

Rare Earth Activated Phosphors for Different Applications

Mihail Nazarov

¹*Institute of Applied Physics, Academy of Sciences of Moldova, Republic of Moldova.*

²*School of Materials and Mineral Resources Engineering Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia*
mvnazarov@mail.ru

Abstract — For the purpose of development of highly energy-efficient light sources, one needs to design highly efficient green, red and yellow phosphors, which are able to absorb excitation energy and generate emissions. Using double activation, energy can be transferred from one luminescent activator to the other one, resulting in more efficient or brighter device operation. Co-activators can be added to a host material to change the color of the emitted light. The incorporation of Eu^{3+} or Tb^{3+} ions into the CaWO_4 crystal lattice modifies the luminescence spectrum due to the formation of the emission centers that generate the specific red and green light. Very efficient new red phosphors based on YNbO_4 and doped by Eu^{3+} , Ga^{3+} , Al^{3+} allow recommend these materials as good candidates for different applications including LED and X-ray intensifying screens. For double activated TAG with Ce^{3+} and Eu^{3+} and for different mole ratio Ce/Eu the color temperature changes from 5500 K (0.331, 0.322) up to 4200 K (0.370, 0.381) and the light becomes “warmer”. Application of TAG:Ce,Eu in the light emitting device shows the better chromaticity coordinates of luminescence and color rendering index of LEDs. Combination of Eu^{2+} with Dy^{3+} in SrAl_2O_4 matrix allows us to create a material that emitted bright light for hours after ending the excitation. In this contribution we present our results on producing some efficient phosphors with improved luminescence properties for different applications: LED and X-ray intensifying screens, marine artificial reefs, biology and medicine.

Index Terms — Luminescence; Optical materials; Phosphors.

I. INTRODUCTION

Rare Earth (RE) phosphors can be separated into two types: broad band emitting owing to the $5d \rightarrow 4f$ transition (Eu^{2+} , Ce^{3+}) or narrow band emitting owing to the transition between the $4f$ levels (Eu^{3+} , Tb^{3+} , Gd^{3+} , Yb^{3+} , Dy^{3+} , Sm^{3+} , Tm^{3+} , Er^{3+} , Nd^{3+} etc).

The luminescence is more intense if the band gap between the excited state and the highest component of the ground state multiplet becomes larger. For example, $\text{Gd} \rightarrow 32100 \text{ cm}^{-1}$ (4 eV), $\text{Tb} \rightarrow 14800 \text{ cm}^{-1}$ (1.8 eV), $\text{Eu} \rightarrow 12300 \text{ cm}^{-1}$ (1.5 eV), $\text{Yb} \rightarrow 10400 \text{ cm}^{-1}$ (1.3 eV), $\text{Dy} \rightarrow 7800 \text{ cm}^{-1}$ (0.96 eV), $\text{Sm} \rightarrow 7400 \text{ cm}^{-1}$ (0.9 eV), $\text{Tm} \rightarrow 6200 \text{ cm}^{-1}$ (0.77 eV), $\text{Er} \rightarrow 5900 \text{ cm}^{-1}$ (0.73 eV), $\text{Nd} \rightarrow 4400 \text{ cm}^{-1}$ (0.5 eV), etc.. Gd is a very good emitter, but the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition occurs in the ultraviolet region (around 310 nm) that is not convenient for practical application. This explains the prominent role played by Tb and Eu as luminescent probes. Moreover, Eu is a unique activator that gives both the broad band and narrow band emissions in dependence on its valences. That's why in this work we focus on some different host lattices activated by Eu and Tb in different combinations with other rare earth elements. The co-activation or double activation by these RE elements is discussed. In double activated phosphors the energy can be transferred from one luminescent activator to the other one, resulting in more efficient or

brighter device operation. If the energy transfer occurs

within the Eu-Tb complex so that it works as a donor-acceptor pair due to small energy gap between excited energy levels 5D_4 (Tb^{3+}) and 5D_1 (Eu^{3+}). Secondly, co-activators can be added to a host material to change the color of the emitted light. Though these Eu and Tb activators are widely used for a long time, there are many questions had to be resolved.

First application we consider in calcium tungstate phosphor. The optical properties of the scheelite crystal have been studied extensively for decades [1-4]. The continuous need for high-performance phosphors renewed the interest in this luminescent material with more than a century of history. Self-activated $\text{CaWO}_4:\text{W}$ is an efficient material emitting blue luminescence related to some tetrahedral WO_4 groups of the scheelite host lattice. However, the luminescence properties of this classic phosphor could be essentially varied by doping with RE ions, in particular with Eu^{3+} and Tb^{3+} , and therefore, some new applications could be proposed. The incorporation of Eu^{3+} or Tb^{3+} ions into the CaWO_4 crystal lattice modifies the luminescence spectrum due to the formation of the emission centers that generate the specific red and green light, respectively [5-8]. Photoluminescence (PL) and cathodoluminescence (CL) investigations are used to evaluate the performance of Eu^{3+} and Tb^{3+} activated CaWO_4 and to put in evidence the interaction between the two activating species.

