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Effects of crystalline growth on structural and luminescence properties of \( \text{Ca}_{(10-3x)}\text{Eu}_{2x}(\text{PO}_4)_6\text{F}_2 \) nanoparticles fabricated by using microwave driven hydrothermal process

Katarzyna Zawisza\(^1\)*, Paulina Sobierajska\(^1\), Guillaume Renaudin\(^2\), Jean-Marie Nedelec\(^2\) and Rafal J. Wiglus\(^z\)*

\(^1\)Institute of Low Temperature and Structure Research, PAS, Okolna 2, 50-422 Wroclaw
\(^2\)Université Clermont Auvergne, CNRS, SIGMA Clermont, ICCF, F-63000 Clermont-Ferrand, France

*Corresponding author: R.Wiglus@int.pan.wroc.pl and K.Zawisza@int.pan.wroc.pl

The \( \text{Eu}^{3+} \) doped fluorapatite nanopowders were synthesized by microwave assisted hydrothermal technique and annealed in the 500 – 1000°C temperature range for 3 h.
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Rafal J. Wiglusz$^1$

$^1$Institute of Low Temperature and Structure Research, PAS, Okolna 2, 50-422 Wroclaw
$^2$Université Clermont Auvergne, CNRS, SIGMA Clermont, ICCF, F-63000 Clermont-Ferrand, France

Abstract

The $\text{Eu}^{3+}$ doped fluorapatite nanopowders were synthesized by microwave assisted 
hydrothermal technique and annealed in the 500 – 1000°C temperature range for 3 h. The europium 
ions concentration was determined to be in the 0.5 – 10 mol% concentration range. The morphology 
and structural properties of $\text{Ca}_{(10-3x)}\text{Eu}_{2x}(\text{PO}_4)_6\text{F}_2$ were determined by using TEM (Transmission 
Electron Microscopy), XRPD (X-Ray Powder Diffraction) techniques as well as the IR (Infrared) and 
Raman spectroscopy. The average nanoparticle sizes were calculated by Rietveld refinement being in 
the range from 30 nm for as-prepared samples to above 100 nm for materials thermally treated at 
1000°C. The particles have grown up in rectangular prism nanorods. The spectroscopic properties of 
obtained materials were observed to be dependent on the dopant concentration and annealing 
temperature and were studied in details. The Judd-Ofelt theory was applied and correlated with 
structural and optical properties to get detailed insight into fluorapatite structures.

Keywords: calcium fluorapatite, europium doping, photoluminescence, spectroscopy, luminescence, 
europium ions, phosphate, nanocrystalline apatite, nanopowder

*Corresponding author:
E-mail: R.Wiglusz@int.pan.wroc.pl and K.Zawisza@int.pan.wroc.pl
Phone: +48-71-395-41-59
Fax: +48-71-344-10-29
Homepage address www.intibs.pl
1. Introduction

The apatite is a large family of compounds widespread in nature. The most ideal representative of it is calcium hydroxyapatite (Ca$_{10}$ (PO$_4$)$_6$(OH)$_2$ – hereafter CaHAp), which can be easily substituted by different ions$^{1}$. Nowadays apatites are extensively applied in many industrial fields as catalysts, laser hosts, luminescent materials, gas sensors, ionic conductors and adsorbants$^{2-5}$. Additionally, these calcium phosphates play an important role as a material for biological applications due to their excellent biological properties. Synthetic apatites are highly similar to biological inorganic matrix of hard tissues in vertebrates and they are characterized by good biocompatibility, osteoconductivity, non-toxicity, non-immunogenicity and bioactivity as the ability to induce the formation of a direct chemical bond with living tissues$^{1,6,7}$. An innovative approach in advanced biomaterials is focused on substances containing elements that are integral components of living system. Since, calcium and phosphorus are main constituents of hard tissue, the calcium phosphate family has caught the attention as fundamental compounds for this goal. According to these numerous advantages this material is widely used and implanted to repair damaged bones and as teeth and bones fillers$^{8,9}$.

