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## The Luminescent Properties of Yttrium Oxyapatite Doped with $\text{Eu}^{3+}$ ions

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### Abstract:

The structural and luminescent properties of  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$  (CYS) silicate based oxyapatite doped with  $\text{Eu}^{3+}$  ions have been reported in this paper. The sample was synthesized using reflux method assisted by urea subsequent degradation. Very specific, shell- and rope-like morphologies were observed by SEM. The powder X-ray diffraction study revealed that the  $\text{Eu}^{3+}$ : CYS system crystallized in a hexagonal lattice structure (space group  $P63/m$ ) characteristic of oxyapatite. In the host oxyapatite structure, a partial replacement of  $\text{Ca}^{2+}$  and  $\text{Y}^{3+}$  ions by luminescent active  $\text{Eu}^{3+}$  ions have been done, and its photoluminescent spectra were analyzed. The performed analysis indicate the presence of  $\text{Eu}^{3+}$  ions in both, nine-fold coordinated  $4f$ , and seven-fold coordinated  $6h$  sites, showing a slight shift towards the blue area in comparison to a typical spectra of other yttrium-silicate phases as hosts.

**Keywords:** Urea assisted reflux method, Europium doped yttrium oxyapatites, Luminescent properties, Crystal structure.

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### 1. Introduction

Recently, luminescent materials have attracted great attention because of their potential application in high-resolution devices such as: cathode ray tubes (CRTs), flat panel display devices, or field emission displays (FEDs) [1, 2]. In the past decade, the sol-gel method became one of the most attractive methods for synthesis of various luminescent ceramics composed of different host materials in which rare earth metal ions have been incorporated, e.g.  $\text{Y}_2\text{SiO}_5:\text{Tb}$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}$  systems for cathodoluminescence,  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Eu}$  and  $\text{Y}_3(\text{Al}, \text{Ga})_5\text{O}_{12}:\text{Tb}$  for field emission displays,  $\text{Y}_2\text{O}_3:\text{Eu}$ ,  $\text{TiO}_2:\text{Eu}$  and  $\text{Zn}_2\text{SiO}_4:\text{Mn}/\text{Tb}$  for photoluminescence, and  $\text{ZnS}:\text{Mn}/\text{Tb}$  and  $\text{Ga}_2\text{O}_3:\text{Eu}/\text{Mn}$  for electroluminescence [3-5]. Recently, solvothermal and hydrothermal methods are particularly investigated because they enable synthesis of the luminescent materials of very interesting morphology [6].

A special attention among the host materials belongs to the  $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$  (RE is Y, Gd or La) oxyapatite, which can be used to host various luminescence active rare earth ions [7-12]. The most prominent structural characteristic of oxyapatites is the possibility of rare earth ions to simultaneously occupy two different crystallographic sites, the nine-fold coordinated  $4f$  site (with  $C_3$  point symmetry) and the seven-fold coordinated  $6h$  site (with  $C_s$  point symmetry) in the hexagonal lattice structure (space group  $P63/m$ ). In this paper, the structural and luminescent properties of low-temperature synthesized  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2:\text{Eu}^{3+}$

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system, obtained by urea assisted sol-gel method, have been studied. Taking in mind that conventional processes of oxyapatite synthesis require significantly higher temperatures than 1000 °C and longer thermal treatments to obtain mono-phase system, the modified procedure of synthesis, used in this study, gives numerous advantages, especially from the aspect of particles nanodesign.

## 2. Experimental

### 2.1. Synthesis

For the synthesis of calcium yttrium oxyapatite of chemical formula  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$ , doped with 1.42 at% of  $\text{Eu}^{3+}$ , silica sol, calcium, yttrium and europium nitrate salts were mixed in the corresponding stoichiometric ratio. The silica sol is prepared by method described in ref. [13], and an average size of  $\text{SiO}_2$  particles was estimated to be 6.7 nm. The synthesis was performed using reflux method, at water boiling temperature during 4 h. The pH value of precursor was adjusted to 9 by adding urea, which brings to an increase of the pH value to the level required for complete hydrolysis of metal ions. After precipitation, the sample was rinsed with deionized water, and then the precipitate was annealed at 800 °C for 4 h. The white powder was obtained.

