Characterization of hydroxyapatite by time-resolved luminescence and FTIR spectroscopy

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Abstract. Time-resolved luminescence and FTIR absorption spectra of undoped and Eu and Ce doped hydroxyapatite nanocrystalline powders prepared by sol-gel method were studied. The luminescence band at 350-400 nm was detected and two decay times (11 ns and 38 ns) was determinated for Ce doped samples. The luminescence spectra and decay kinetics were analized for Eu doped nanopowders. The Eu^{3+} ion was incorporated in different Ca sites. The process of energy transfer to Eu^{3+} excited state ($^5D_0$) was detected from luminescence decay kinetics.

1. Introduction

Hydroxiapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAp) is a biomedical material – component of bone and teeth. During recent years HAp studies became topical in view of material non-toxicity, biocompatibility, important for different clinical and biological applications (drug delivery, implants, in *vivo* imaging etc.) [1]. The HAp doped with rare earth (RE) ions is fluorescent materials prospective for lightening [2]. The HAp can be synthesized a nanopowder by sol-gel, hydrothermal and others methods [3.4]. The luminescence properties of HAp were studied in limited number of papers and mostly contain the Eu^{3+} luminescence studies [1,3, 5]. The time-resolved luminescence is described in limited number of papers.

The HAp has hexagonal structure, space group $P6_3/m$ [6] and two non equivalent Ca^{2+} positions are – Ca(I) and Ca(II). Therefore the rare earth (RE) ions substitute for Ca^{2+} in HAp structure in two non-equal local positions and the RE ions luminescence was used as a local structure probe.

In this paper we will present the results of synthesis of undoped as well as doped with Eu and Ce HAp nanocrystalline powders. The XRD and FTIR studies were carried out for the controlling the structure and vibration spectra of prepared HAp. The luminescence properties - spectra and decay kinetics of HAp nanopowders were measured and analyzed.

2. Experimental

FTIR absorption spectra were recorded using spectrometer Bruker EQUINOX55 with KBr pellet method. The crystalline phases were identified by X-ray difractometer (Bruker AXS D8 Advance).
The luminescence spectra and decay kinetics were measured under YAG:Nd laser (266 nm, 2 ns) excitation.The luminescence was recorded through monohromator with a phonon counting head (HAMAMATSU H8259) and photon counting board FastComTech module P 7887 with 500 channels and minimal time bins 250 ps. The radioluminescence was excited by X-rays (30 kV, 10 mA) through a Be window; the monochromator SHAMROC303 coupled with CCD camera ANDOR iDUS DU401A-BV was used for the spectra registration. All experiments were carried out at 300K.

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3. Results and discussion

3.1.1. Sample synthesis.
The sol-gel (co-precipitation) method was used for undoped and doped with Eu or Ce HAp nanocrystals synthesis. The synthesis was carried out by using the sheme similar to described in [7].

The starting materials was $[(NH_4)_2HPO_4]$, $(CaNO_3)_2 \cdot 4H_2O$ and RE nitrates. The concentration of RE was calculated in at.%. During the reaction the NH_4OH was used to keep constant pH=10. After the reaction and washing in deionised water the powders were dried at 80 ^oC 72 h. All samples were prepared under the same conditions.

3.1.2. XRD difraction.
The XRD was measured to clear up the crystallinity of synthesized powders. Fig.1. shows the XRD patterns of undoped HAp, Ce and Eu doped HAp. The XRD pattern shows only HAp with well-crystallized hexagonal structure (JCPDS Nr.09-0432) and other phases were not found. The grain sizes calculated from XRD patern by Debay-Scherr's formula was 20-25nm.