It is expected that the presence of fluorine ions in the apatite structure is enhancing the physical and biological properties comparatively to hydroxyapatite$^8$. Synthetic fluorapatite (Ca$_{10}$ (PO$_4$)$_6$F$_2$ – hereafter CaFAp) is harder, stiffer, possesses better chemical and thermal stability, higher acid resistance, lower solubility in water compared to CaHAp$^{10}$. It is known that fluorine ions release from CaFAp could lead to inhibition of bacteria metabolism$^{11}$. According to this, F$^-$ ions prevent and control dental caries, stimulate bone cells proliferation and differentiation$^{12}$. Furthermore, this essential microelement is necessary for the normal dental and bone formation in living systems$^{13,14}$. In response to the consumption of fluorinated water CaFAp is formed on the outer layer of the tooth$^{15}$. In vitro studies have confirmed biocompatibility of calcium fluorapatite and have shown release of F$^-$ ions in a controlled rate. Moreover, it has been demonstrated that it exhibits integration with hard tissue and longer resorption time that ordinary CaHAp$^{12,13,15}$. Due to these advantages fluorapatite is considered as a biological material and as a fluorescence bioprobe for bio-imaging and biosensing.
Fluorapatite crystallizes in hexagonal space group \( P6_3/m \) (No. 176) with unit cell formula \( \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \), which contains ten calcium cations in two nonequivalent sites. There are four \( \text{Ca}(1) \) ions with nine-fold \( C_3 \) symmetry (Wyckoff position 4f, coordinates \([1/3,2/3,z]\)), each surrounded by nine oxygen atoms, and six \( \text{Ca}(2) \) ions with seven-fold \( C_5 \) symmetry (Wyckoff position 6h, coordinates \([x,y,1/4]\)), each coordinated by six oxygen atoms and one fluoride atom. Rare earth ions can locate in both calcium sites depending on local charge compensation\(^{16,17} \). The \( F^- \) ion has smaller size (1.28 Å) than \( \text{OH}^- \) (1.37 Å) hence fluorine ions pack closely which results in smaller cell volume\(^{10} \). The success of rare-earth doping is expected in view of similarity in ionic radius of lanthanide ions and calcium ion and high affinity to \( \text{PO}_4^{3-} \). Moreover, it is important to note that substitution of \( \text{OH}^- \) groups by \( F^- \) ions could contribute to the enhancement of luminescence efficiency\(^{18} \). The presence of \( \text{OH}^- \) groups in matrix leads to strong non-radiative energy migration caused by coupling between lanthanide ions and \( \text{OH}^- \) vibrations\(^{19} \). Materials containing fluorine ions are characterized by low phonon energy\(^{18} \).

The optical properties of the fluorapatites doped with rare earth ions such as \( \text{Nd}^{3+} \), \( \text{Pr}^{3+} \), \( \text{Tm}^{3+} \), \( \text{Eu}^{3+} \), \( \text{Yb}^{3+} / \text{Ho}^{3+} \), \( \text{Er}^{3+} / \text{Yb}^{3+} \) have been studied. These investigation were concerning mostly polycrystalline powders and single crystals as phosphors and laser hosts.

2. Experimental

2.1. Synthesis of \( \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2: \text{Eu}^{3+} \) nanoparticles

The nanocrystalline powders of fluorapatite doped with \( \text{Eu}^{3+} \) ions were prepared by microwave stimulated hydrothermal method. Concentration of the europium(III) ions has been set to 0.5, 1, 2, 3, 5, 10 mol\% in proportion to the overall molar content of \( \text{Ca}^{2+} \) ions. As starting substrates have been used analytical grade of \( \text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O} \) (99+% Acros Organics), \( \text{NH}_4\text{H}_2\text{PO}_4 \) (99.995% Alfa Aesar), \( \text{NH}_4\text{F} \) (98% Alfa Aesar), \( \text{Eu}_2\text{O}_3 \) (99.99% Alfa Aesar) and \( \text{NH}_3\cdot\text{H}_2\text{O} \) (99% Avantor Poland) for pH adjustment. At first, the stoichiometric amounts of \( \text{Eu}_2\text{O}_3 \) were digested in an excess of the \( \text{HNO}_3 \) (ultrapure Avantor Poland) to obtain water soluble nitrates and then europium(III) nitrates were re-crystalized three times. Subsequently, calcium nitrate was dissolved in deionized water together with europium nitrate. The suitable amount of ammonium phosphate dibasic and then ammonium fluoride were added to the mixture leading to fast precipitation of the by-product. The pH of the
dispersion was modulated to 10 by adding ammonia, transferred into the Teflon vessel and set in the microwave reactor (ERTEC MV 02-02). After 90 min of the microwave stimulated hydrothermal processing at 280°C and under autogenous pressure of 60 atm., a nanocrystalline powder was obtained. Powder was washed with de-ionized water several times and dried at 70°C for 24 h in order to get the final product. In order to receive well-crystallized product and get rid of residual amorphous phase thermal treatment in the temperature range of 500-1000°C was applied.

