⁻⁵ Pa). The spectral resolution was 5 cm⁻¹.

The time-resolved photoluminescence (PL) spectra and PL decays were measured using modified Quanta Master system from Photon Technology International (PTI). An Q-switched Nd³⁺:YAG laser equipped with Optical Parametric Resonator (Opolette from OPOTEK Inc.) has been used as the pulsed excitation source. The laser equipped with Optical Parametric Resonator (Opolette from OPOTEK Inc.) has been used as the pulsed excitation source. The time-resolution was 5 cm⁻¹. The time-resolved photoluminescence (PL) spectra and PL decays were measured using modified Quanta Master system from Photon Technology International (PTI). An Q-switched Nd³⁺:YAG laser equipped with Optical Parametric Resonator (Opolette from OPOTEK Inc.) has been used as the pulsed excitation source. The laser equipped with Optical Parametric Resonator (Opolette from OPOTEK Inc.) has been used as the pulsed excitation source. The time-resolution was 5 cm⁻¹.

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3. Results and discussion

Fig. 1 shows SEM image obtained for Tb³⁺ doped phosphor synthesized by sol-gel method. It can be seen that the structure of powder is granular with a number of individual grains sticking very close to each other, resulting in the formation of irregularly shaped agglomerates. Analyzing several SEM images, we have found that the typical grain size is around 25–50 nm, while the size of the agglomerates is widely distributed, typically around 100 nm. Similar results were obtained for Eu³⁺ doped phosphor.

Fig. 2 shows the XRD patterns measured for Eu³⁺ and Tb³⁺ doped phosphors. In both cases, the diffraction lines were identified (ICDD no. 38-0222) as arising from the cubic form of YAlO₃, having the garnet structure (Y₃Al₂O₁₂ = Y₃Al₂(AlO₄)₃), which can be represented by the formula Y₃Al₃(AlO₄)₃ = YAIO₃ [9]. Noteworthy, this crystalline phase of YAIO₃ has been observed before for undoped phosphors [9,15] obtained, e.g. by the traditional solid-state reaction method or soft chemistry route. It was suggested by Yamaguchi et al. [9] that YAIO₃ in the garnet structure is tolerant to the presence of Al³⁺ in both six-fold (octahedral) and four-fold (tetrahedral) coordination as well as to the replacement of half of the six-coordinated aluminum by yttrium, as represented by the formula Y₃Al₃(AlO₄)₃. In the case of Y₃Al₃O₁₂ garnet structure, Y atoms are dodecahedral coordinated [18], and the point symmetry group of Y site is D₂. Moreover, Al atoms in Y₃Al₃O₁₂ garnet are present in two different sites. The first Al site has octahedral point symmetry C₃ and the second Al site has tetrahedral point symmetry S₄ [19]. Taking into account the above information, we may expect that there are two distinct sites occupied by yttrium in Y₃Al₃(AlO₄)₃ = YAIO₃. The first one is the D₂ site (dodecahedral coordination) and the second one is C₃ site (octahedral coordination, which results from the substitution of one of the Al sites by Y). However, it should be emphasized that the above mentioned symmetry is only the ideal case (correct for Y₃Al₃O₁₂) and in the real cubic YAIO₃ crystal, the C₃ site symmetry may be lowered (e.g. to C₁ or C₃ according to the branching rules) due to the substitution of Al by significantly larger Y ion. Similarly, we may also expect the lowering of the D₂ site symmetry, e.g. due to substitution of Y³⁺ by Eu³⁺ or Tb³⁺ ion. As suggested for Tb:Fe₃O₁₂ garnet, this kind of substitution may result in the lowering of the Tb³⁺ site symmetry from D₂ to C₂ [20].

![Fig. 1. SEM image obtained for Tb:YAIO₃ phosphor.](image)

![Fig. 2. XRD results obtained for Tb and Eu doped phosphors.](image)

![Fig. 3. FT-IR spectra measured for Eu and Tb doped YAIO₃ phosphors.](image)
The presence of the cubic garnet form of YAlO₃ was evidenced also by the FT-IR absorption measurement. Fig. 3 shows the infrared spectra obtained for both powders. The absorption bands at 783, 717, 682 cm⁻¹ are due to the stretching vibrations of AlO₄ tetrahedron, the bands at 564, 510, 449 and 427 cm⁻¹ are due to the stretching vibrations of AlO₆ octahedron and the bands at 389 and 370 cm⁻¹ are due to bending of AlO₄ tetrahedron or stretching Y–O vibrations [9]. The obtained energies are characteristic for the cubic form of YAlO₃, and they are slightly (but considerable) lower than the equivalent absorption bands of the cubic Y₃Al₅O₁₂. We have found also other IR bands at 321, 285, 215, 156 and 120 cm⁻¹. However, due to the lack of available literature data concerning this spectral region, these bands remain unidentified for the moment.