Next interesting phosphor with improved properties presented in this work is yttrium niobium-tantalate $\text{Y}(\text{Ta,Nb})\text{O}_4$. The yttrium tantalate (YTao_4) and yttrium

niobate (YNbO₄) systems are of great interest from fundamental scientific point of view and also for various spectroscopic applications. The blue light emission from host lattice could be shifted toward longer wavelengths when rare earth ions Eu³⁺ or Tb³⁺ replace partially the yttrium ions in these materials. In these phosphors, activated by rare earth elements, the host-lattice emission centers and the rare earth emission centers contribute both to the overall luminescence. The growing interest toward luminescence properties in the vacuum ultraviolet and in the visible spectral range is due to industrial demands for new applications. Efficient phosphors based on YNbO₄ and doped by Eu³⁺, Ga³⁺, Al³⁺ were synthesized with different fluxes under different thermal conditions and investigated under UV, X-ray excitation and Raman spectroscopy. The samples co-doped by Al³⁺ and Ga³⁺ show higher intensity under UV and X-ray excitation in comparison with YNbO₄:Eu³⁺ phosphors. The model of redistribution energy transfer from ⁵D₁ level to ⁷F_J is proposed. Monoclinic fergusonite crystal structure and excellent luminescent properties under X-ray and UV excitation allow recommend these phosphors as good candidates for different applications including LED and X-ray intensifying screens.

Yttrium aluminum garnet Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce) and terbium aluminum garnet Tb₃Al₅O₁₂:Ce³⁺ (TAG:Ce) are used as a phosphors for white light emitting diodes using the principle of luminescence conversion. However, the color impression of such conversion on the base of a blue diode and these phosphors is too "cold", a red component is missing. The common way to improve the emission spectra of lighting devices is with co-activation of the conversion phosphors, for example with Eu³⁺, which shows an intense line emission in the red. Results of co-doping TAG:Ce with Eu³⁺ are presented in this work.

In this article we propose also a new interesting direction in the study and biology application of persistent materials: namely underwater investigations of persistent luminescence. A new multiphase blue-green phosphor based on SrAl₂O₄ was synthesized and applied in marine conditions in the development of an artificial luminescent reef. The possibility of algae cultivation and fish attraction by the light of artificial reef is discussed.

Therefore, it seems attractive to develop new phosphor materials with high efficiency and color saturation or modify well-known compositions by co-doping them with different combinations of efficient RE activators.

II. EXPERIMENTAL

2.1. CaWO₄:Eu³⁺, Tb³⁺

CaWO₄:RE phosphor samples described in this work were prepared by solid state reaction from homogeneous mixtures consisting of luminescent-grade CaWO₄ as host lattice, WO₃ and Eu₂O₃ (99,99% Jansen Chemical) and/or Tb₄O₇ (Johnson Matthey "Specpure") as activating system, and alkaline salts as flux. CaWO₄ used as precursor in phosphor synthesis was prepared from highly purified CaCl₂ and Na₂WO₄ solutions. The synthesis mixtures containing flux and equivalent amounts of WO₃ and Eu₂O₃ or Tb₄O₇ were homogenized and fired at 900 °C. The prepared powders were carefully washed, dried, and sieved.

The incorporation of trivalent RE ions into the CaWO₄ crystalline lattice could proceed in two major ways. Either 2RE³⁺ replace 3Ca²⁺ ions, or a pair of RE³⁺ and M⁺ replace 2Ca²⁺ ions (where M⁺ = alkaline ion). In our sample preparation conditions, alkaline salt acts as a mineralizing agent and also as a source of compensating ion. Based on this principle, a series of synthesis mixtures was prepared according to the general phosphor formula Ca_{1-2x-2y}Eu_xTb_yM_{x+y}WO₄.

2.2. (Y, M)NbO₄:Eu³⁺ (M: Al, Ga)

There are few papers on the improvement of the red emission of YNbO₄:Eu³⁺ under different excitations. Some attempts have been made when other trivalent ions (Gd³⁺, for example) partially substituted yttrium in the host lattice [9]. The effects of the substitution of trivalent ions such as Al³⁺ and Ga³⁺ for Y³⁺ was investigated by Lee et al.[10]. In this work, (Y, M)NbO₄:Eu³⁺ (M: Al, Ga) powders were synthesized by a flux method, and then the effects of the replacement of Al³⁺ and Ga³⁺ on the red emission under n-UV and X-ray excitation were investigated first. (Y,M)NbO₄:Eu³⁺ (M: Al, Ga) powders were fabricated by firing the stoichiometric mixtures of Y₂O₃, Nb₂O₅, Al₂O₃, Ga₂O₃, and Eu₂O₃ powders. LiCl (7 wt %) was added as a flux to promote a solid state reaction and the luminescent properties by accelerating the kinetics for the compound formation due to the increased diffusion coefficients. The purities of all the powders were 99.99%. The amount of Eu₂O₃ was in the range of 0 - 45 mol %. After ballmilling the mixtures for 24 hours, they were fired at 1300 °C for 12 hours in an electric tube furnace flowing N₂ gas.

