

Growing of Sm^{3+} doped polycrystalline calcium fluorapatite from aqueous solutions

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Polycrystalline samples of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ (calcium fluor-apatite, FAP) and of Sm^{3+} doped FAP have been obtained by precipitation from aqueous solutions. The optimum conditions to obtain single-phase polycrystalline doped and undoped FAP are $\text{pH} = 4.7$ and $T = 80^\circ\text{C}$. Effect of physicochemical conditions on the sample characteristics has been studied. The luminescence and luminescence excitation spectra of FAP doped with samarium have been measured. The spectra obtained are identified as those of Sm^{3+} .

Методом осаждения из водных растворов получены поликристаллические образцы $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ (фторапатита кальция, ФАП) и ФАП, активированного Sm^{3+} . Оптимальными условиями получения монофазного, поликристаллического, допированного и не допированного ФАП являются $\text{pH} = 4.7$ и $T = 80^\circ\text{C}$. Изучено влияние физико-химических условий на характеристики образующихся осадков. Измерены спектры люминесценции и её возбуждения для образцов ФАП, допированных ионами самария. Полученный спектр люминесценции, идентифицируется как спектр люминесценции Sm^{3+} .

In the frame of lighting problem, apatite-like structures $\text{Me}_{10}(\text{ZO}_4)_6\text{X}_2$ ($\text{Me} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{Z} = \text{P}, \text{V}$; $\text{X} = \text{F}, \text{Cl}, \text{OH}\dots$) are considered now to be materials of good promise for light converting coatings, large-frame plasma displays, UV protecting coatings, etc. Such materials include, in particular, calcium fluorapatite (FAP) $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ doped with rare-earth elements (RE) such as Nd^{3+} , Sm^{3+} , Eu^{3+} , etc. [1]. Since the apatite crystal lattice contains two non-equivalent positions of the metal atoms in different local environment symmetry, the controllable replacement of Me^{2+} ions ($\text{Me} = \text{Ca}, \text{Sr}, \text{Ba}$) in the matrix with RE ions at the growth step makes it possible to regulate the spectral and luminescence properties of the materials [2]. The RE ions can replace the calcium one in two non-equivalent crystallographic positions of the lattice, depending on the growing method and local charge compensation [3].

Traditionally, the apatite-like material synthesis are synthesized using the solid-

phase and hydrothermal methods as well as various vacuum sputtering techniques [4–6]. The powders, including the nanocrystal ones, as well as coatings with a pre-specified phase compositions, are difficult to obtain proceeding from multicomponent compounds, because the synthesis control in a system consisting of several precursors is a complicated task. Among alternative and promising ways to polycrystalline coatings, disperse structures and nanocrystals of apatite-like materials, the low-temperature precipitation of precursor salts from supersaturated aqueous solutions is worth to mention [7, 8]. It is known [9] that introduction of impurity ions into an aqueous solution may result in a decreased supersaturation relative to the main crystallizing phase and, due to inhibiting effect, in decreased growth rate and changed growth mechanism as well as in changed phase composition and structure of the growing microcrystals. There are numerous works [7, 8, 10] aimed at study of formation and

Table 1. Elemental analysis results for pure and Sm-doped FAP.

Sample	Element, %						
	Ca	P	F	C	O	Sm	Impurity
FAP	29.3	17.5	5.4	36.2	11.0	–	< 0.6
FAP: Sm^{3+} ($C_{\text{Sm}^{3+}} = 1\%$)	27.5	16.2	5.1	30.7	19.8	< 0.3	< 0.4

growth of alkali-earth haloapatites (including those doped with various metal ions) from aqueous solutions. Nevertheless, the growth of haloapatites activated with RE elements as well as of mixed apatites $\text{Me}^I_{10-x}\text{Me}^{II}_x(\text{PO}_4)_6\text{F}_2$ and, in particular, of FAP, are scarcely studied to date. The purpose of this work is to study the effect of the growing conditions from aqueous solutions (temperature, pH, dopant concentration, annealing) on the phase composition, structure and morphology of polycrystalline FAP: Sm^{3+} .

