

## Luminescent ceramics based on polycrystalline calcium fluoroapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{3+}$

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The FAP and  $\text{FAP}:\text{Eu}^{3+}$  powders have been prepared using precipitation from aqueous solution. The as-prepared powders were compacted into tablets at 660 MPa and sintered in oxygen atmosphere at 600–1200°C. XRD analysis has shown that within the whole range of sintering temperature, the samples contain crystalline fluorapatite along with a small amount of amorphous phase, which decreases as the sintering temperature rises. The sintering temperature elevation results in extension of the coherent scattering area size ( $L = 42$  to  $54$  nm). The  $\text{FAP}:\text{Eu}^{3+}$  ceramics density attains 84.67 % at  $T_{\text{sint}} = 1100^\circ\text{C}$  and decreases above that value. As the temperature increases, the average grain size grows from 5 to 15  $\mu\text{m}$  and the porosity decreases. The photoluminescence efficiency of  $\text{Eu}^{3+}$  in the FAP structure is maximum for ceramics sintered at 1100°C.

Порошки фторапатита кальция (ФАП) и  $\text{ФАП}:\text{Eu}^{3+}$  получены методом осаждения из водных растворов. Свежеприготовленные порошки компактировались в таблетки при 660 МПа и спекались в атмосфере кислорода в диапазоне температур  $T_{\text{sint}} = 600$ – $1200^\circ\text{C}$ . По данным XRD, во всем диапазоне температуры спекания наряду с кристаллической фазой ФАП, присутствует небольшое количество аморфной фазы, которое с ростом температуры спекания уменьшается. С ростом температуры увеличивается размер областей когерентного рассеяния ( $L = 42$ – $54$  нм). Плотность керамики  $\text{ФАП}:\text{Eu}^{3+}$  достигает 84.67 % при  $T_{\text{sint}} = 1100^\circ\text{C}$  и выше этого значения снижается. С увеличением  $T_{\text{sint}}$  средний размер зерен растет от 5 до 15 мкм и снижается пористость. Выход фотолюминесценции  $\text{Eu}^{3+}$  в структуре ФАП максимален для керамики, спеченной при 1100°C.

Recently, the ceramics on the basis of apatite-like materials is under intense investigation [1–6]. Such materials are used successfully in prosthetics and implant manufacturing due to their unique properties such as biocompatibility, bioactivity, ion exchange ability, etc. [5, 7–10]. The hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$  (HAP) ceramics of various porosity is used widely as bone fillers and bone substitutes. The compact ceramics on the basis of nanocrystalline HAP and fluoro substituted HAP prepared by solid phase method has been studied in [11, 12]. The structure and morphology proposed by the authors was shown to be the

most acceptable in bone regeneration. The structure analog of calcium hydroxyapatite, namely, fluoroapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  (FAP) as well as other halogen-phosphates activated with rare earth ions are of good prospects in manufacturing of crystal lumino-phors, light converting coatings, UV protecting coatings, laser materials, etc. [13, 14].

Unlike the HAP ceramics, the FAP one is still investigated insufficiently. In [15, 16], the FAP ceramics has been obtained in argon and oxygen atmosphere. The fluoroapatite phase has been shown to be stable up to 1180°C. The argon atmosphere provides the maintaining of constant density at

higher temperatures than in the ceramics synthesized under oxygen. The strontium substituted glass ceramics of calcium fluoroapatite for medical purposes has been prepared in [17]. The authors have shown that strontium introduction into the Ca-FAP structure effects insignificantly the structure, nucleation and crystallization processes of the glass ceramics. Introduction of magnesium ions into calcium fluoroapatite ceramics causes changes in the ceramics crystallinity and morphology and appearance of additional  $\text{Mg}_2\text{F}(\text{PO}_4)$  phase at elevated temperatures [18]. In connection with development of novel luminescent ceramic materials, of importance is the search for appropriate matrices, optimization of the synthesis conditions, and studies of the ceramics properties being of interest for potential technical applications. Thus, the purpose of this work is to synthesize and study the ceramics on the basis of polycrystalline FAP and FAP activated with europium ions.