2.3. Tb₃Al₅O₁₂:Ce³⁺, Eu³⁺

The powder samples have been prepared by a conventional solid state reaction. According to the nominal composition of Tb₃Al₅O₁₂:Ce³⁺, Eu³⁺, the starting materials Tb₄O₇; Al₂O₃; CeO₂ and Eu₂O₃ (99% for Al₂O₃, 99.9% for all other oxides) are weighed and milled. Synthesis took place in a furnace heated by induction using a sealed alumina tube in a reducing atmosphere of H₂/N₂ to stabilize the Tb³⁺ state. The crucible was made out of Al₂O₃. BaF₂, LiF and H₃BO₃ as flux materials were used. The synthesis lasted approximately 2 h at temperature of about 1500 °C. The samples were prepared with different Ce (1, 3, 5 mol %) and Eu (1, 3, 5, 7, 9, 11, 13 mol %) concentrations.

2.4. SrAl₂O₄:Eu²⁺, Dy³⁺

Artificial rock and block made of steel slag hybrid matrix were developed recently in Japan [11,12]. We propose experimental artificial glow reef to make from concrete and sand to provide hard surface. The main goal of these reefs is to cultivate the algae in future and to attract the fish. For this purpose the artificial block must be luminescent and preferably excite the green light. The persistent phosphor SrAl₂O₄:Eu²⁺, Dy³⁺ as a phosphorescence material and polymer epoxy as a coating layer are proposed. Strontium aluminate phosphor doped with Eu²⁺ and co-doped with Dy³⁺ SrAl₂O₄:Eu²⁺, Dy³⁺ were prepared by solid state reaction approach using strontium carbonate (SrCO₃; Aldrich, 99.9 %), aluminum oxide (Al₂O₃), europium oxide

(Eu₂O₃; Aldrich, 99.99 %) and dysprosium oxide (Dy₂O₃; Aldrich, 99.99 %) as the starting materials. Small amount (0.2 mol %) of H₃BO₃ was used as a flux. Prior to heating at 1250°C, the reagents were ground using a ball mill to form a homogeneous mixture. First, the dry milling was used for 30 minutes and then continued by wet-mixing machine for 30 minutes. The resulting slurry was dried at 150°C for 3 hours to remove the water content. After fully dried, the mixed white powder was placed in a small alumina crucible and then fired at 1250°C for 2 hours under a mild reducing atmosphere. Graphite crucible was used to create the reducing atmosphere and to ensure complete reduction of Eu³⁺ to Eu²⁺ and to crystallize and form the luminescence centers. The mixing – milling process to get smaller particle size and homogenous mixture was used after calcination. An epoxy layer of SrAl₂O₄:Eu²⁺,Dy³⁺ phosphor were deposited on reef surface by brushing technique.

III. RESULTS AND DISCUSSION

3.1. Luminescence of Eu³⁺ and Tb³⁺ activated CaWO₄ phosphors

The low (0.5-1 keV) and high (20-30 keV) voltage cathodoluminescence modes including color CL and PL with different excitation wavelengths (147, 254, 365 nm) were applied to investigate the luminescence properties and the energy transfer processes in CaWO₄, activated by trivalent Eu³⁺ and Tb³⁺ ions.

The PL and CL spectra of the same material are rather similar; however, there is some difference between the PL and CL related with excitation, generation rate and volume. In general, the CL spectra are richer because only the electron beam excitation can induce transition between all the defect levels, including those created by surface type of imperfections. Observed characteristic blue emission at 400-500 nm is related with some tetrahedral WO₄ groups of the scheelite host lattice. The specific green emission bands at 497 and 553 nm can be attributed to electronic transition inside the Tb-center. 4 red emission bands at 596, 622, 661, 711 nm are caused by transition from emitting level ⁵D₀ to ⁷F₁, ⁷F₂, ⁷F₃, ⁷F₄ for trivalent ions of europium. The dependence of the CL emission intensity on the activator concentration is shown in Fig.1. The variation of the main emission peaks of Eu and Tb with their concentration is clearly seen. As a result, the overall chromaticity also changes, strongly depending on the activator ratio and concentration.

The specific green emission band of Tb centers that is situated at 543 nm is due to electronic transition ⁵D₄→⁷F₅ inside Tb³⁺ ion with 4f⁷ configuration. In order to obtain an efficient green luminescence, the activator concentration has to be at least 2.5 mole %.

Emission lines of Eu³⁺ ion correspond to transitions from the excited ⁵D₀ level to the ⁷F_J (J = 1, 2, ...) levels of the 4f⁶ configuration (transition from J = 0 to J = 0 being forbidden, because the total orbital momentum is not changed).