The initial FAP was precipitated from aqueous solutions by mixing together in a glass the CaCl_2 and KH_2PO_4 solutions containing KF in the presence of acetate buffer under controlled temperature. The total solution volume was 280 mL. The mixture temperature was 20, 37, or 80°C, the solution pH was adjusted to 4.7, 5.5, or 6.5. The FAP: Sm^{3+} was obtained at pH = 4.7 and $T = 80^\circ\text{C}$. The activation was done by introducing samarium chloride, the activator concentration being 1 and 3 at. %. The precipitates formed were washed, dried at 60°C and annealed in air at 500°C for 40 h. The phase composition of the samples was examined by XRD (DRON-4 instrument, Fe K_α emission, $\lambda = 1.93728 \text{ \AA}$, the scanning angle 2θ range 10 to 70 deg). The coating crystallinity extent (the average size of crystalline blocks) was calculated from the XRD line half-width using the Selyakov-Scherer equation. The microstructure characteristics of the synthesized samples were studied using scanning electron microscopy (SEM) (JEOL-820). The elemental composition was determined using a photoelectron spectrometer Kratos XPS-800 as well as X-ray fluorescence (XRF) analysis. The luminescence and luminescence excitation spectra were recorded using an automated SDL-2 set (LOMO, St.Petersburg). The XRF and elemental analysis have shown that the ratios of main components in the powders amount $\text{Ca}/\text{P} = 1.67 \pm 0.02$ and $\text{Ca}/\text{F} = 5.42 \pm 0.05$, thus corresponding to FAP stoichiometry (see Table 1). The presence of carbon is due to hydrocarbons adsorbed from the environ-

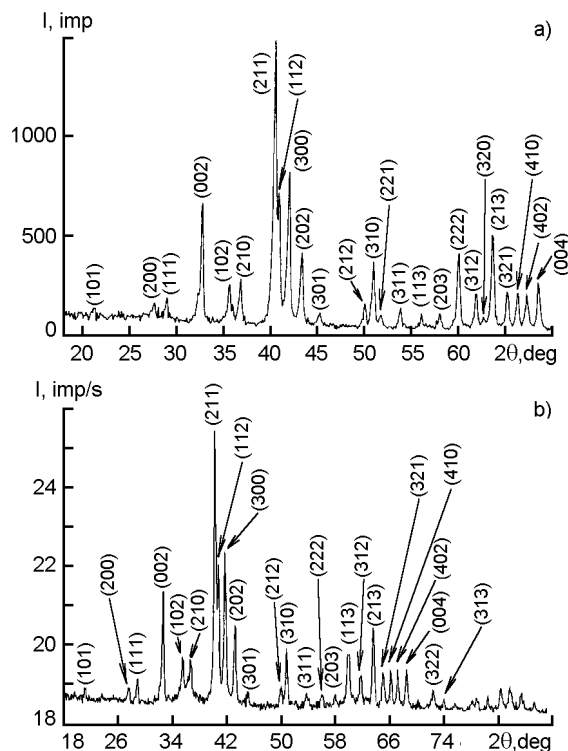


Fig. 1. XRD patterns of nominally pure FAP (a) and FAP: Sm^{3+} (1 at.%) (b) precipitated from aqueous solutions at $T = 80^\circ\text{C}$ and pH = 4.7.

mental air. The impurities (Na, K) in a total amount less than 1 % are due to the presence of those components in the initial solutions.

