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Abstract.   The nanoparticles of hydroxiapatite and fluorapatite doped with Er/Yb and Tm/Yb were synthesized and characterized by FTIR, XRD, SEM and TEM methods. The results of up-conversion luminescence studies were presented for the samples as prepared, annealed at 500°C and at 900-1000 °C. At annealing above 800°C the ceramic state was formed. It is shown that fluorapatite host is more appropriate than hydroxiapatite host for rare ions luminescence and up-conversion processes. The post preparing annealing of nanarticles significantly enhanced the luminescence intensity. The Tm/Yb doped fluorapatite shows intense up-conversion luminescence in 790-800 nm spectral region and is potentially useful for biomedical applications.

1. Introduction

Hydroxiapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAp) and fluorapatite $Ca_{10}(PO_4)_6F_2$ (FAp) are well known biomaterials being the main components of bones and teeth. The synthetic HAp and FAp are bio-compatible materials and are studied mainly due to their biomedical applications, for example as coating material for metallic implants, dental implantology, drug delivery and deep tissue bio-imaging [1-3]. The energy levels and up-conversion luminescence mechanisms of Yb/Er and Yb/Tm ions in a number of hosts were described in details in the review article [3]. HAp and FAp are not mentioned among the typical host materials for up-converion luminescence the. The most studied up-conversion luminescence material is NaYF4:Yb:Er. It is shown in [4] that up-conversion luminescence of NaYF4:Yb:Er is applicable for cancer therapy and imaging.

The rare-earth (RE) doped HAp and FAp are prospective luminescent biomarkers, especially if the high efficiency of up-conversion luminescence in nanoparticles (NP) is be achieved.

However, up to date only few papers are devoted to up-conversion luminescence studies in FAp. In [5] the 543 nm and 654 nm luminescence bands were detected under 980 nm excitation due to up-conversion process of FAp:Yb/Ho. According to our knowledge the data of FAp: Yb/Er and FAp:Yb/Tm up-conversion luminescence are not available.

The FAp:Yb/Tm has a great potential for tissue bio-imaging since the Tm ion has one luminescence band at ~800 nm and it fits well in the window of optical transparency of biological tissues. This indicates the importance of present studies.

The FAp has similar to HAp hexagonal structure with space group *P63/m* [6] with only difference - the fluoride ions substitute OH groups in HAp lattice. The structure has two non equivalent Ca^{2+} positions: Ca(I) and Ca(II). The analysis of luminescence spectra and luminescence decay kinetics of Eu^{3+} doped HAp described in [7] showed that Eu^{3+} can substitute for Ca^{2+} in both non-equivalent sites in HAp.

The presence of residual molecular impurities can distort the symmetry of luminescence center, thus modifying the configuration coordinate and leading to luminescence quenching. Therefore in the present investigation the Fourier Transform Infrared absorption (FTIR) study was caried out for detection of some molecular impurities of as prepared samples and those after thermal treatment. Another possible channel for efficient quenching of luminescence is due to excitations trapping at surface states, followed by non radiative recombination. This channel effciency is NP size dependent.

In the present work the FAp codoped with Er/Yb and Tm/Yb NP were synthesized and characterized. The work is devoted to studies of luminescence processes under x-ray excitation and 980 nm laser line excitation.

2. Experimental

2.1. Sample synthesis and annealing.

The FAp synthesis procedure was performed similar to HAp synthesis described in our previous paper [8]. The starting materials were $(NH_4)_2HPO_4$, $Ca(NO_3)_2 \cdot 4H_2O$, Er_2O_3, Tm_2O_3, Yb_2O_3 and NH_4F. The RE oxides were dissolved in HNO_3 (1:3) and the obtained solutions of nitrate salts were added to $Ca(NO_3)_2 \cdot 4H_2O$ and stirred for 30 min at 80°C. The $(NH_4)_2HPO_4$ and NH_4F solutions were kept at constant pH=10 by adding NH_4OH. The obtained solution was drop-wise added to the solution of nitrate salts during 1h at 80°C. The prepared white suspension was stirred for 3h at 80°C and then cooled to room temperature and aged for 4h. The sediment was filtered through 3 µm membranes filter and washed in deionized water. The FAp powders were dried at 110°C 24h. The activator concentrations were calculated in at% units. For samples doped with Er/Yb and Tm/Yb the concentration of activators was 2 at% of Yb and 1 at% of Er or Tm.

The study was carried out on NP as prepared and after annealing at 500°C or 900°C in air. Above ~800°C the ceramic samples were obtained.

2.2. Experimental equipments.

The FTIR absorption spectra were registered with KBr pellet method using spectrometer Bruker EQUINOX55. The X-ray diffractometer (Bruker AXS D8 Advance) was used for structure identification; grain size was calculated from FWHM according to Scherrer's formula.