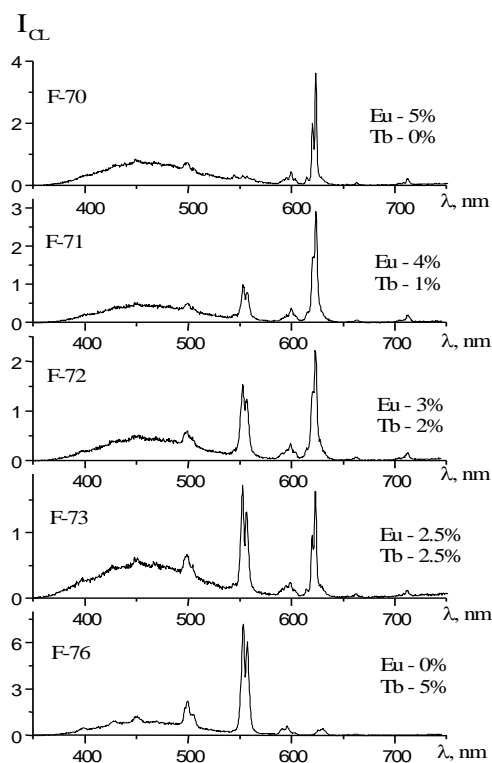


Fig.1. CL spectra of CaWO₄:Eu, Tb samples (codes F70-F76) prepared with different activator concentrations

The weak emission in the vicinity of 590–600 nm is due to the magnetic dipole transition ⁵D₀→⁷F₁. The strong emission around 610–630 nm is due to the hypersensitive electric dipole transition of ⁵D₀→⁷F₂, induced by the lack of inversion symmetry at the Eu³⁺ site. In order to obtain an efficient red luminescence, the activator concentration of Eu has to be at least 2.5 mole %.

CL spectra and PL spectra are very similar, thus indicates that the mechanism of energy transfer is the same, whatever the excitation is. Both methods of investigations, namely PL and CL spectroscopy, put in evidence a continuous increase of the red emission band and a considerable decrease of the green emission band (Fig.2). Experimental results showed that no activator quenching effect could be noticed in this concentration range, so that the possible effect of concentration quenching is not to be taken into consideration. To explain the experimental PL and CL results, two- and three-level models taking into account an interaction between Tb³⁺ and Eu³⁺ are proposed. The detailed analysis is given in ref. [13].

According to the proposed model, the Tb³⁺ emission intensity decreases nonlinearly whereas the Eu³⁺ emission intensity increases linearly with activator concentration. These calculations are in agreement with the experimental data, as shown in Fig.2. When Eu³⁺ and Tb³⁺ were simultaneously introduced in equal amounts at relatively low concentration (up to 1.5%), the linear dependence can be noticed and the mutual activators interaction needs not to be accounted. The simple two-level model could be used in this case. At higher concentration the activators interaction has to be taken into consideration to explain the results.

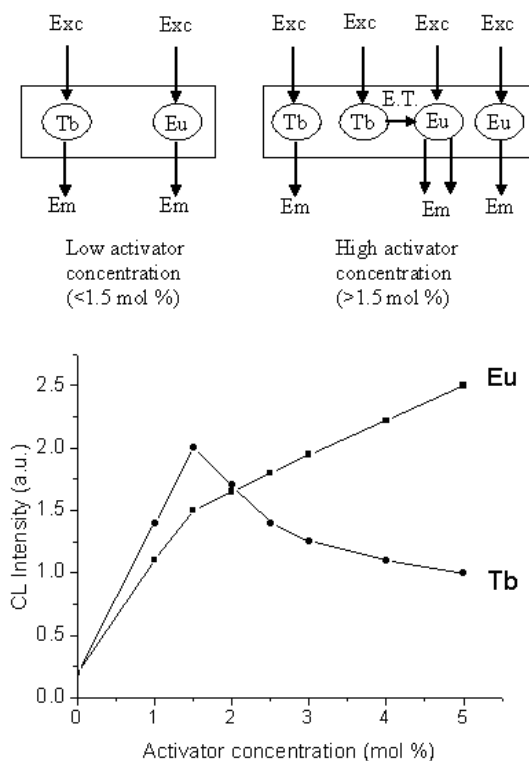


Fig.2. Dependence of the CL intensity of the specific Eu³⁺ red band at 612 nm and Tb³⁺ green band at 543 nm on activator concentration.

The proposed models are confirmed further by numerous measurements with different excitations such as high and low voltage CL, PL including UV and VUV, and X-ray luminescence. This model is available in the most matrices, such as yttrium tantalate, yttrium niobate, calcium tungstate [14], zink silicate [15,16], porous silicon [17], porous phosphate [18], zeolite-Y[19], calcium molybdate [20], and others.