### 2.2. Characterizations

The powder X-ray diffraction (XRD) method was used for the phase analysis of such obtained powder, as well as for the estimation of the average crystallite size value and the lattice parameters. Diffraction pattern was collected on a Philips 1710 diffractometer equipped with  $\text{Cu } K_{\alpha 12}$  radiation. The data were collected in the  $2\theta$  range from 9 to 70° with a scanning step of 0.05°, and exposition time of 5 sec per step. The average crystallite size of  $\text{Eu}^{3+}$ -doped calcium yttrium oxyapatite was determined from the line broadening of (002) reflection using Scherrer equation:  $d = K\lambda/B\cos\theta$ , where  $d$  - is the average diameter of the crystallites (in nm),  $K$  - is the shape factor (0.9),  $B$  - is the full width at half maximum of reflection,  $\lambda$  - is the wavelength of the employed X-rays and  $\theta$  is the Bragg diffraction angle.

The specific surface area of powder was estimated using the nitrogen gas absorption BET method (Sorptomatic 1990, Termoquest CE Instruments). 0.20 g of the sample was thoroughly degassed for 3 h at 150 °C, and then the absorption measurement was performed. Under assumption that the synthesized particles are spherical in shape, the average diameter of the particles was estimated using equation:  $d_{\text{bet}} = 6/\rho S_w$ , where  $S_w$  - is the specific surface area, and  $\rho$  - is the density of the  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$  oxyapatite powders (we used theoretical value,  $\rho = 4.2 \text{ g/cm}^3$ ).

The morphology and agglomerate size distribution of the powder were observed by scanning electron microscopy (SEM, JEOL JSM-5300).

Photoluminescence properties of  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2:\text{Eu}^{3+}$  powder were studied by Perkin Elmer LS45 luminescence spectrometer, equipped with the excitation source (an optical parametric oscillator (OPO) pumped by the third harmonic of the Nd:YAG laser). The emission was analyzed using HR250 monochromator (Jobin-Yvon). The data was collected using an ICCD camera (Princeton Instrument). In order to limit the contribution of the  ${}^5\text{D}_1$  emission, the photoluminescence spectra were obtained with 1 ms time delay after the laser pulse. The emission spectra were recorded after excitation into the strongest  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  absorption band.

### 3. Results

#### 3.1. XRD study

Fig. 1 shows the XRD patterns of  $\text{Ca}_2\text{Y}_{8-x}\text{Eu}_x(\text{SiO}_4)_6\text{O}_2$  ( $x=0.0142$ ) oxyapatite powder after thermal treatment at 800 °C. Pretty narrow diffraction peaks pointed out on a well crystallized grains and low density of strains inside crystal structure. As  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$  is isostructural with natural oxyapatite phase  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , all reflections were indexed in the space group (*S.G.*)  $P6_3/m$ , as follow: 22.1° (200), 23.3° (111), 26.3° (002), 28.7° (120), 29.2° (102), 32.2° (121), 32.8° (112), 33.3° (300), 47.4° (222), 48.8° (213), 50.3° (123), 51.9° (402), and 52.6° (004) (in agreement with JCPDS Card 27-93). The experimental XRD patterns were analyzed by *FullProf* program in a full profile-matching mode (Fig.1). The refined lattice parameters were found to be:  $a = b = 9.360(1)$  Å,  $c = 6.790(1)$  Å. The average crystallite size obtained using Sherrer equation was found to be about 45 nm.

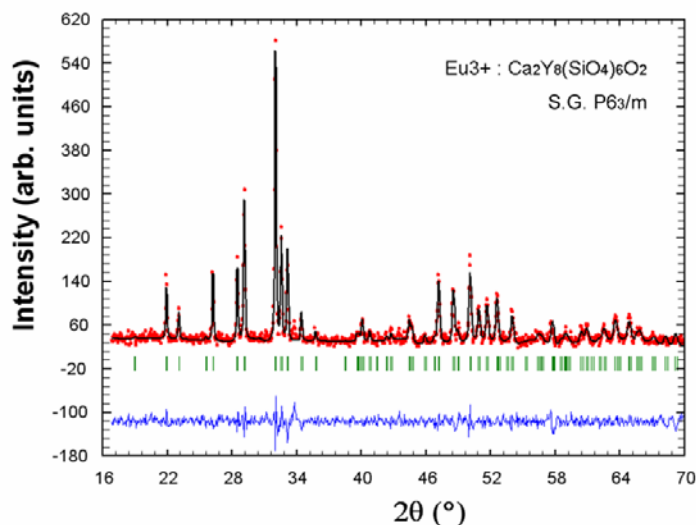


Fig. 1. Experimental (dots) and refined (line) XRD diffraction pattern of  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2:\text{Eu}^{3+}$  powder annealed at 800 °C.