In Fig. 1, presented are the XRD data for the initial nominally pure FAP and for FAP: Sm^{3+} ($C_{\text{Sm}^{3+}} = 1 \text{ at.}\%$) obtained by precipitation at pH = 4.7 and $T = 80^\circ\text{C}$. The XRD patterns contain the set of main reflections corresponding to the FAP crystal lattice. No amorphous phases are found. In the apatite crystal lattice, Ca^{2+} ion occupies two non-equivalent crystallographic positions, namely, Ca(I) one with C_3 symmetry is surrounded by nine oxygen atoms while Ca(II) one with C_s symmetry is coordinated with six oxygen and one fluorine atoms [11]. As the heterovalent Sm^{3+} ions enter the FAP structure ($r(\text{Sm}^{3+}) = 1.13 \text{ \AA}$, $r(\text{Ca}^{2+}) = 1.06 \text{ \AA}$ [12]), the charge compensation, according to the Goldschmidt rule

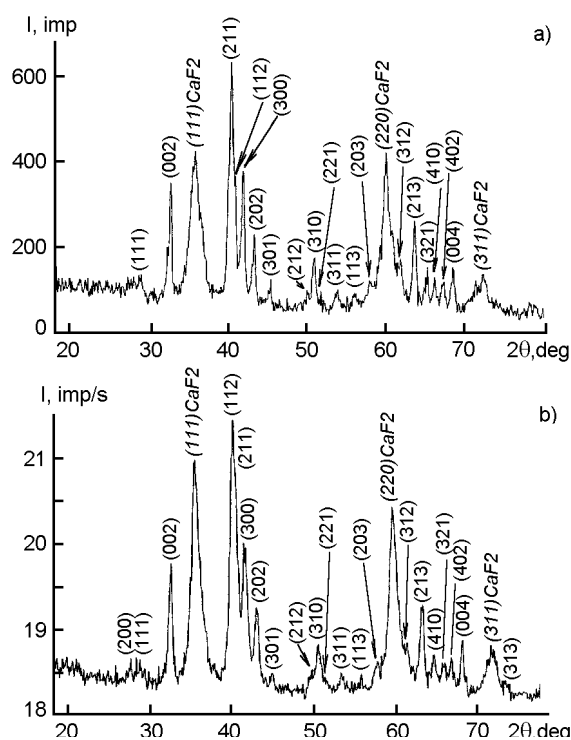


Fig. 2. XRD patterns of FAP precipitated at $T = 20^\circ\text{C}$ (a) and at pH = 6.5 (b).

and to [2], may occur by way of mechanism $3\text{Ca}^{2+} \rightarrow 2\text{Sm}^{3+} + \text{V}_{\text{Ca}^-}$ (V_{Ca^-} being a calcium vacancy). The vacancy may be in various crystallographic positions relative to Sm^{3+} ion. Doping of FAP with heterovalent Sm^{3+} ions ($C_{\text{Sm}^{3+}} = 1\%$) (see Fig. 1b) results in enlarged FAP crystal lattice parameters, $a = 9.401 \text{ \AA}$, $c = 6.882 \text{ \AA}$ (for pure calcium fluoro-apatite, $a = 9.3475 \text{ \AA}$, $c = 6.8646 \text{ \AA}$, Fig. 1a) [13]. For FAP doped with $C_{\text{Sm}^{3+}} = 3\%$, $a = 9.390 \text{ \AA}$, $c = 6.888 \text{ \AA}$. When FAP was doped with Pb^{2+} ions having ionic radius exceeding considerably that of Ca^{2+} ($r(\text{Pb}^{2+}) = 1.32 \text{ \AA}$), the increase of Pb^{2+} concentration from 5% to 10% has resulted in linear changes of the FAP crystal lattice parameters from $a = 9.401 \text{ \AA}$, $c = 6.892 \text{ \AA}$ to $a = 9.440 \text{ \AA}$, $c = 6.909 \text{ \AA}$, respectively. Proceeding from the broadening of X-ray reflections for the FAP powders, the coherent scattering field (the crystalline block) size has been estimated. For the nominally pure FAP obtained at pH = 4.7 and $T = 80^\circ\text{C}$, the size is $L = 43 \text{ nm}$. Introduction of samarium ions ($C_{\text{Sm}^{3+}} = 1\%$, 3 at.%) results in an insignificant diminution of the nanocrystalline block size down to 43 and 39 nm, respectively.