3.2. Red phosphors YNbO₄:Eu³⁺, Al³⁺ and YNbO₄:Eu³⁺, Ga³⁺ with high-emission properties

Now we show the luminescence properties of YNbO₄ phosphors doped by Eu³⁺, Ga³⁺, Al³⁺ under X-ray excitation. The improved about 1.5 times emission of these phosphors, respectively, than that of YNbO₄:Eu³⁺ was ascribed to the redistribution of energy transfer from excited levels.

The introduced activators can be excited directly by excitation source or by energy transfer transition from the host lattice. In the lattice of Rare Earth doped yttrium niobate the doped luminescent centers, such as Eu³⁺, occupy the Y sites. The NbO₄³⁻ groups can absorb excitation energy through O²⁻→Nb⁵⁺ charge transfer transition respectively, and transfer the energy to Rare Earth luminescent centers, which give rise to the corresponding characteristic emission. Low intensity of host lattice luminescence is observed in non-doped phosphor and disappeared due to energy transfer in activated samples. The system Y_{1-x}Eu_xNbO₄ was studied more thoroughly because it illustrates clearly the importance of excitation energy transport through the

lattice in order to obtain efficient phosphors.

Under X-ray excitation the relatively strong ⁵D₀→⁷F₄ transition intensity is appeared. Usually this emission is very weak under UV excitation. Furthermore, comparing the luminescence under UV (254 nm) and the broad X-ray excitation, it was found that the relative intensity of ⁵D₀→⁷F_J (J=1, 2, 4) emission peaks of Eu³⁺, so called branch ratios, varies significantly with the activation excitation energy. Under UV excitation, the ⁵D₀→⁷F₄ emission is mostly trapped by the empty upper levels. On the contrary, it is more likely that such empty levels can be readily filled under X-ray excitation. This explains the appearance of visible ⁵D₀→⁷F₄ transition and the increment of the luminescence intensity of Eu³⁺ emission centers under X-ray excitation.

The influence of codoping YNbO₄:Eu³⁺ by Al³⁺ and Ga³⁺ on the luminescence properties under X-ray excitation was studied. First, the optimum concentration of Al³⁺ = 2 mol % and Ga³⁺ = 1 mol % was established. Since the ionic radii of Al³⁺ (0.54 Å) and Ga³⁺ (0.62 Å) were much smaller than that of Y³⁺ (0.88 Å), the crystal field surrounding Eu³⁺ (0.95 Å) ions was expected to be altered considerably, resulting in the change of photoluminescence properties. The highest intensities under X-ray excitation were found for samples (Y_{0.7}Al_{0.2}NbO₄:Eu_{0.1}³⁺) and (Y_{0.8}Ga_{0.1}NbO₄:Eu_{0.1}³⁺) doped by Eu³⁺ 10 mol%.

The emission spectra of all Eu³⁺ phosphors show similar features, and have been involved in the following emission lines: ⁵D₀→⁷F₁, ⁵D₀→⁷F₂, ⁵D₀→⁷F₃ and ⁵D₀→⁷F₄. Other transitions from ⁵D₀ to ⁷F₀, ⁷F₅ and ⁷F₆ levels are also allowed from the selection rules for the transition between Stark components of Eu³⁺ in symmetry of the actual crystal field, but luminescence intensities are too weak. Furthermore, there appears to be an energy transfer from host to activator. Additionally, the transition from ⁵D₁ to ⁷F₁ level is also possible and we examined this transition more carefully. Position of the ⁵D₁→⁷F₁ transition for all the samples is the same (538 nm) and no shift was observed. It means that no phase changes with incorporation Ga and Al is appeared. The abrupt decrease of luminescence in Y_{0.8}Ga_{0.1}NbO₄:Eu_{0.1}³⁺ (absolutely the same for Y_{0.7}Al_{0.2}NbO₄:Eu_{0.1}³⁺) in comparison with YNbO₄:Eu³⁺ about 1.5 times can be explained by the redistribution of energy transfer from excited Eu³⁺ state ⁵D₁. One additional part of energy from excited level ⁵D₁ transfers nonradiative to the lowest level ⁵D₀ and then radiative to all the levels of ground state decreasing intensity in ⁵D₁→⁷F₁ transition and increasing general luminescence in other transitions. We checked the intensities of Al and Ga doped materials in all emission lines including the most important ⁵D₀→⁷F₂ (612 nm) emission transition and found that the intensity increased about 1.5 times. The proposed mechanism is schematically presented in Fig.3. The samples codoped by Al³⁺ and Ga³⁺ show higher intensity under n-UV and X-ray excitation in comparison with YNbO₄:Eu³⁺ phosphors. Monoclinic fergusonite crystal structure and excellent luminescent properties under n-UV and X-ray excitation allow recommend these phosphors as good candidates for different applications.