The initial powders precipitates of FAP and FAP activated with trivalent europium ions were obtained by early described procedure [19,20]. The FAP and  $\text{FAP:Eu}^{3+}$  powders were sintered in oxygen atmosphere at temperatures ranging from 600 to 1200°C. The powders to be sintered were compacted previously under 660 MPa into tablets 1.5 mm thick tablets of 100 mm diameter. The phase composition of the samples obtained was studied using XRD (DRON-4, Fe  $K_\alpha$  emission,  $\lambda = 1.93728 \text{ \AA}$ , the scan angle range  $2\theta$  10–70°). The size of coherent scattering area in the sintered samples was calculated from the XRD line half-width using the Selyakov-Scherrer equation. The microstructure characteristics of the samples was studied using a JSM-820 scanning electron microscope equipped with the microanalysis system. The luminescence and its excitation spectra were recorded using an automated SDL-2 setup (LOMO, St.-Petersburg).

According to the elemental analysis data, the ratios of main components in the FAP and  $\text{FAP:Eu}^{3+}$  ceramics amounted as follows: Ca/P, 1.5 to 2.1; Ca/F, 5.1 to 7.0, that is close to the FAP stoichiometry. The europium concentration was  $1 \pm 4 \text{ at. \%}$ . The XRD analysis has shown that when europium ions are entered the FAP structure in an amount up to 4 at.%, the XRD patterns contain a set of main reflections corresponding to FAP. Above that value, a two-component system is formed consisting of FAP and  $\text{EuPO}_4$ . That is why the further

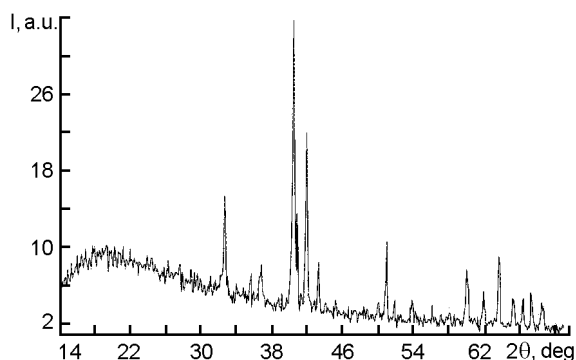


Fig. 1. XRD pattern for  $\text{FAP:Eu}^{3+}$  ceramics sintered at 1000°C.

studies were carried out using ceramics containing 4 at. % Eu.

Fig. 1 presents the XPA results for  $\text{FAP:Eu}^{3+}$  ceramics sintered in oxygen atmosphere. The XRD patterns for samples obtained within the whole sintering temperature range contain a set of main reflections corresponding to FAP crystal lattice. The reflections are narrow enough, thus evidencing the presence of large crystallites. Since it is very difficult to obtain the stoichiometric FAP ( $\text{Ca/P} = 1.67$ ), the formation of additional impurity phases, such as CaO,  $\text{CaF}_2$ , etc., is quite possible. It has been shown [15] that the sintering of non-activated calcium fluoroapatite in argon atmosphere above 1100°C causes the appearance of additional CaO phase (due to hydrolysis of  $\text{CaF}_2$  impurity phase), the CaO amount increasing as the temperature is elevated. At  $\text{FAP:Eu}^{3+}$  powder sintering under oxygen atmosphere, the absence of CaO phase is due to its dissolution in the liquid phase corresponding to the FAP/impurity eutectics, in particular, with fluorite as the impurity phase.