When studying the temperature effect on the sample phase composition, the following

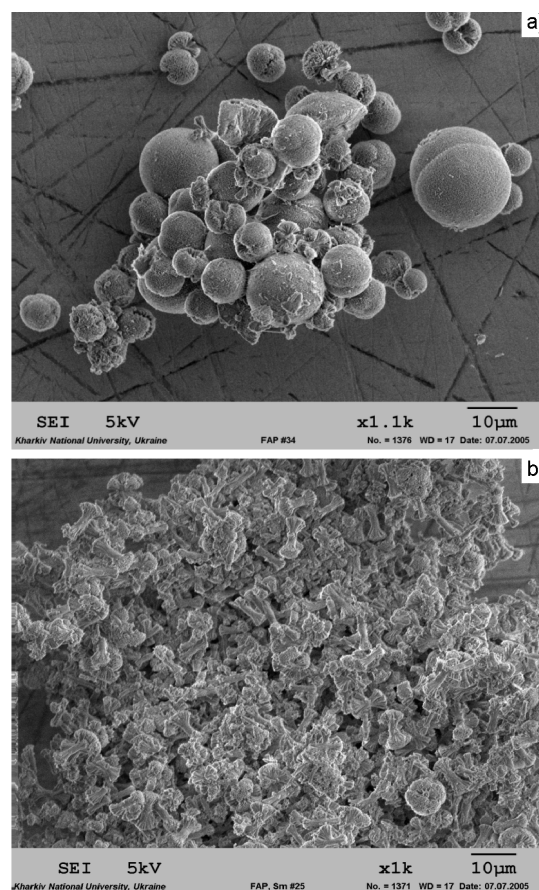


Fig. 3. EM images of nominally pure FAP (a) and FAP: Sm^{3+} (1 at.%) (b).

regularities have been revealed. The solution temperature lowering down to $T = 20^\circ\text{C}$ at pH = 4.7 (Fig. 2a) results in formation of additional CaF_2 phase and a diminution of the nanocrystalline block size (for the sample obtained, $L = 30 \text{ nm}$). Effect of the solution pH on the sample phase composition at a constant temperature has been studied, too. At pH = 5.5 and $T = 37^\circ\text{C}$, the single-phase FAP with the crystal block size of 29 nm has been obtained. As pH is raised to 6.5, the dissociation extent of HF increases and, as a result, the fluorine ion concentration in the solution rises. Moreover, the pH increase favors a higher supersaturation of the solution in CaF_2 phase, thus initiating its formation (Fig. 2b). As the solution pH increases, the nanocrystalline blocks become diminished down to $L = 21 \text{ nm}$. The XRD analysis data are summarized in Table 2.

The results of FAP and for FAP: Sm^{3+} ($C_{\text{Sm}^{3+}} = 1 \text{ at.}\%$) morphology analysis using SEM are presented in Fig. 3. The crystallites are seen to form spherical conglomerates of 5 to 15 μm size (Fig. 2a). The electron microscopic image of a Sm^{3+}

Table 2. Summary of X-ray phase analysis for experimental samples.

Sample	pH	T , °C	L(FAP), nm	L(CaF_2), nm	FAP lattice parameters	
					a , Å	c , Å
FAP	4.7	80	43	–	9.37	5.89
FAP	4.7	20	30	8	9.39	6.88
FAP	5.5	37	29	–	9.40	6.88
FAP	6.5	37	21	11.5	9.42	6.89

(1 at.%) doped FAP sample shows that the impurity entering causes changes in the crystallite size and shape. The crystallites grow in a denser plate-like shape and the size there of attains 10 μm . These shape and size changes can be supposed to be due to the inhibiting effect of the impurity [9].