2.2. Characterization

The X-ray powder diffraction (XPRD) patterns were measured in the 3-120° 2θ range by using an X'Pert Pro PANalytical X-ray diffractometer equipped with Ni-filtered Cu Kα₁ radiation (Kα₁ = 1.54060 Å, V = 40 kV, I = 30 mA). The experimental XRD patterns were compared with the standard from Inorganic Crystal Structure Database (ICSD) and analyzed. The microstructure and morphology of synthesized nanofluorapatites were investigated by High Resolution Transmission Electron Microscopy (HRTEM) using Philips CM-20 SuperTwin microscope, operating at 200 kV. Specimen for HRTEM was set up by dispersing a small amount of sample in methanol and putting a droplet of the suspension on a copper microscope grid covered with perforated carbon.

The IR measurements were performed at 295 K in KBr pellets using the FT-IR Biorad 575C spectrometer in the range of 3800-400 cm⁻¹. Raman spectra were measured using a Bruker FT 100/S spectrometer with YAG:Nd laser excitation (1064 nm). Both IR and Raman spectra were recorded with a spectral resolution of 2 cm⁻¹.

The Rietveld refinements of X-ray powder patterns were performed for each sample with the program FullProf.2k and Maud 2.68 software. The used procedure (both data-collection and refinement strategy) corresponded to the general guidelines for structure refinement using the Rietveld method (whole-profile) formulated by the International Union of Crystallography Commission on Powder Diffraction. The initial structural parameters of fluorapatite, Ca₁₀(PO₄)₆F₂, were taken from: space group P6₃/m, Z = 1, a = 9.363 Å and c = 6.878 Å, 7 independent atomic positions: two Ca positions in sites 4f (z = 0.0012) and 6h (x = 0.2415, y = 0.0071), one P position in site 6h (x = 0.3982, y = 0.3689), and three O positions in sites 6h (x = 0.3268, y = 0.4850 and x = 0.5881, y = 0.4668), 12i (x = 0.3415, y = 0.2569, z = 0.0704) and one F position in site 2a. Eu³⁺ cations were allowed to substitute Ca²⁺
cation in the two Ca(1) and Ca(2) calcium sites by considering the following vacancy mechanism:

\[ 3Ca^{2+} \rightarrow 2Eu^{3+} + \square \]  

(1)

The initial structural parameters of europium phosphate phases were taken from literature for EuPO$_4$ monazite$^{34}$ and for Eu$_3$PO$_7$ (isostructural to Nd$_3$PO$_7$)$^{35}$.

The excitation spectra were measured using FLS980 Fluorescence Spectrometer from Edinburgh Instruments equipped with 450 W Xenon lamp. The excitation of 300 mm focal length monochromator was in Czerny-Turner configuration. The excitation arm was supplied with holographic grating of 1800 lines/mm grating blazed at 250 nm. The luminescence spectra were recorded using Jobin-Yvon THR1000 monochromator equipped with Hamamatsu R928 photomultiplier and 1200 lines/mm grating blazed at 500 nm. As an excitation source the third harmonic of a pulsed YAG:Nd laser ($\lambda_{exc} = 266$ nm) was used. The spectral resolution was 0.1 nm. All the emission and excitation spectra were respectively corrected to the detector sensitivity and excitation source intensity.

The luminescence kinetics measurements were performed using Jobin-Yvon THR1000 monochromator equipped with R928 Hamamatsu photomultiplier using as the excitation source pulsed YAG:Nd laser (3$^{rd}$ harmonic, \( \lambda_{exc} = 266 \) nm). The decay profiles were collected using a LeCroy WaveSurfer 400 MHz oscilloscope. The decay curve fitting was performed with the help of Origin 9.1 software.

3. Results and Discussion

3.1. Structure and morphology analysis

The formation of the Ca$_{(10-3x)}$Eu$_{2x}$(PO$_4$)$_6$F$_2$ nanocrystals doped with 2x Eu$^{3+}$ ions (where 2x = 0.5, 1, 2, 3, 5, 10 mol%) were observed by the XRD measurement as a function of optical ions concentration and annealing temperatures 600°, 800° and 1000°C (see Figures 1 and s1). All materials synthesised by hydrothermal procedure presented detectable crystallinity at entire range of applied post-heat treatment temperatures (as-synthesised – 1000°C/3h).