The Lyra (Tescan) SEM and Tecnai G20 (FEI) TEM equipments were used for samples morphology testing.

The luminescence was excited with X-rays (30 kV, 10 mA, W-target) through a Be window or with 980 nm laser diode irradiation (optical power 0.78 W). For the luminescence spectra registration the monochromator SHAMROC303 coupled with ANDOR iDUS DU401A-BV CCD camera was used. All experiments were carried out at 300K.

3. Results and discussion

3.1. TEM and SEM

The as prepared HAp and FAp NP consisted of cigar-shaped nanorods with diameters in the range of 30-50 nm and ~200 nm lengths (Fig.1a). After annealing the grains enlarged (Fig.1b), achieving diameters 40 – 60 nm and agglomerated; after sintering at high temperature the porous ceramic was obtained (Fig.1c).
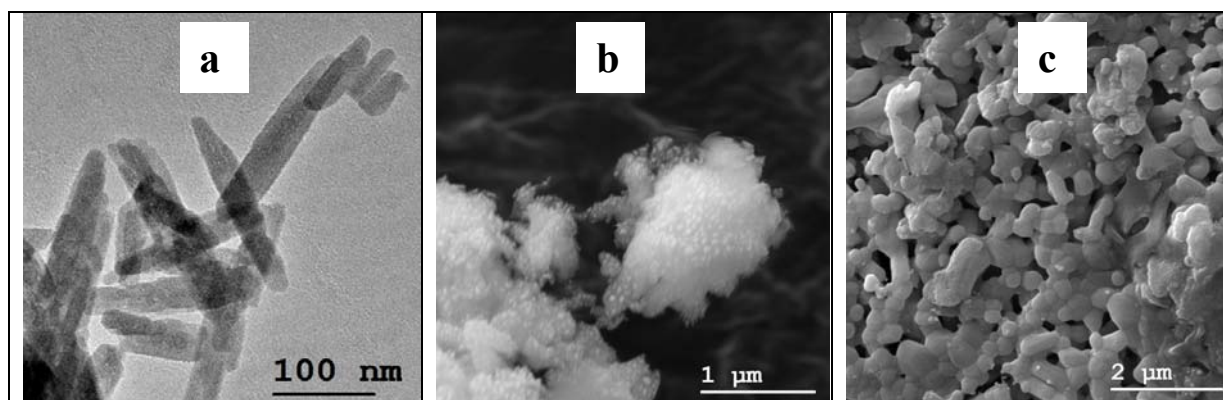
Fig.1. TEM micrograph of the undoped (as prepared) HAp (a), SEM images of FAp:Er/Yb sample annealed at 500 ^{o}C 2h (b) and FAp:Er/Yb ceramic sintered at 1000 ^{o}C 15 h (c).

3.2. XRD.

The HAp and FAP have hexagonal structure (P63/m). The XRD results for as prepared NP were compared with JCPDS cards number 00-009-0432 (HAp) and 00-15-0876 (FAp). Additional phases in RE doped NP were not detected. The grain sizes calculated according to Scherrer's formula are 20-30 nm for as prepared HAp and FAP and ~40-50 nm after 2h calcinations at 500 ^{o}C. These sizes are close to those obtained from TEM and SEM images for the corresponding samples.

3.3. FTIR

The FTIR absorption spectra of the prepared HAp and FAp NP show the absorption peaks associated with stretching and bending modes of the hydroxyl, PO_4^{3-} and carbonate groups [8,9]. The main aim of this study is to analyse the annealing effect on hydroxyl and carbonate group modes in FAp. For the comparison the HAp spectra are shown. The traces of carbonate group bands in as prepared NP were identified according to the [8,10,11]. Fig. 2a and b shows the FTIR spectra for as prepared and annealed HAp and FAp NPs.
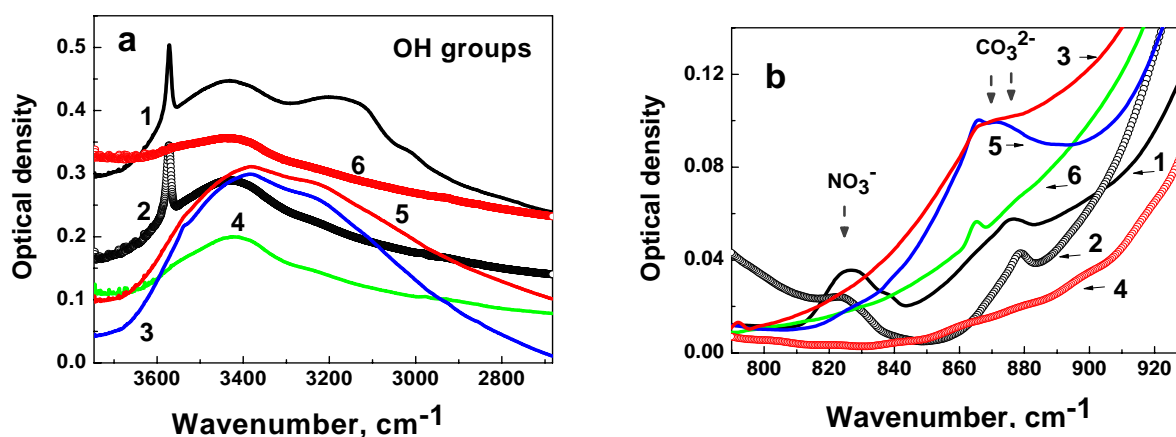