No additional phases have been revealed in diffraction pattern of ceramics obtained in our experiments. The samples sintered at low temperatures consist of amorphous phase that is indicated by a wide halo at small angles. The amorphous phase amount decreases as the temperature rises. In parallel, the amount of crystalline calcium FAP increases, as is evidenced by increasing intensity of diffraction lines. The diffraction pattern for samples sintered at 1100 and 1200°C contain the reflection set of the essentially single-phase FAP. Table 1 summarizes the XPA results of  $\text{FAP:Eu}^{3+}$  ceramics. The FAP lattice parameters, both  $a$  and  $c$  ones, are seen to be essentially constant (the changes are within the calculation

Table 1. Summarized XPA data for FAP:Eu<sup>3+</sup> ceramics

Ceramics	$T_{sinter}, ^\circ\text{C}$	XRD analysis		
		$a \pm 0.03, \text{\AA}$	$c, \text{\AA}$	$L, \text{nm}$
FAP:Eu <sup>3+</sup>	0	9.37	6.88	42
FAP:Eu <sup>3+</sup>	600	9.39	6.89	42
FAP:Eu <sup>3+</sup>	1000	9.38	6.89	77.5
FAP:Eu <sup>3+</sup>	1100	9.49	6.89	51.5
FAP:Eu <sup>3+</sup>	1200	9.40	6.90	54

error) within the whole temperature range. However, the coherent scatter are size ( $L$ ) grows as the sintering temperature rises.

Fig. 2 presents the dependence of the FAP:Eu<sup>3+</sup> ceramics density on the sintering temperature. The density and porosity of the samples were determined using hydrostatic weighing. The density and porosity data are summarized in Table 2. It is seen from the Fig. 2 and Table 2 that the density increases with the sintering temperature and attains a maximum at 1100°C. Above that temperature, the grain growth becomes substantial and favors the intergranular porosity that is responsible for the density decrease. The ceramics porosity decreases as the density increases. The minimum porosity value of 6.8 % is attained at the maximum density  $\rho = 84.67$  % of theoretical value.

The morphology of the ceramics obtained was studied by scanning electron microscopy. The images are shown in Figs. 3 and 4. It is seen from Fig. 3 (a, b) that the grain size increases from 5 to 15  $\mu\text{m}$  as the sintering temperature rises. The porosity is minimum in both non-activated and activated ceramics sintered at 1100°C.

Due to specific features of the FAP crystal structure, the charge compensation at

Table 2. Summarized density and porosity data for FAP:Eu<sup>3+</sup> ceramics

Ceramics	$T_{sint}, ^\circ\text{C}$	$\rho_{abs}, \%$	$\rho_{rel}, \%$	$P(\text{porosity}), \%$
FAP:Eu <sup>3+</sup>	0	2.37	74.06	19.4
FAP:Eu <sup>3+</sup>	600	2.42	75.89	17.3
FAP:Eu <sup>3+</sup>	1100	2.71	84.67	6.8
FAP:Eu <sup>3+</sup>	1200	2.60	81.23	19.1

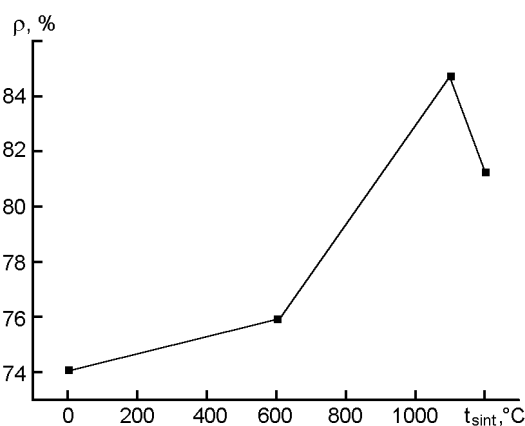
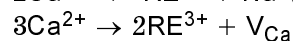
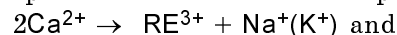


Fig. 2. Dependence of relative density of ceramic samples on the sintering temperature.