Fig. 4 shows time-resolved PL spectra of Eu²⁺ doped phosphor obtained at resonant 465 nm excitation wavelength, which corresponds to ⁵D₀→⁷F₂ transition [21]. The spectra were recorded for different time delays (T₉) set relatively to the excitation pulse. The spectrum shown in Fig. 4a was obtained for T₉ = 0 ms (just after the excitation pulse), and the spectrum shown in Fig. 4b was measured for T₉ = 3 ms. In the case of T₉ = 0 ms spectrum, the observed infra 4f-shell transition lines were identified as ⁵D₀→⁷F₀, ⁵D₀→⁷F₁, ⁵D₀→⁷F₂, ⁵D₀→⁷F₃ and ⁵D₀→⁷F₄ [21]. In the case of T₉ = 3 ms spectrum the observed transitions are ⁵D₀→⁷F₁, ⁵D₀→⁷F₂, ⁵D₀→⁷F₃ and ⁵D₀→⁷F₄. Besides ⁵D₀→⁷F₂ band, each of the observed emission lines is split into several Stark components.

There are two major differences between spectrum shown in Fig. 4a and b. First of all, it can be seen that the ⁵D₀→⁷F₂ transition remains constant at T₉ = 0 ms, but it vanishes for T₉ = 3 ms. This result will be important for further discussion.

The second noticeable difference between T₉ = 0 and T₉ = 3 ms spectra is the shape of ⁵D₀→⁷F₂ band. Comparing the time resolved spectra shown in Fig. 4a and b one can see that the intensity decay of the broad ⁵D₀→⁷F₂ band is not the same over the whole spectral range (e.g. the intensity decays faster in the middle of the band than at the edges). Since the band shape changes with time we deal with non-single exponential PL decay of this band. The most probable explanation of this complex time-evolution of ⁵D₀→⁷F₂ band is that for T₉ = 0 we observe (at least) two emission bands overlapping each other. These emission bands may originate from Eu³⁺ ions placed in different lattice sites and each of the emission bands have different relaxation kinetic. Noteworthy, the ⁵D₀→⁷F₂ dipole transition is hypersensitive to the site symmetry of Eu³⁺ ions [22]. In particular, depending on the point group symmetry of Eu³⁺ ion, ⁵D₀→⁷F₂ level can be split into maximum (2J + 1) = 5 Stark components. In this way, depending on the actual ion site, the ⁵D₀→⁷F₂ emission band may have different spectral shape. Taking into account that besides shape these bands may differ also in terms of their PL lifetimes, the non-uniform decay of ⁵D₀→⁷F₂ emission can be understood.

Fig. 5 shows the time-resolved PL spectra of Tb³⁺ doped phosphor obtained for resonant 488 nm excitation wavelength which corresponds to ⁵D₄→⁷F₃ transition. The spectrum shown at the bottom of Fig. 5 was obtained for T₉ = 0 ms, and the spectrum shown at the top of Fig. 5 was measured for T₉ = 7 ms. In contrast to the results obtained for Eu³⁺ doped phosphor, the Tb³⁺ emission recorded for different T₉ does not show any clear qualitative differences. For both spectra, five main PL bands can be seen that originate from radiative transitions between Stark-split multiplets of Tb³⁺ ion 4f electrons. The observed transitions are ⁵D₄→⁷F₉, ⁵D₄→⁷F₇, ⁵D₄→⁷F₅, ⁵D₄→⁷F₃ and ⁵D₄→⁷F₀ [21], with ⁵D₄→⁷F₃ transition being the most intensive.