Fig.2. FTIR spectra of HAp and FAp NP in OH stretching (a) and CO_3^{2-} , NO_3^- (b) bending (ν_2) vibration modes region.
(1-HAp as prepared; 2 – HAp annealed at 800 ^{o}C 3h; 3 – FAp as prepared; 4 – FAp annealed at 500 ^{o}C 2h; 5 - FAp:Er/Yb as prepared; 6 - FAp:Er/Yb annealed at 500 ^{o}C 2h).

OH groups. In HAp the well resolved narrow OH band at 3572.8 cm^{-1} is not changing during annealing. The OH groups responsible for this narrow band are the components of HAp chemical composition. The wide bands at 3436.4 and 3170 cm^{-1} are partly reduced during annealing and the OH groups responsible for these bands are located on surface states.

In FAp only the wide OH bands were detected and these OH bands were annealed successfully. It is very important since the OH groups in FAp are the impurity ions and can affect the processes of charge and energy transfer. In FAp samples doped with RE ions the same wide OH bands are detected and annealing processes were observed similarly to undoped FAp.

CO_3^{2-} groups. In HAp NP the band at 878 cm^{-1} due to CO_3^{2-} group is well expressed and the annealing of this band is not efficient up to annealing temperature 800 ^{o}C. The CO_3^{2-} group band in FAp (867 cm^{-1}) is slightly shifted relatively to the peak position in HAp and is efficiently annealed even at 500 ^{0}C (Fig. 2 b).

NO_3^- groups. In HAp, the band at 825 cm^{-1} is due to nitrate ions [12] and this band is noticeably reduced during annealing. In FAp nanopowders this band was not detected even for the as prepared powders.

The molecular ions were incorporated during synthesis as the fragments from reagents or from the surrounding atmosphere. The presence of such ions can affect luminescence characteristics because these molecular ions can both have their own specific luminescence bands and interact with luminescence centers changing the luminescence yield.

3.4. Luminescence

The RE doped HAp and FAp NP are prospective materials as luminescent biomarkers, especially if the up-conversion luminescence is used. The radioluminescence and up-conversion luminescence under excitation in near infra-red spectral region were studied in the as prepared and annealed in air FAp:Er/Yb and FAp:Tm/Yb samples.

Our study of HAp:Er/Yb NP luminescence has revealed that the intensity of luminescence is low even for NP annealed at 900 ^{0}C in air. The reason of luminescence low intensity in RE doped HAp is possibly due to presence of OH$^-$, NO$_3^-$ and CO$_3^-$ groups with high thermal stability. Thus our attention was drawn to FAp samples since in FAp molecular impurities were annealed effectively (Fig. 2a and b) and FAp has a low phonon energy [10-11] – an important characteristic for up-conversion luminescence.
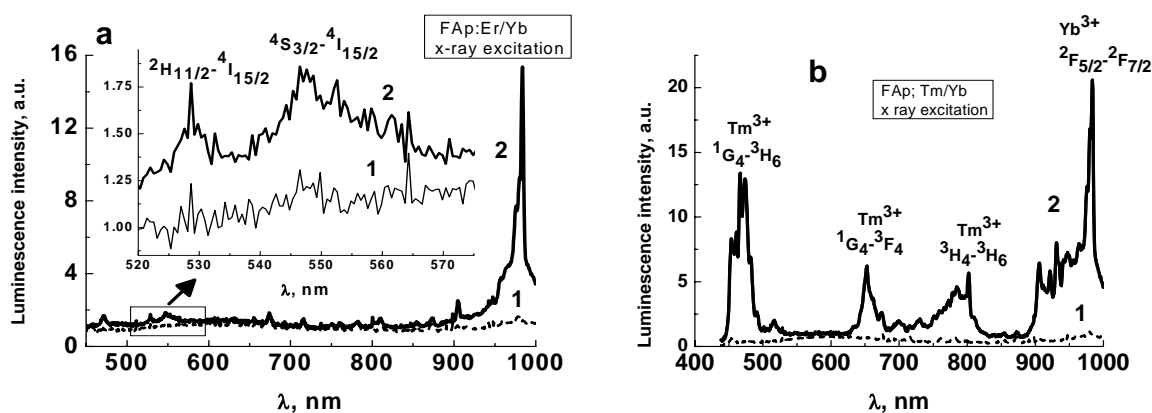