the introduction of heterovalent Eu<sup>3+</sup> ions ( $r(\text{Eu}^{3+}) = 1.13 \text{\AA}$ ,  $r(\text{Ca}^{2+}) = 1.06 \text{\AA}$  [21]), may proceed according to various mechanisms, in accordance with the Goldschmidt rule and in agreement with [22]. In the Ca(I) position where the calcium ion is surrounded with 9 oxygen atoms, two charge compensation mechanisms are possible:



( $\text{V}_{\text{Ca}}$  being calcium vacancy). The vacancy may be positioned in various crystal-

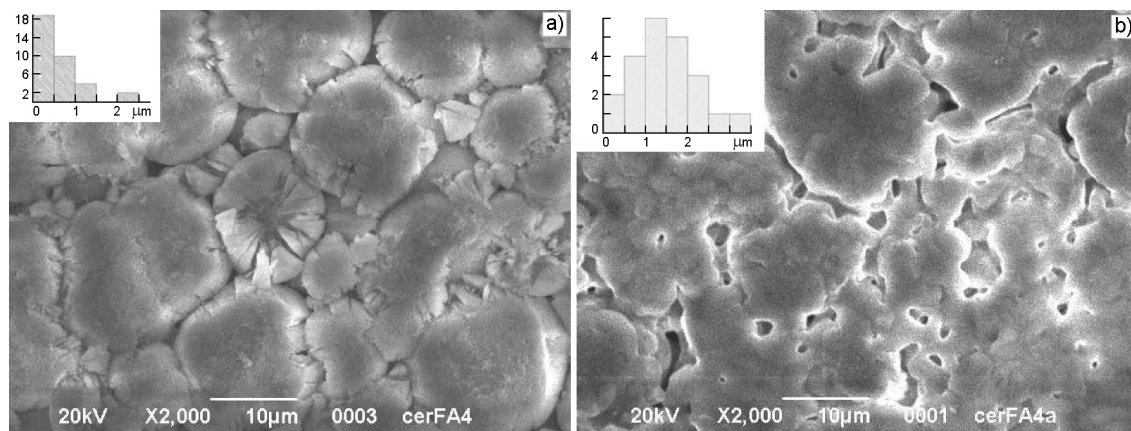


Fig. 3. Morphology of non-activated FAP samples: as-prepared FAP (a) and FAP sintered at 1000°C (b).

