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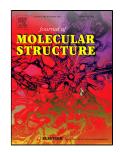
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### Europium concentration effect on characteristics and luminescent properties of hydroxyapatite nanocrystalline powders

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#### Abstract

Series of Eu-apatites were synthesized by precipitation from aqueous solutions with the Eu/Ca atomic ratio from 0.5% to 5% at T = 90 °C. Resulting precipitates were studied using different experimental techniques including X-ray powder diffraction, infrared and raman spectroscopy, scanning electron microscopy, EDX and photoluminescent spectroscopy.

Eu-doped Ca-deficit nanosized non-stoichiometric hydroxyapatite with high water content has been obtained throughout the experiment. Europium content in the synthesized apatites reaches 0.24 apfu (Eu/Ca = 2.5%). Relations between Eu content is the solution and precipitate have been established. It was shown that Eu-monacite starts to precipitate as secondary phase at Eu/Ca ratio in starting solution 1% or higher. Maximum luminescence is observed in apatite with ~2% Eu/Ca ratio (which equals to ~0.2 apfu and corresponds to 3% Eu/Ca ratio in the starting solution). As an important and brand-new result, apatite with 2% Eu/Ca ratio can be considered as the most appropriate material for the producing biolabels for luminescent research in medicine and biology.

#### Introduction

Apatite is the main mineral component of the bone and tooth tissue<sup>1–3</sup>. Because of this fact apatite is highly biocompatible and therefore the most important object of interest in the field of the bone-engineering<sup>4–6</sup>. For example, apatite is utilized as biological active coating for metal implants<sup>7</sup> and in prosthetics<sup>8</sup>. Apatite also can be used as the mean of the drug delivery<sup>9</sup> or for simultaneously release of multi drugs into the organism<sup>10,11</sup>.

One of the approaches to the improving of the apatite-based materials for medical purposes is the doping apatite with specific ions to impart new properties to it. Apatite structure is surprisingly tolerate to the multiple ionic substitutions in all crystallographic positions<sup>1,2,12</sup>, therefore revealing many possible ways for obtaining new apatite-based materials with different desired properties granted by specific dopants<sup>7,13–15</sup>.

Doping apatites with the rare-earth elements (REE) grants them various luminescent properties<sup>16–18</sup>, which allows to use such doped apatites as luminescent labels for biological and medical research<sup>19–21</sup>. Natural apatites can contain significant amounts of REEs (up to 1.26 atoms per unit cell), with light REE (from La to Sm) preferring Ca(2) crystallographic site<sup>22</sup>.

Present research is focused, however, on the synthetic Eu-doped apatites. Among other REEs Eu possesses several properties beneficial for the material engineering.

First,  $Eu^{3+}$  ions have strong red emission upon visible radiation and non-degenerated excited level <sup>5</sup>D<sub>0</sub> which facilitates interpretation of luminescence spectra.  $Eu^{3+}$  ions are also well-known as structural probes due to the presence of hypersensitive transitions<sup>23,24</sup>. Second, doping apatites with Eu increases their biocompatibility<sup>25,26</sup> and grants antibacterial properties to it<sup>16,27</sup>.

Existing researches devoted to the Eu-bearing apatites, however, don't reveal the concentration maximum of luminescence of the Eu-doped apatite and don't provide deep insight into the apatite properties in wide range of doping concentrations<sup>16,28–34</sup>.

Main goal of our study was to determine the dependence between the luminescent properties of

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