Fig. 6a and c shows PL decays obtained for Eu³⁺ and Tb³⁺ doped YAlO₃ phosphors, respectively. In the case of Eu³⁺, the excitation wavelength used for the measurement was λ_EXC = 580 nm (⁵D₀→⁷F₂ transition) while the emission decay was monitored at λ_EM = 607 nm (⁵D₀→⁷F₂ transition). For Tb³⁺ doped phosphors the excitation wavelength was λ_EXC = 488 nm (⁵D₄→⁷D₉ transition) and emission was detected at λ_EM = 546 nm (⁵D₄→⁷F₅ transition). The obtained decay traces were then analyzed by means of the Maximum Entropy Method (MEM) which yields discrete distributions of the PL decay lifetimes [23]. This approach is especially suitable for the analysis of complex PL decays as it allows to fit the data without any assumptions on the analytic form of the decay function. Particularly, we do not have to assume that the PL decay is described by single or double exponential function. Nevertheless, such conclusion can be drawn on the basis of the lifetime distributions obtained by MEM [23]. It should be also mentioned here that
in the case of MEM analysis even pure exponential decay process have Gaussian-like lifetime distribution with finite width (unless the data is completely noiseless). Therefore, even broad distributions obtained by MEM do not necessarily imply non-exponential dynamics.

The result of MEM analysis performed for the Eu$^{3+}$ PL decay is shown in Fig. 6b. The obtained lifetime distribution is bimodal and consist of two well-resolved, Gaussian-like peaks centered at 1.1 and 4.5 ms. These peak-lifetimes values coincide very well with the lifetimes obtained from fitting the PL decay with function of the form $I(t) = \sum_i A_i \exp(-t/\tau_i)$, where $i = 2$. Therefore, the above results allow us to conclude that the PL decay of the $^5D_0$ level of Eu$^{3+}$ is double-exponential.

The most straightforward interpretation of the double-exponential decay is the presence of two major Eu$^{3+}$ sites in the YAlO$_3$ nanopowder which differ in terms of local symmetry or chemical environment. In the first site the lifetime of $^5D_0$ level is short, about 1.1 ms. Interestingly, this value is very close to the lifetime measured for $^5D_0\rightarrow^7F_2$ band, as shown in the inset to Fig. 4a. Moreover, since the PL decay measured for $^5D_0\rightarrow^7F_2$ band was single-exponential we may conclude that the first site of Eu$^{3+}$ ion, characterized by the short $^5D_0$ level lifetime, is the site responsible for $^5D_0\rightarrow^7F_2$ emission. It should be noted here that the radiative $^5D_0\rightarrow^7F_0$ transition is electric and magnetic dipole forbidden but weak $^5D_0\rightarrow^7F_0$ emission may appear, e.g. due to crystal-field induced J-mixing effect [24]. Nevertheless, the $^5D_0\rightarrow^7F_2$ transition is only allowed in the following 10 site symmetries: C$_s$, C$_i$, C$_v$, C$_3$, C$_4$, C$_i$, C$_{2v}$, C$_{3v}$, C$_{4v}$, and C$_{6v}$, according to the ED selection rule [25]. Moreover, $^5D_0\rightarrow^7F_2$ transition of the Eu$^{3+}$ ion is often observed in the materials in which the site symmetries of this ion are relatively low, for example in many glasses [24]. This suggest that the part of Eu$^{3+}$ ions characterized by the short $^5D_0$ level lifetime (1.1 ms) are very likely located in a distorted lattice sites very close to the YAlO$_3$ nanocrystal surface. On the other hand, the second Eu$^{3+}$ site characterized by the long $^5D_0$ level lifetime (4.5 ms) is most probably related to the sites occupying D$_2$ or C$_2$ sites inside the YAlO$_3$ nanocrystal volume. The Eu$^{3+}$ ions located inside the phosphor volume. On the other hand, for $T_D = 0$ ms, we observe the superposition of emission lines from both sites. It is also worth to mention that the PL measured for $T_D = 3$ ms shows feature characteristic for Eu$^{3+}$:Y$_2$Al$_2$O$_2$ emission [27]: the magnetic dipole transition, $^5D_0\rightarrow^7F_1$, is relatively strong in comparison to the electric dipole transition, $^5D_0\rightarrow^7F_2$. This is the major difference in comparison to the orthorhombic Eu$^{3+}$:YAlO$_3$ (perovskite structure) where Eu$^{3+}$ emission is concentrated mainly in the $^5D_0\rightarrow^7F_2$ electric dipole transition [27].

Fig. 6d shows the result of MEM analysis performed for Tb$^{3+}$:YAlO$_3$ phosphor. Again, the obtained lifetime distribution is bimodal with Gaussian-like peaks centered at 2.3 and 5.0 ms, confirming that also in the case of Tb$^{3+}$ the PL decay is double-exponential. We would like to underline that without MEM analysis this result could have been missed since for the first glance the PL decay shown in Fig. 6c is almost a straight line (in semi-log scale).