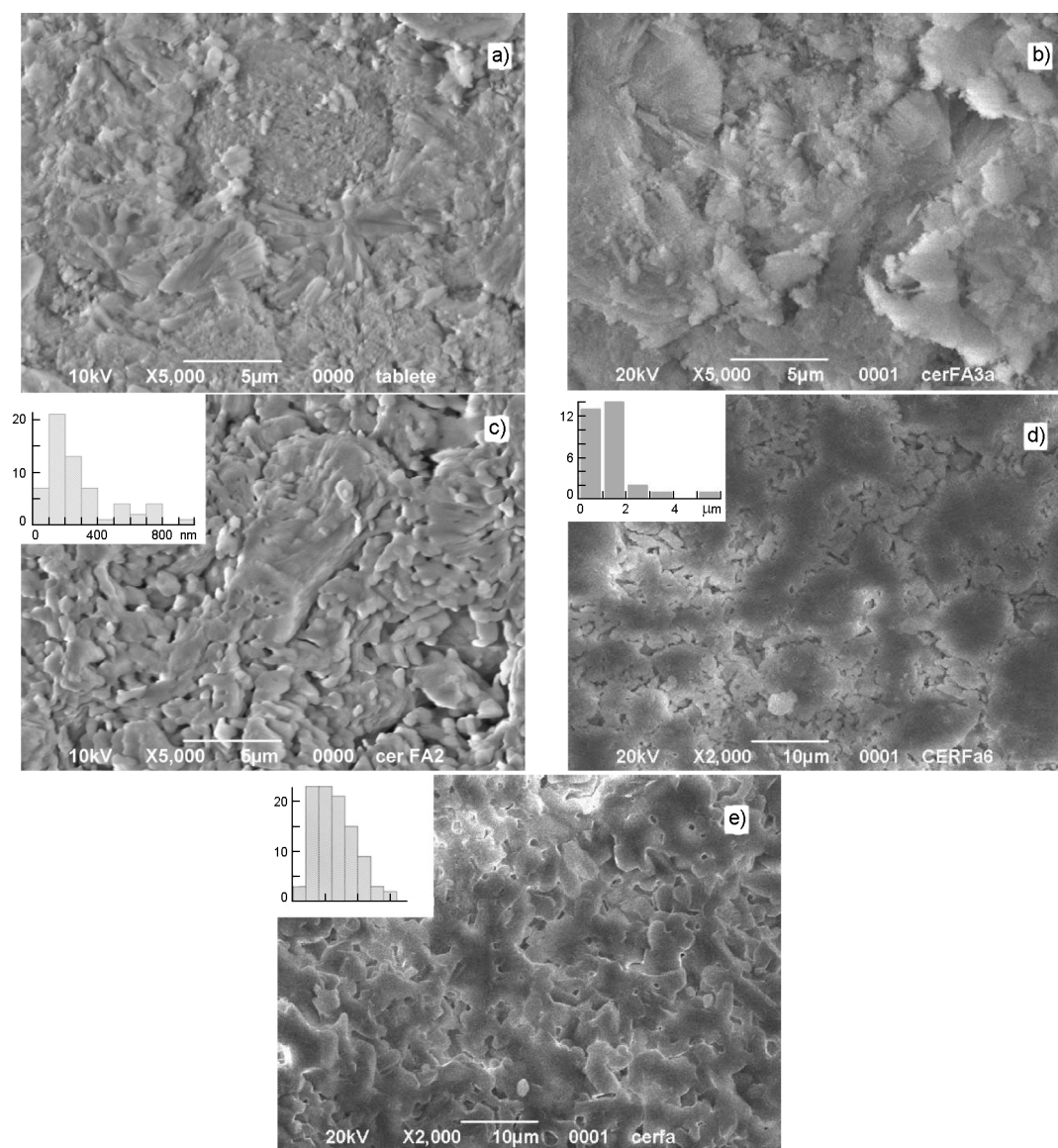
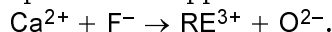


Fig. 4. Morphology and porosity distribution of FAP:Eu<sup>3+</sup> ceramic samples sintered in oxygen atmosphere at temperatures (°C): 0 (a); 600 (b); 1000 (c); 1100 (d); 1200 (e).

lographic positions with respect to europium ion. The first mechanism is the least probable, since the potassium ion radius exceed considerably that of calcium ( $r(\text{K}^+) = 1.33 \text{ \AA}$ ,  $r(\text{Ca}^{2+}) = 1.06 \text{ \AA}$ ). The presence of potassium and sodium ions is due to the impurities in the initial components. This mechanism is most often described in literature where Na<sup>+</sup> or K<sup>+</sup> is introduced into the FAP structure along with a divalent cation, thus compensating trivalent RE ion [23]. The second mechanism is more probable for our systems and supposes the presence of defects, in particular, calcium vacancy formation. In the Ca(II) position, calcium ion is

surrounded with 7 oxygen atoms that form the phosphate tetrahedrons. Here, the crystal field is deformed due to substitution of fluorine ion for oxygen one and the charge compensation supposes the scheme



When studying the dependence of Eu<sup>3+</sup> luminescence integral intensity on europium concentration in the FAP matrix, a peak of luminescence yield was observed in the activator concentration range of 3.5 to 4 at. %. In our opinion, that dependence is due to a strong concentration quenching of Eu<sup>3+</sup> luminescence in the fluoroapatite matrix.