#### 3.2. SEM and BET investigations

The SEM images of  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2:\text{Eu}^{3+}$  powder, shown in Fig. 2, give insight into a morphology of the powder. As it can be seen, particles are agglomerated and form aggregates of shell- and rope-like shape.

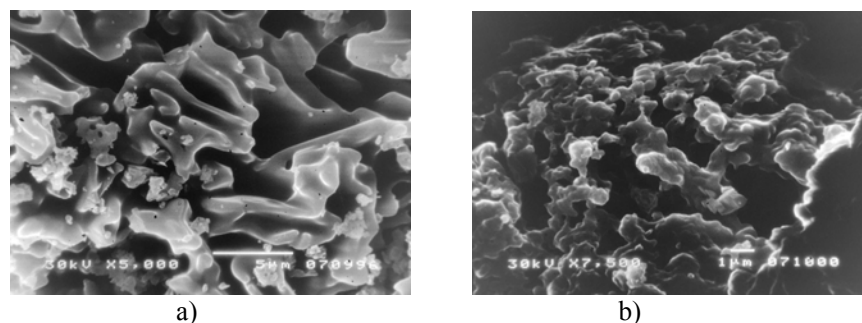
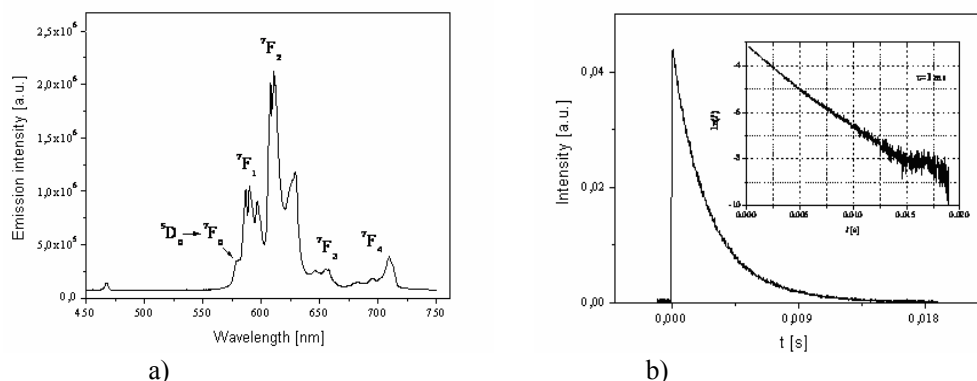


Fig. 2. Typical morphology of  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2:\text{Eu}^{3+}$  particles; a) shell-like platelets; and b) rope-like rings.

The platelet size of shells is up to 5  $\mu\text{m}$ , with small broken pieces in between, less than 1  $\mu\text{m}$  in size (Fig. 2a). On the other side, the rope-like agglomerates (Fig. 2b) are consisted of spherical particles less than 1  $\mu\text{m}$  in size which are probably built of assembly of even smaller particles. The particles size value obtained by BET analysis was found to be  $\sim 55$  nm, and is very close to the average crystallite size obtained by XRD analysis ( $\sim 45$  nm).

### 3.3. Photoluminescence properties

The fluorescence spectra of  $\text{Eu}^{3+}$ -doped  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$ , excited by 476.5 nm wavelength, is shown on the Fig 3a.



**Fig. 3.** Emission spectra of  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2:\text{Eu}^{3+}$ : a) typical emission bands; b)  $^5\text{D}_0$  decay profile lifetime line at room temperature. Estimated lifetime is 3 ms.