As can be seen, pure hexagonal phases corresponding to the reference standard of the Ca$_{10}$(PO$_4$)$_6$F$_2$ (ICSD – 9444$^{33}$) are observed for samples doped up to 3 mol% of Eu$^{3+}$ ions and annealed up to 900°C. Above terminal concentration of 3 mol%, one can observed phases separation due to the limited solubility of europium(III) ions in fluorapatite and appearance of extra EuPO$_4$ at around 2θ = 29°. Above post-heat treatment temperature of 900°C, it is
observed an occurrence of additional $\text{Ca}_3(\text{PO}_4)_2$ phase due to escaping of fluorine ions and dehydration process of fluorapatite. All samples heat-treated at 1000°C contained $\text{Ca}_3(\text{PO}_4)_2$ phase.

![X-ray powder diffraction patterns](image)

**Figure 1.** X-ray powder diffraction patterns of the $\text{Ca}_{10-3x}\text{Eu}_{2x}(\text{PO}_4)_6\text{F}_2$ annealed at 600°C/3h depending on optical ions concentration (upper) and the $\text{Ca}_{9.85}\text{Eu}_{0.1}(\text{PO}_4)_6\text{F}_2$ depending on annealed temperature.

The quality of structural Rietveld refinement was checked by $R$-values to detect the consistency with a hexagonal structure. However, a difference in the observed and
calculated patterns is the best method to evaluate the Rietveld refinement. Moreover, other parameters with additional functions were applied to find a structural refinement with better quality and reliability. As can be seen, Figure 2 shows a good agreement between the observed XRD pattern and the theoretical fit calculation for Ca$_{9.85}$Eu$_{0.1}$(PO$_4$)$_6$F$_2$ obtained at 500°C which implicate the success of the Rietveld refinement method as displayed by the small differences of the $(Y_{\text{Obs}} - Y_{\text{Calc}})$ intensity. The base lines during this method were used. The projection of the unit cell with the indication of the coordination polyhedra are presented in Figure 3 whereas results of calculations are given in Table 1.