The luminescence spectrum of FAP:Eu<sup>3+</sup> ( $C_{\text{Eu}} = 4 \text{ at. \%}$ ) (Fig. 5) contains four most

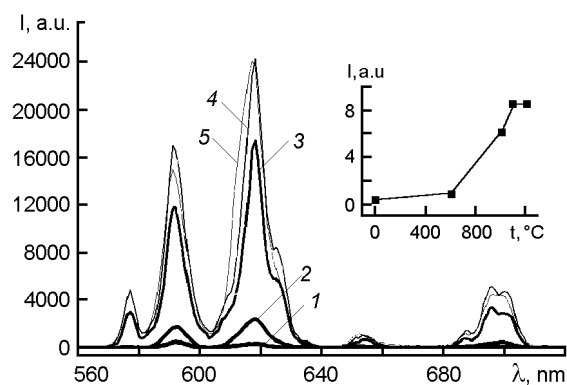


Fig. 5. Luminescence spectra of FAP:Eu<sup>3+</sup> ceramics sintered in oxygen atmosphere at temperatures (°C): 0 (1); 600 (2); 1000 (3); 1100 (4); 1200 (5).

intense groups of lines with maxima at 578, 589, 618, and 697 nm, corresponding to main transitions  $^5D_0 \rightarrow ^7F_0$ ,  $^5D_0 \rightarrow ^7F_1$ ,  $^5D_0 \rightarrow ^7F_2$  and  $^5D_0 \rightarrow ^7F_4$  of trivalent europium excited at 395 nm. The bands corresponding to the magneto-dipole ( $^5D_0 \rightarrow ^7F_1$ ) and electric-dipole (supersensitive)  $^5D_0 \rightarrow ^7F_2$  transitions predominate. The relatively low intensity of  $^5D_0 \rightarrow ^7F_0$  transition as compared to the  $^5D_0 \rightarrow ^7F_2$  one as well as the total number of bands in the spectrum evidence that Eu<sup>3+</sup> ions in the structure of all the studied ceramic samples are localized predominantly in the low symmetry Ca(II) position with the local C<sub>s</sub> symmetry. The maximum intensity of europium luminescence is observed in the samples sintered at 1100°C. The correlation between the luminescence intensity and the sintering temperature is shown schematically in the inset to Fig. 5.

Thus, we have obtained luminescent ceramics on the basis of calcium fluoroapatite activated with europium ions. It has been shown that europium occupies predominantly the Ca(II) position in the FAP crystal lattice. The luminescence intensity increases sharply in the activator concentration range of 3.5 to 4 at. %. The luminescence intensity decrease at a further increase of the activator concentration is due to concentration quenching of Eu<sup>3+</sup> luminescence in the FAP matrix. The optimum sintering temperature providing the maximum Eu<sup>3+</sup> pho-

toluminescence yield in the FAP structure has been established to be 1100°C.

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## **Люмінесцентна кераміка на основі фторапатиту кальцію $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{3+}$**

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Порошки фторапатиту кальцію (ФАП) та ФАП: $\text{Eu}^{3+}$  отримано методом осадження з водних розчинів. Свіжоприготовлені порошки компактувались у таблетки при 660 МПа та спікались у атмосфері кисню у діапазоні температур  $T_{\text{sint}} = 600\text{--}1200^\circ\text{C}$ . За даними XRD, у всьому діапазоні температур спікання поряд з кристалічною фазою ФАП присутня невелика кількість аморфної фази, яка з ростом температури спікання зменшується. З ростом температури спікання збільшується розмір областей когерентного розсіювання ( $L = 42\text{--}54$  нм). Густина кераміки ФАП: $\text{Eu}^{3+}$  досягає 84.67 % при  $T_{\text{sint}} = 1100^\circ\text{C}$  і вище цього значення знижується. Зі збільшенням  $T_{\text{sint}}$  середній розмір зерен зростає від 5 до 15 мкм та пористість знижується. Вихід фотолюмінесценції  $\text{Eu}^{3+}$  у структурі ФАП є максимальним для кераміки, спеченої при  $1100^\circ\text{C}$ .