The spectral and luminescence measurements have shown that unannealed samples of both initial and doped FAP are not luminescent at room temperature. Annealing of the samples in air at 500°C results in appearance of an intense luminescence. The luminescence spectra evidence that samarium ions enter the FAP crystal lattice in the trivalent state Sm^{3+} (Fig. 4). The luminescence was excited in the band peaked at $\lambda_{ex.} = 402$ nm. It is seen (Fig. 4a) that in the 300–490 nm range, the luminescence excitation spectrum of $\text{FAP}:\text{Sm}^{3+}$ consists of three groups of poorly resolved bands, the highest intensity lines being just 361, 374, 402, and 470 nm ones. Similar to the luminescence excitation spectrum, the luminescence spectrum of $\text{FAP}:\text{Sm}^{3+}$ contains three highest intensity groups of lines peaked at 562, 597, and 643 nm. According to [14], those groups of lines are due to intra-configuration electron transitions from the lower excited level $^4G_{5/2}$ (metastable state) to the ground multiplet levels $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$.

Thus, our investigation has shown that single-phase polycrystalline FAP and $\text{FAP}:\text{Sm}^{3+}$ can be obtained using precipitation from aqueous solutions. The optimum precipitation conditions are pH = 4.7 at $T = 80^\circ\text{C}$ as well as pH = 5.5 at $T = 37^\circ\text{C}$. The crystallites of the samples studied consist of nanocrystalline blocks of 21–43 nm size. The temperature lowering down to 20°C results in formation of additional CaF_2 phase and a diminution of the block size. Increased pH causes formation of two-phase FAP/ CaF_2 system and the block size diminution. In the case of pH increase, the amount of CaF_2 is larger than in the sample

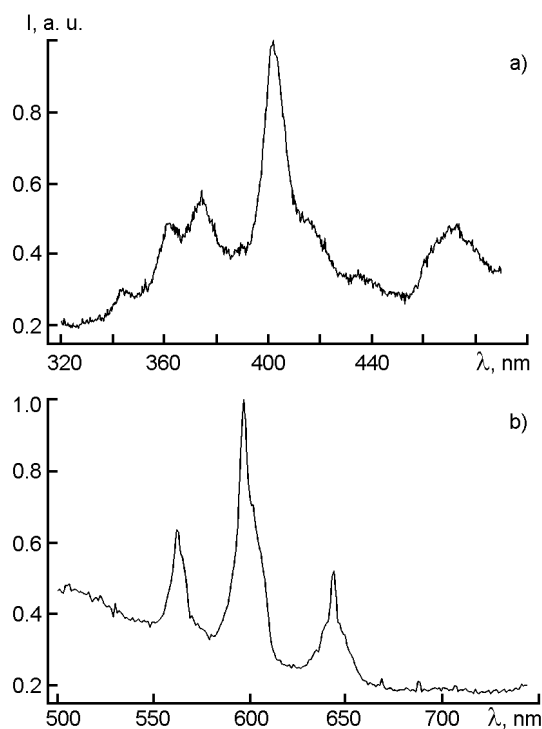


Fig. 4. Luminescence excitation ($\lambda_{lum.} = 597$ nm) (a) and luminescence ($\lambda_{ex.} = 402$ nm) (b) of $\text{FAP}:\text{Sm}^{3+}$ (1 at.%) crystals.

obtained at low temperature, that is evidenced by increased intensity of CaF_2 lines as compared to that of fluorapatite lines. The presence of samarium has been confirmed by X-ray fluorescence and elemental analysis. Samarium has been found to enter the calcium fluorapatite crystal lattice as a substitution impurity and does not initiate the formation of any additional phases. The as-prepared samples have been found to be not luminescent. The annealed samples show a luminescence identified as that of trivalent samarium.

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Вирощування полікристалічного фторапатиту кальцію, активованого Sm^{3+} , з водних розчинів

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Використовуючи метод осадження з водних розчинів отримано полікристалічні зразки $Ca_{10}(PO_4)_6F_2$ (фторапатиту кальцію, ФАП) і ФАП, активованого Sm^{3+} . Оптимальними умовами отримання монофазного полікристалічного допованого та недопованого ФАП є: $pH = 4.7$ і $T = 80^\circ C$. Вивчено вплив фізико-хімічних умов на характеристики отриманих осадів. Отримано спектри люмінесценції та її збудження для зразків ФАП та ФАП, активованого іонами самарію. Отриманий спектр люмінесценції ідентифікується як спектр люмінесценції Sm^{3+} .