The fluorescence spectrum of  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2:\text{Eu}^{3+}$  oxyapatite, obtained upon excitation at 396 nm (Fig. 3a), shows all characteristic emissions lines for  $\text{Eu}^{3+}$  ions which correspond to the transition lines  $^5\text{D}_0$ - $^7\text{F}_J$  ( $J=0, 1, 2, 3, 4$ ). The emissions from higher  $^5\text{D}_J$  ( $J>0$ ) levels have not been observed, which can be ascribed to the fact that the energy gaps between  $^5\text{D}_2$  and  $^5\text{D}_1$ , as well as between  $^5\text{D}_1$  and  $^5\text{D}_0$  levels of  $\text{Eu}^{3+}$ , which are  $2500\text{ cm}^{-1}$  and  $1750\text{ cm}^{-1}$  respectively, silicate groups (with  $\nu_{\text{max}} = 950\text{ cm}^{-1}$ ) are able to bridge, thus joining the gaps between the higher lying levels of the  $\text{Eu}^{3+}$  ion and the  $^5\text{D}_0$  level. The most prominent  $^5\text{D}_0$ - $^7\text{F}_2$  emission of  $\text{Eu}^{3+}$  ions belongs to the hypersensitive, forced electric dipole transition, which is highly sensitive on the symmetry of  $\text{Eu}^{3+}$  surrounding [1-2]. Generally, the  $^7\text{F}_J$  energy levels of free  $\text{Eu}^{3+}$  ions ( $4f^6$  electron configuration) in a crystal lattice split under the effect of crystal field depending on the symmetry of  $\text{Eu}^{3+}$  site and the number  $J$ . In hexagonal oxyapatite structure, the crystal fields with  $C_3$  and  $C_s$  symmetry cause splitting of both  $^5\text{D}_0$ - $^7\text{F}_1$  and  $^5\text{D}_0$ - $^7\text{F}_2$  levels into 3 lines, respectively.  $^5\text{D}_0$ - $^7\text{F}_0$  emission line can not be split because  $J=0$ . So the number of  $^5\text{D}_0$ - $^7\text{F}_0$  lines can be an indication of the number of different  $\text{Eu}^{3+}$  luminescent centers. It is well known that two  $^5\text{D}_0$ - $^7\text{F}_0$  lines indicate that the  $\text{Eu}^{3+}$  ions probably simultaneously occupy two different sites in the host oxyapatite lattices, e.g.  $4f(C_3)$  sites and  $6h(C_s)$  sites [7]. The explanation for such prediction can be as follows. The nine-fold coordinated  $4f$  site can accommodate larger cations (bigger space), while the seven-fold coordinated  $6h$  site is favorable for higher charge cations due to the fact that a cation in this site is surrounding by one free oxygen  $\text{O}(4)$  ion. The  $\text{Eu}^{3+}$  has larger effective ionic radii than  $\text{Y}^{3+}$  (0.120 and 0.1075 nm for nine-coordinated  $\text{Eu}^{3+}$  and  $\text{Y}^{3+}$  ions, respectively) and higher charge (+3), which are favorable for  $4f$  site and  $6h$  site, respectively. The competition of these two tendency cause simultaneous occupation of both,  $4f$  and  $6h$  sites by  $\text{Eu}^{3+}$  ions. The  $4f$  site has no free oxygen ion in its surrounding, while the  $6h$  site has one (at a very short distance). Consequently, the seven-fold coordinated  $\text{Eu}^{3+}$  ions ( $6h$ ) are expected to be more covalently bonded than the nine-fold coordinated  $\text{Eu}^{3+}$  ( $4f$ ). Therefore, the  $^5\text{D}_0$ - $^7\text{F}_0$  emission line at the

lower energy is assigned to  $\text{Eu}^{3+}$  ions in  $6h$  site, and second at higher energy to  $\text{Eu}^{3+}$  ( $4f$ ) site. It is obvious that the  ${}^5\text{D}_0\text{-}{}^7\text{F}_0$  line of  $\text{Eu}^{3+}$  ( $4f$ ) is significantly broader than the  ${}^5\text{D}_0\text{-}{}^7\text{F}_0$  transition line of  $\text{Eu}^{3+}$  ( $6h$ ). This is because the crystal field at the  $4f$  site varies, giving rise to an inhomogeneous broadening of the spectral lines. On the contrary, the  ${}^5\text{D}_0\text{-}{}^7\text{F}_0$  transition line of  $\text{Eu}^{3+}$  ( $6h$ ) is very narrow, because the  $6h$  sites exclusively belong to  $\text{Y}^{3+}$ .