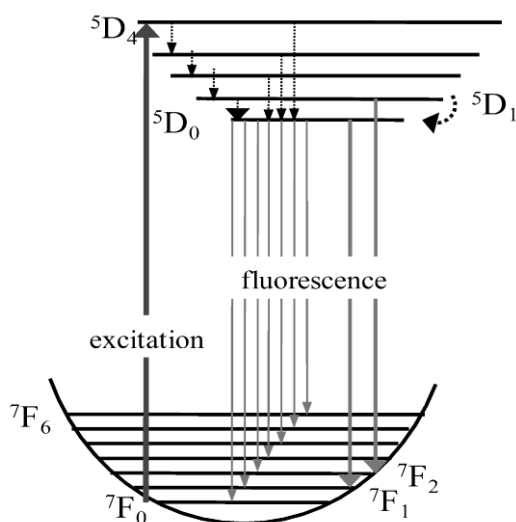


Fig.3. A schematic model of stimulated Eu^{3+} luminescence in $(\text{Y,Al,Ga})\text{NbO}_4$ phosphors.

3.3. Yttrium and Terbium Aluminate Phosphors co-activated by Eu^{3+}

For the application in the blue LED a yellow phosphor with improved luminescence properties it is interesting to obtain Ce^{3+} and Eu^{3+} luminescence simultaneously in garnets, especially for the low energy Ce^{3+} excitation around 460 nm. The energy transfer between Ce^{3+} and Eu^{3+} ions in garnets has not yet been investigated in details. However this pair is well-known for $\text{YOCl}:\text{Ce}^{3+},\text{Eu}^{3+}$ and $\text{YAlO}_3:\text{Ce}^{3+},\text{Eu}^{3+}$. In the latter case, the energy transfer should be highly effective due to the overlap of the luminescence of Ce^{3+} and the strong absorption of the ${}^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+} at about 390 nm. In garnet, the photon energy in the Ce^{3+} luminescence is different from the ${}^7F_0 \rightarrow {}^5L_6$ and also from the ${}^7F_0({}^7F_1) \rightarrow {}^5D_2$ (464 nm) transition energies. Doping with 1-3-5 mol % Ce yields a broad-band of $5d \rightarrow 4f$ luminescence Ce^{3+} . In addition to the direct Ce^{3+} excitation, the Eu^{3+} contribution to the luminescence is also expected.

To understand the luminescence mechanism in cerium-europium double activated terbium aluminum garnet phosphor the selectively excited emission was measured.

The emission spectra consist of a broad band corresponding to the $\text{Ce}^{3+} 5d \rightarrow {}^2F_7$ transition and of the series of sharp lines arising from $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_J$ transitions. (Fig.4). From the analysis the experimental results one can conclude that the excitation of Eu^{3+} occurs via the Ce^{3+} quenching luminescence. This means that the Ce^{3+} ion acts as a sensitizer for the Eu^{3+} luminescence. The Eu^{3+} luminescence can also be activated by a Tb^{3+} sensitizing which is not too surprising as an energy transfer from Tb^{3+} to Eu^{3+} is well-known^[32, 33]. Therefore the Tb^{3+} host lattice acts as a sensitizer for the activator Eu^{3+} but also as an activator itself showing host lattice emission. The fluorescence of Tb^{3+} in the TAG is due to the transitions from the Stark components of the 5D_4 level to the Stark components of the 7F_J levels but the low energy excitation used in blue LED (460 nm) is not enough to excite these levels. 227 nm excitation and more is needed to excite the

host lattice. Nevertheless, one can expect the transfer of energy from the Ce^{3+} to Tb^{3+} lattice ion due to a slight overlap of the Ce^{3+} luminescence in TAG with the ${}^7F_6 \rightarrow {}^5D_4$ absorption band of Tb^{3+} (483 nm).

Emission spectra of the blue LED including of cerium-europium double activated terbium aluminum garnet phosphor with improved luminescence properties in the light emitting device is demonstrated in Fig.4. Some additional Eu^{3+} peaks and broadening of the spectra in the red region significantly improves the color rendering index (CRI) and luminescent properties of LED.

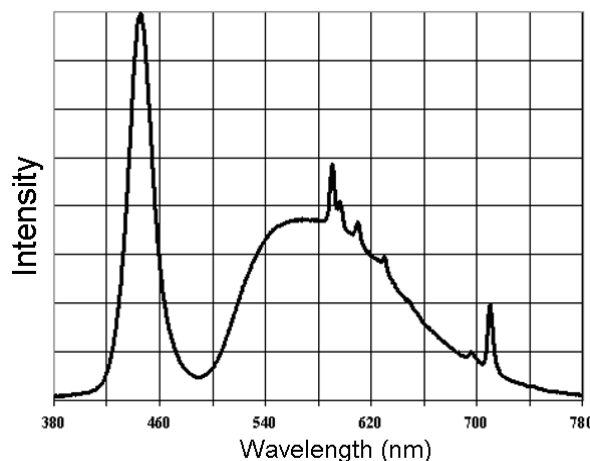


Fig.4. Emission spectra of the blue LED including TAG: $\text{Ce}^{3+}, \text{Eu}^{3+}$

3.4. A marine reef application for $\text{SrAl}_2\text{O}_4:\text{Eu}$ Dy-based persistent luminescence phosphors

Persistent phosphors can emit light for a long time from seconds to many hours after the excitation has ended. The irradiation used may be UV, visible light, X-ray, gamma radiation, as well as usual sun light.