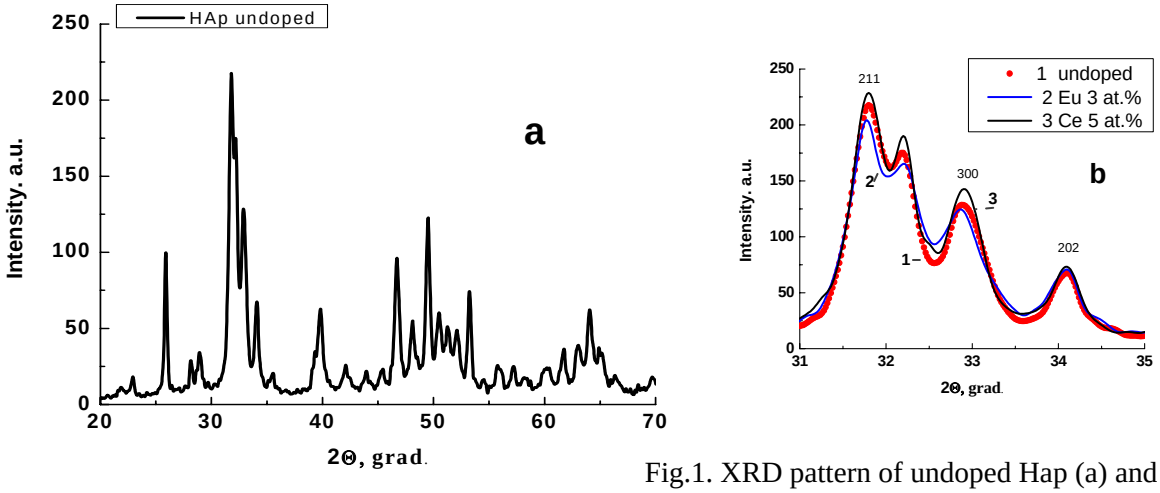

Fig.1. XRD pattern of undoped Hap (a) and doped with 3 at. % Eu and 5 at.% Ce (b)

3.1.3.FTIR
The FTIR absorption spectra of the obtained HAp nanopowders (Fig.2) show the absorption peaks concerned with stretching (ν) and bending modes (δ) of the hydroxyl, PO_4^{3-} and carbonate groups [4,8]. The narrow peak at 3570 cm^{-1} (O-H stretching mode for hydroxil group in regular HAp sites) confirms the synthesis HAp structure [9]. Along with PO_4^{3-} group vibration bands the traces of carbonate group bands [10] were identified (Fig.2).

3.1.4.Luminescence
In prepared undoped HAp sample the wide luminescence band peaking at 420 nm was detected at 300K. The time-resolved eksperiments showed that band consist of two peaks with different decay times (~6.5 ns and ~8.7 ns). The band must be due to two non-equal PO_4^{3-} groups.

In Ce doped samples the luminescence band at 350-400 nm was detected and two decay times (11 ns and 38 ns) was determinated (Fig.3). The decay time 38 ns are close to that observed for Ce^{3+} luminescence in other materials [11]. The two close bands are due to Ce ion ground state splitting to $^5F_{5/2}$ and $^2F_{7/2}$ (splitting 1800 cm^{-1}).

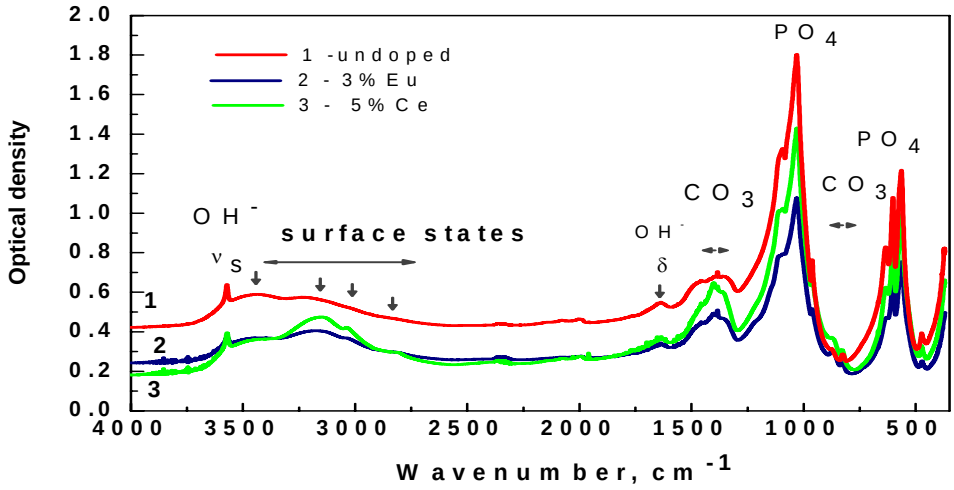

Fig.2.FTIR spectra of HAp nanopowders

Table 1. FTIR absorption peak positions and types of bonds of prepared HAP

Peak position, cm^{-1}	3570	3438 3151 3032	1468 1383 1346	1630	1110 1089 1030	960	873 821	634	602	573 563	472
Marking	ν	ν	ν_3	δ	ν_3	ν_1	δ	δ	ν_4	ν_4	δ
Type of bonds	OH^-	Surface OH^-	CO_3	H_2O	PO_4	PO_4	CO_3	OH^-	P-O	PO_4	O-P-O