The  $4f$  sites and  $6h$  sites alternate in the host lattices, i.e.  $4f$  ( $\text{Ca}^{2+}$ ,  $\text{Y}^{3+}$ ) -  $6h$  ( $\text{Y}^{3+}$ ). So it can be expected the formation of  $\text{Eu}^{3+}(4f)\text{-O}^{2-}\text{-Y}^{3+}(6h)$  and  $\text{Eu}^{3+}(6h)\text{-O}^{2-}\text{-Ca}^{2+}(4f)$  in the host lattices. The next neighbor of  $\text{Eu}^{3+}(4f)\text{-O}^{2-}$  is  $\text{Y}^{3+}$ , so the energy position of  $\text{Eu}^{3+}(4f)$   ${}^5\text{D}_0\text{-}{}^7\text{F}_0$  is almost similar. As far as  $\text{Eu}^{3+}(6h)\text{-O}^{2-}$  is concerned, its next neighbor is  $\text{Ca}^{2+}$  ion which will influence the degree of covalence of  $\text{Eu}^{3+}(6h)\text{-O}^{2-}$  bond. This causes increased degree of covalence of  $\text{Eu}^{3+}(6h)\text{-O}^{2-}$  bond making a red shift for  $\text{Eu}^{3+}(6h)$   ${}^5\text{D}_0\text{-}{}^7\text{F}_0$ .

Fig. 3b shows the fluorescence decay curves of the  ${}^5\text{D}_0$  emitting level obtained when the sample was excited at 590 nm ( $\lambda_{\text{cm}} = 613$  nm). The fluorescence decay profiles can be adjusted by a single-exponential function in the longer times, while a non-exponential part is observed for the shorter time. The lifetime estimated from this curve is found to be 3 ms, what is quite high value for europium species with low non-radiative energy transfer probability. This fact makes this material very promising from the aspect of optoelectronic applications.

#### 4. Conclusions

In this paper we revealed synthesis procedure, as well as structural and luminescent properties of  $\text{Eu}^{3+}$ -doped  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$  oxyapatite. The sample is obtained from the precipitate synthesized via urea assisted reflux method at  $\text{pH} = 9$ , which subsequently underwent annealing at  $800^\circ\text{C}$  in air. The XRD analysis confirmed high purity of the sample, giving rise to the high advantages of this over other methods of synthesis. An oxyapatite structure is obtained at significantly lower temperature (about  $500^\circ\text{C}$ ), comparing a classical solid state reaction. The average crystallite size was found to be 45 nm (XRD), what is in comparison with the average particle size obtained by BET method ( $\sim 55$  nm).  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2\text{:Eu}^{3+}$  nanoparticles aggregate into bigger, spherical particles, 1  $\mu\text{m}$  in size, which further form shell- and rope-like agglomerates order of 1 to 5  $\mu\text{m}$ . The photoluminescence spectra analysis indicate that  $\text{Eu}^{3+}$  ions simultaneously occupied two different sites inside host calcium yttrium oxyapatite lattices,  $4f$  and  $6h$  sites (*S.G. P63/m*), causing splitting of both  ${}^5\text{D}_0\text{-}{}^7\text{F}_1$  and  ${}^5\text{D}_0\text{-}{}^7\text{F}_2$  emission levels of  $\text{Eu}^{3+}$  ions into 3 lines, respectively.

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**Садржај:** Структурне и луминесцентне особине оксиапатита  $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$  (CYS) допираног  $\text{Eu}^{3+}$  јонима приказане су у овом раду. Узорак је синтетисан рефлукс методом, уз постепену деградацијом урее. Врло специфична, икољколика и ужаста, морфологија честица уочена је помоћу скенирајуће електронске микроскопије. Дифракција X-зрака показала је да је  $\text{Eu}^{3+}$ : CYS систем кристалисан у хексагоналној структурној решетки, карактеристичној за оксиапатит. У структури оксиапатита као домаћина, изведена је делимична замена  $\text{Ca}^{2+}$  и  $\text{Y}^{3+}$  јона са луминесцентно активним  $\text{Eu}^{3+}$  јонима чији су фотолуминесцентни спектри анализирани. Дата анализа указује на присуство  $\text{Eu}^{3+}$  јона на оба места, 4f са координацијом 9 и 6h са координацијом 7, показујући благи помак ка плавој области у поређењу са типичним спектром других итријум-силикатних фаза, као домаћина  $\text{Eu}^{3+}$  јона.

**Кључне речи:** рефлукс метода, еуропијумом допирани итријум оксиапатит, луминесцентне особине, кристална структура.