Persistent luminescence has intrigued people for hundreds of years. The situation drastically changed about 16 years ago when Matsuzawa et al. discovered bright and long-lasting luminescence in $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ [21]. By codoping the green-emitting phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ (already showing a relatively strong and long-lasting afterglow by itself) with the rare earth element dysprosium (Dy^{3+}), they were able to create a material that emitted bright light for hours after ending the excitation (simultaneously and independently, Takasaki et al. reported similar results [22]). They found an afterglow with both a far higher initial intensity and a much longer lifetime compared to traditional $\text{ZnS}:\text{Cu,Co}$. These investigations have led to a renewed research interest, and it promoted the use of these green-emitting persistent phosphors in signalization, glow-in-the-dark toys, emergency signs, dials and displays, textile printing, medical diagnostics, and many other applications. Applications of persistent luminescence phosphors are rapidly expanding.

In this article we propose a new direction in study and biology application these materials, namely underwater investigations of persistent luminescence. A new multiphase blue-green phosphor based on SrAl_2O_4 was synthesized and applied in real sea conditions.

The real underwater experiments in sea conditions were carried out in Pulau Payar, Malaysia. First, the artificial blocks covered by $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} and excited by the sun light were installed on the ocean floor with different relief (agropora corals, rocks, sand) and at different deep from 2 up to 6 meters. Fig.5 shows the process of installation artificial luminescent block on real stone in the sea at the deep about 5 meters.



Fig.5. Installation of concrete matrix covered by $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+}

Next step was the underwater luminescence investigations. All blocks showed the bright blue-green luminescence from all the places independently of relief and deep. One of the examples is demonstrated in Fig.6.



Fig.6. Blue-Green color luminescence of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} from 5 meters deep in real sea conditions

After some minutes the fishes were interested in a new luminescent object and gathered around it (Fig.7). Finally, the black-tip shark was also interested in luminescence and came near our artificial sample.

There is a risk of forever damaging the existence of thousands natural reefs because of tsunami or other cataclastic phenomena. We need to know how to restore or sometimes to improve reefs and marine ecosystems. Therefore, measuring and interpreting the impact of human actions on the diversity on marine and oceanic life represent one way to prevent ecological disasters and predict possible environmental changes.



Fig.7. The fishes are attracted by bright and long-lasting luminescence of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+}

4. CONCLUSIONS

Double activation of phosphors is a promising technique for improving luminescent properties of materials.

The double activation of CaWO_4 with Tb^{3+} and Eu^{3+} , in the presence of alkaline salts as flux, gives the possibility to synthesize phosphors with variable chromatic emissions. Variable luminescence colors could be obtained when calcium tungstate phosphors containing 0-5 mole % activator ions were exposed to relatively low excitation energies, such as 365 or 254 nm ultraviolet radiations. Under high energy excitation such as VUV (147 nm) radiation or electron beam, white light could be observed. Due to very good chromatic variability, $\text{CaWO}_4:\text{Eu},\text{Tb}$ powders are potentially utilizable in the manufacture of fluorescent lamps for advertising signs, or other color rendering devices.

New efficient phosphors based on YNbO_4 and doped by Eu^{3+} , Ga^{3+} , Al^{3+} show higher intensity under n-UV and X-ray excitation in comparison with $\text{YNbO}_4:\text{Eu}^{3+}$ phosphors. The model of redistribution energy transfer is proposed and discussed. Monoclinic fergusonite crystal structure and excellent luminescent properties allow recommend these phosphors as good candidates for different applications. In particular, $\text{Y}_{1-y}\text{Al}_y\text{NbO}_4:\text{Eu}^{3+}$ and $\text{Y}_{1-z}\text{Ga}_z\text{NbO}_4:\text{Eu}^{3+}$ can be the promising red phosphors for white LEDs using n-UV chips

For double activated TAG with Ce^{3+} and Eu^{3+} and for different mole ratio Ce/Eu the color temperature changes from 5500 K (0.331, 0.322) up to 4200 K (0.370, 0.381) and the light becomes "warmer". Application of TAG:Ce,Eu in the light emitting device shows the better chromaticity coordinates of luminescence and color rendering index of LEDs.

Multiphase blue-green persistent phosphor with turquoise luminescence was synthesized and applied for sea investigations. For the first time the experiments with artificial stone covered by $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ based phosphor were carried out in real sea conditions in Malaysia. Strong and bright blue-green (turquoise) luminescence was observed and registered under the water. Fishes were attracted by the light of the artificial reef. The possibility of algae cultivation is discussed.