Fig.3. Luminescence spectra under x-ray excitation FAp:Er/Yb (a) and FAp:Tm/Yb (b) NP as prepared (1) and annealed 3h at 900 ^{o}C (2)
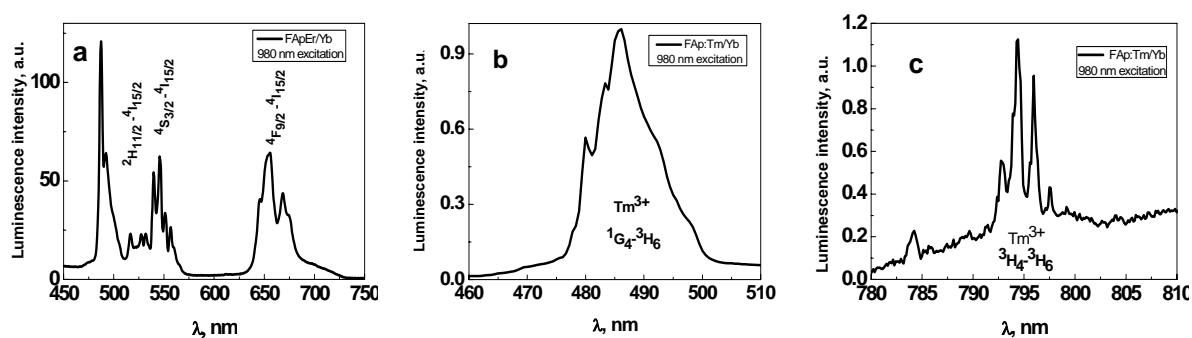
Fig.4. The up-conversion luminescence spectra of FAp:Er/Yb (a) and FAp:Tm/Yb (b,c) annealed 3h at 900°C.

Under X-ray excitation of annealed FAp NP the Yb^{3+} luminescence band (980 nm) is detected along with Er and Tm ion luminescence (Fig.3a and b). The luminescence intensity is negligible in the as prepared NP, but it increases considerably after annealing as well as after sintering (Fig.3a and b).

The up-conversion luminescence spectra of the annealed FAp:Er/Yb samples (Fig.4a) show the Er ion transitions at 525 nm ($^2H_{11/2}$-$^4I_{15/2}$), 545 nm ($^4S_{3/2}$- $^4I_{15/2}$) and 652 nm ($^4F_{9/2}$-$^4I_{15/2}$). The 490 nm band in the up-conversion spectra is the laser diode second harmonic line and is not detected under x-ray excitation. Attention should be drawn to the fact that spectra consist of red-green-blue lines, so white luminescence was obtained in the up-conversion process. This effect is important for new light sources and needs further research.

In FAp:Tm/Yb the ~479-495 nm, ~648 nm and ~795-800 nm luminescence bands are assigned to Tm^{3+} transitions under X-ray excitation. Note that the 648 nm luminescent transition (from $^1G_4$ to $^3F_4$ state) is detected under X-ray excitation and is not observed under 980 nm excitation. The $^3F_4$ state is one of excited states of Tm^{3+} ion involved in the up-conversion process. Therefore it is suggested that in the upconversion process the nonradiative transition from $^3H_5$ state to $^3F_4$ state provides the efficient population of $^3F_4$ state and thus the probability of radiative transition from $^1G_4$ to $^3F_4$ state becomes negligible. The radiative transition from $^3H_4$ state to the $^3H_6$ state is responsible for luminescence within 795 – 800 nm. The more detailed description of the upconversion processes can be found in [3].

The $^3H_4$-$^3H_6$ radiative transition (~800 nm) of Tm^{3+} can be excited with 980 nm laser and is due to energy transfer from Yb^{3+} ion to Tm^{3+} ion in FAp:Tm/Yb. Since this luminescence falls in tissue transparency window, the further studies are important from biological point of view.

4. Conclusions

The single hexagonal crystal structure is confirmed in the as prepared HAp and FAp NP. RE ion doping does not create additional phases. Analysis of FTIR spectra shows that during the post preparing annealing at 500 °C the OH and CO_3^{2-} groups practically disappear in both undoped FAp and RE ions doped FAp.

The FAp NP is more suitable for the observation of RE luminescence and up-conversion processes than HAp NP. Our data of up-conversion luminescence reveal that the post preparing sintering at 900-1000°C of FAp NP significantly enhances the luminescence intensity. The FAP:Tm/Yb provides the intense up-conversion luminescence and potentially

can be used for biomedical applications, especially taking into account that the 800 nm luminescence band ($^3H_4$-$^3H_6$ transition of Tm^{3+} ion) is located close to optical transparency window of biological tissues.

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