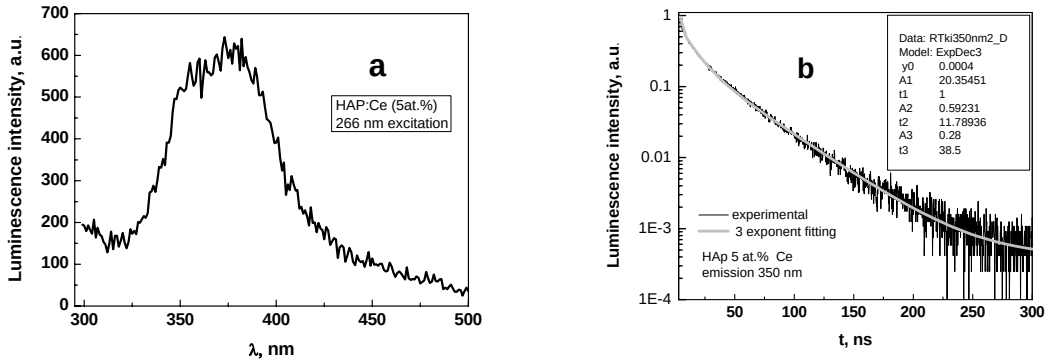

Fig.3. Luminescence spectrum (a) and luminiscence decay kinetic for HAp:Ce nanopowder.

The red luminescence of HAp: Eu is evidence of incorporation of Eu^{3+}. The spectra were recorded under 266 nm laser excitation and under X-ray excitation. The peak positions and the ratio of peak intensities are the same showing that both excitations band-to-band and charge transfer are efficient for Eu doped HAp. The luminescence spectra and luminescence decay kinetic of HAp:Eu nanopowder are presented in Fig.4. The band at 592 nm is characteristic of luminescence center with inversion center (magnetic dipole transition). The band at 619 nm is most intense and it is due to the Eu^{3+} center without inversion symmetry (electrical dipole). Hence the Eu^{3+} ion incorporates in two different sites

in prepared HAp nanopowders. In [5] two sites C_3 and Cs was discussed for the Eu^{3+} incorporation in HAp.

The decay kinetics at 579 nm, 592 nm and 700 nm are close (~1.1 ms at 300K) (Fig.4b). The decay time of 619 nm band is ~540 μs that shows the different site symmetries of incorporatyed Eu^{3+} ions.

The rising front of the luminescence kinetics was detected for 592 nm, 619 nm and 700 nm bands. This behavior is related to energy transfer process during the excited state ($^5D_0$) formation.

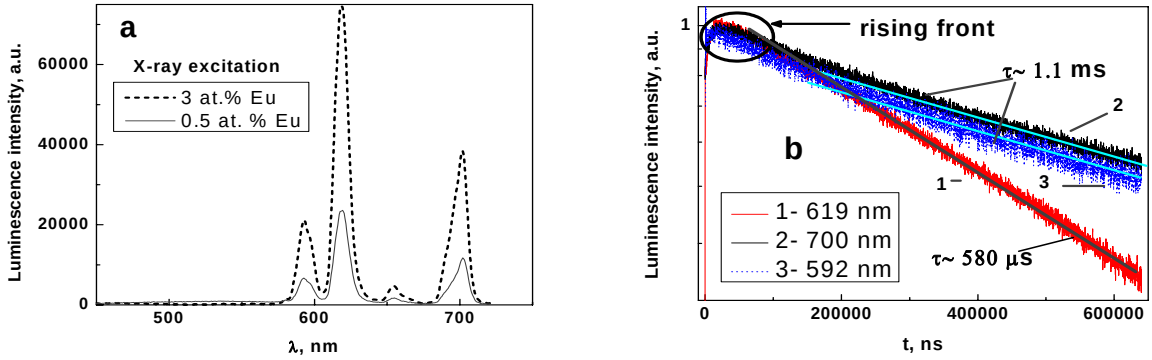

Fig.4. Luminescence spectra (a) and decay kinetics (b) of HAp:Eu nanopowders.

4. Conclusions

The analysis of XRD and FTIR absorption confirm the synthesis hexagonal HAp structure and the vibration spectrum did not showed traces of additiomal molecular impurities. The luminescence band peaking at 420 nm in undoped HAp nanopowders consist of two sub-bands with decay times τ_1 ~ 6.5 ns and τ_2~8.7 ns. We suggest that this luminescence is due to two different PO_4 groups in HAp structure. The Eu^{3+} luminescence spectra and decay kinetics were analyzed. It is shown that the mechanism of exited state ($^5D_0$) formation is complicate and includes the energy transfer process. The Eu^{3+} incorporates in Ca(I) position with C_3 site symmetry and in Ca(II) position with C_s symmetry.

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