REFERENCES

- [1] Forgaciu F, Popovici E-J, Ciocan C, Ungur L, Vadan M. Calcium tungstate phosphors with well-defined particle sizes. in *SIOEL '99: Sixth Symposium on Optoelectronics*. Bucharest, Romania, SPIE, 2000.
- [2] Blasse G, Grabmeyer B C. *Luminescent Materials*: Springer Verlag, Berlin, Heidelberg, 1994
- [3] Uitert L G. Luminescence of Insulating Solids for Optical Masers, in Goldberg P, ed. *Luminescence of Inorganic Solids* Academic Press, 1966.
- [4] Grasser R, Pompe W, Scharmann A. Defect luminescence in tungstates. *J.Lumin.*, 1988, **40-41**: 343.
- [5] Nazarova T A, Nazarov M V, Saparin G V, Obyden S K, Ivanikov I P, Popovici E J, Forgaciu F. Colour Cathodoluminescence and Photoluminescence of Powder Samples. *European Microscopy and Analysis*, 2001, **70**: 19.
- [6] Popovici E-J, Nazarov M, Jeon D Y, Muresan L, Nazarova T A, Indrea E, Hristea-Simoc A. Photo- and cathodoluminescence investigation of CaWO₄:Eu,Tb phosphors. in *ROMOPTO 2003: Seventh Conference on Optics*, Romania, SPIE, 2004.
- [7] Forgaciu F, Popovici E-J, Ungur L, Vadan M, Vasilescu M, Nazarov M. Synthesis of europium- or terbium-activated calcium tungstate phosphors. in *ROMOPTO 2000: Sixth Conference on Optics*. Bucharest, Romania, SPIE, 2001.
- [8] Saparin G V, Obyden S K. Colour in the microworld: real colour cathodoluminescence mode in scanning electron microscopy. *European Microscopy and Analysis* 1993(March): 7.
- [9] Wang H, Yu M, Lin C, Liu X, Lin J. Synthesis and Luminescence Properties of Monodisperse Spherical Y₂O₃:Eu³⁺@SiO₂ Particles with Core-shell Structure. *J.Phys.Chem.C*, 2007, **111**(30): 11223.
- [10] Lee E Y, Nazarov M, Kim Y J. Red Emission Properties of (Y, M)NbO₄:Eu³⁺ (M: Al, Ga) Phosphors under Near-UV Excitation. *J.Electrochem. Soc.*, 2010, **157**(3): J102.
- [11] T. Takahashi and K. Yabuta. "New Applications for Iron and Steelmaking Slag" NKK Technical review No.87 (2002)
- [12] N. Isoo et al. "Evaluation of Carbonated Solid Block as Artificial Reef Material". *Journal of the Japanese Society of Fisheries Science*, No.66, pp.647-650 (2000).
- [13] M.V. Nazarov and Do Young Noh. "New generation of europium and terbium activated phosphors from synthesis to application" //Pan Stanford Publishing, Singapore, 2011
- [14] Holloway W W, Kestigian M, Newman R. Direct Evidence for Energy Transfer Between Rare Earth Ions in Terbium-Europium Tungstates. *Phys.Rev.Lett.*, 1963, **11**(10): 458.
- [15] Zhang Q Y, Pita K, Kam C H. Sol-gel derived zinc silicate phosphor films for full-color display applications. *J.Phys.Chem. Solids*, 2003, **64**(2): 333.
- [16] Natarajan V, Murthy K V R, Jayanth Kumar M L. Photoluminescence investigations of Zn₂SiO₄ codoped with Eu³⁺ and Tb³⁺ ions. *Solid State Commun.*, 2005, **134**(4): 261.
- [17] Moadhen A, Elhouichet H, Canut B, Sandu C S, Oueslati M, Roger J A. Evidence for energy transfer between Eu³⁺ and Tb³⁺ in porous silicon matrix. *Mat.Sci.Eng.: B*, 2003, **105**(1-3): 157.
- [18] Elhouichet H, Daboussi S, Ajlani H, Najar A, Moadhen A, Oueslati M, Tiginyanu I M, Langa S, Foll H. Strong visible emission from porous GaP doped with Eu and Tb ions. *J.Lumin.*, 2005, **113**(3-4): 329.
- [19] Chen W, Sammynaiken R, Huang Y. Photoluminescence and photostimulated luminescence of Tb³⁺ and Eu³⁺ in zeolite-Y. *J. Appl.Phys.*, 2000, **88**(3): 1424.
- [20] Zhang Z-J, Chen H-H, Yang X-X, Zhao J-T. Preparation and luminescent properties of Eu³⁺ and Tb³⁺ ions in the host of CaMoO₄. *Mat. Sci.Eng., B*, 2007, **145**(1-3): 34.
- [21] T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama. "A new long phosphorescent phosphor with high brightness, SrAl₂O₄:Eu²⁺,Dy³⁺". *J. Electrochem. Soc.* **1996**, *143*, 2670–2673.
- [22] H. Takasaki, S. Tanabe, T. Hanada. "Long-lasting afterglow characteristics of Eu, Dy codoped SrO-Al₂O₃ phosphor". *J. Ceram. Soc. Jpn.* **1996**, *104*, 322–326.