Taking into account the results obtained for Eu$^{3+}$ doped phosphor, we ascribe the fast and slow component of the PL decay to Tb$^{3+}$ ions placed in two different sites as well. Most probably, the fast decay (2.3 ms) is due to the Tb$^{3+}$ ions placed in a disordered site, e.g. in the vicinity of YAlO$_3$ nanocrystal surface, while the slow decay (5.0 ms) is related to the Tb$^{3+}$ ions inside the bulk of YAlO$_3$ nanocrystal. This conclusion can be supported by our previous findings which concerned Tb$^{3+}$ doped YAlO$_3$ inside the porous anodic alumina (PAA) template [28]. In this work we have shown that when YAlO$_3$ is amorphous, the $^5D_4$ lifetime of Tb$^{3+}$ is fast, around 1–2 ms. However, after annealing at temperature above 900 °C, this lifetime is significantly elongated up to around 4 ms, due to the ordering and crystallization of YAlO$_3$. This result confirms directly that Tb$^{3+}$ lifetime is longer in a well-ordered crystal environment (e.g. inside the bulk of YAlO$_3$ nanocrystal) than in amorphous YAlO$_3$ matrix. Noteworthy, the lifetime of $^5D_4$ state measured for Tb$^{3+}$ in bulk Y$_2$Al$_2$O$_2$ crystal is 3.7 ms [29]. This is somewhere in between of 2.3 and 5.0 ms obtained in our experiment, making direct comparison of the lifetime rather impossible.

It should also be pointed out that, according to Choi et al. [16] and Moon et al. [17], it is possible to synthesize mixed structural phases of Eu$^{3+}$-doped YAlO$_3$ phosphor, e.g. the mixture of cubic and orthorhombic forms. Since the optical properties of Eu$^{3+}$ ions in the cubic and orthorhombic YAlO$_3$ hosts are different, we may expect that the optical properties of the mixture are complex. In particular, depending on the relative amount of both phases, the photoluminescence decay of such phosphor may be double-exponential. In the case of the orthorhombic YAlO$_3$, the decay time of $^5D_4$ state of Eu$^{3+}$ is 1.69 ms [27], while for $^5D_4$ state of Tb$^{3+}$ the decay time is around 1.70 ms [30]. These values are far from the long lifetime components obtained in our experiment, but are similar to the short lifetime components. Nevertheless, since we have not observed any measurable amount of the orthorhombic YAlO$_3$ phase in the investigated phosphors, we may exclude the possibility that the obtained short lifetime components are due to the presence of Eu$^{3+}$/Tb$^{3+}$-doped orthorhombic YAlO$_3$. More likely, the short lifetimes could be related to some admixture of the amorphous YAlO$_3$ phase, but, again, there is no evidence for the presence of any significant amount of such phase in the investigated phosphors.

4. Conclusions

A sol-gel method of synthesis of Tb and Eu doped YAlO$_3$ phosphors was put forward. It has been demonstrated that phosphors prepared by this method and annealed at 1000 °C crystallize in the cubic garnet phase, which can be represented by the formula Y$_2$Al$_5$(AlO$_4$)$_3$. Time-resolved spectroscopy and Maximum Entropy Method have been used for the lifetime analysis of europium $^7D_0$
and terbium $^5\text{D}_4$ states. It has been shown that in both cases the photoluminescence decay is double-exponential, with lifetime of 1.1 and 4.5 ms in the case of Eu$^{3+}$ and 2.3 and 5.0 ms in the case of Tb$^{3+}$. Moreover, for both phosphors, the faster decay component was ascribed to the ions occupying low-symmetry sites, probably in the vicinity of the nanocrystal surface, while the slower decay component was related to the ions present in the bulk of YAlO$_3$ nanocrystal. For both dopants, the long-lifetime component of Tb$^{3+}$ and Eu$^{3+}$ emission is longer than the equivalent lifetimes in the bulk Y$_3$Al$_5$O$_{12}$ crystal, and much longer than the equivalent lifetimes in the orthorhombic YAlO$_3$.

Acknowledgments

In Poland, this study was financed by the National Science Center as a research project NN507321240. In addition, the FT-IR spectra were measured thanks to the grant no. DEC-2011/03/D/ST3/02640. We also would like to thank Iryna Nikolaenko from Belarusian State University of Informatics and Radioelectronics for her help with the samples preparation. This work was partially supported by Belarusian Foundation for Basic Research.

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