Table 1. Unit cell parameters ($a$, $c$), cell volume ($V$), grain size as well as refine factor ($R_w$) for the Ca$_{10-3x}$Eu$_{2x}$(PO$_4$)$_6$F$_2$ prepared at different temperatures calculated by Maud 2.68 software.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>size [nm]</th>
<th>$R_w$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>single crystal$^{ab}$</td>
<td>9.480(0)</td>
<td>6.900(0)</td>
<td>537.02(7)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5%</td>
<td>9.388(4)</td>
<td>6.895(1)</td>
<td>526.32(5)</td>
<td>41.15</td>
<td>2.0</td>
</tr>
<tr>
<td>1%</td>
<td>9.374(8)</td>
<td>6.886(1)</td>
<td>524.11(7)</td>
<td>36.51</td>
<td>1.7</td>
</tr>
<tr>
<td>2%</td>
<td>9.377(9)</td>
<td>6.888(0)</td>
<td>524.60(8)</td>
<td>30.86</td>
<td>1.5</td>
</tr>
<tr>
<td>3%</td>
<td>9.386(0)</td>
<td>6.892(0)</td>
<td>525.82(0)</td>
<td>27.23</td>
<td>1.4</td>
</tr>
<tr>
<td>800°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5%</td>
<td>9.366(3)</td>
<td>6.878(4)</td>
<td>522.58(2)</td>
<td>67.23</td>
<td>2.1</td>
</tr>
<tr>
<td>1%</td>
<td>9.352(5)</td>
<td>6.870(3)</td>
<td>520.42(9)</td>
<td>47.94</td>
<td>2.5</td>
</tr>
<tr>
<td>2%</td>
<td>9.364(5)</td>
<td>6.877(9)</td>
<td>522.34(3)</td>
<td>50.00</td>
<td>3.0</td>
</tr>
<tr>
<td>3%</td>
<td>9.356(4)</td>
<td>6.871(3)</td>
<td>520.93(9)</td>
<td>44.39</td>
<td>2.8</td>
</tr>
<tr>
<td>1000°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5%</td>
<td>9.363(0)</td>
<td>6.873(1)</td>
<td>521.81(1)</td>
<td>168.39</td>
<td>2.9</td>
</tr>
<tr>
<td>1%</td>
<td>9.368(2)</td>
<td>6.878(4)</td>
<td>522.79(4)</td>
<td>146.65</td>
<td>3.2</td>
</tr>
<tr>
<td>2%</td>
<td>9.347(7)</td>
<td>6.866(0)</td>
<td>519.57(0)</td>
<td>118.91</td>
<td>3.1</td>
</tr>
<tr>
<td>3%</td>
<td>9.363(1)</td>
<td>6.875(0)</td>
<td>521.96(6)</td>
<td>138.78</td>
<td>3.0</td>
</tr>
<tr>
<td>as-prepared</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500°</td>
<td>9.381(6)</td>
<td>6.887(3)</td>
<td>524.97(0)</td>
<td>32.70</td>
<td>1.9</td>
</tr>
<tr>
<td>600°</td>
<td>9.375(8)</td>
<td>6.886(3)</td>
<td>524.24(4)</td>
<td>35.65</td>
<td>2.1</td>
</tr>
<tr>
<td>700°</td>
<td>9.374(8)</td>
<td>6.886(1)</td>
<td>524.11(7)</td>
<td>36.51</td>
<td>1.7</td>
</tr>
<tr>
<td>800°</td>
<td>9.363(8)</td>
<td>6.878(2)</td>
<td>522.28(8)</td>
<td>39.38</td>
<td>2.2</td>
</tr>
<tr>
<td>900°</td>
<td>9.361(0)</td>
<td>6.874(3)</td>
<td>521.67(9)</td>
<td>89.39</td>
<td>2.8</td>
</tr>
<tr>
<td>1000°</td>
<td>9.368(2)</td>
<td>6.878(4)</td>
<td>522.79(4)</td>
<td>146.65</td>
<td>3.2</td>
</tr>
</tbody>
</table>
The general trend has been observed that all unit cell parameters decrease with an increase in the annealing temperature or otherwise, with an increase in the particle size. Lower unit cell parameters were observed for all nanopowders compared to the Ca$_{10}$(PO$_4$)$_6$F$_2$ single crystal, as a result of the so-called particle size effect. The totally refined amount of europium, considering the substituted ions into the CaFAp and the Eu$^{3+}$ ions from additional europium phosphates, is closely correlated to the europium amount incorporated into the matrix during the synthesis. Two samples were slightly deviating from the targeted values of Eu$^{3+}$ ions concentration: 2x = 3% and 2x = 2% for the thermal treatment at 800°C (see Figure s2). The lack of refined Eu$^{3+}$ ions amount could be attributed to a small amount of EuPO$_4$ phase (less than 1 wt % of monazite would be enough to reach the targeted value). Up to 2x = 2%, samples are single phase whatever the temperature of the heat treatment. For 2x = 3%, samples are still single phase except for the higher thermal temperature of 1000°C. For higher 2x values 5% and 10%, all samples contain monazite as secondary phase (between 3 and 10 weight percent, see Figure s3). And for the 2x = 10% sample heat treated at 1000°C a third Eu$_3$PO$_7$ phase is also present. Clearly, these observations indicate that: 1/ the calcium to europium substitution is limited to a maximal value around 4% in CaFAp, 2/ the higher is the thermal treatment, the lower is this substitution level. The unit cell volume is not so much affected by the calcium to europium substitution. Nevertheless, the general trend can be extracted from the unit cell volume variation associated to the thermal treatment: the first moderate heat treatment at 500°C induces shrinkage of the unit cell volume and the following 800°C and 1000°C heat treatment show an increase of the unit cell volume. A heat treatment of 1000°C is needed to exceed the level observed for the as-prepared samples. The a lattice parameter evolutions are similar to those of the unit cell volume. The c lattice parameter evolutions are somehow different: the c lattice parameter is slightly decreasing with increasing in heat treatment temperature, and the Eu$^{3+}$ ions substitution is becoming dependent on heat treatment: the higher is the calcium to europium substitution, the smaller is the c lattice parameter after heat treatment (see Table 1). This observation seems to indicate that the location of the Eu$^{3+}$ ions (either Ca(1) or Ca(2) site) is temperature dependent. For comparison, the following ionic radii can be found: Ca$^{2+}$ 1.06 Å and Eu$^{3+}$ 1.01 Å for a seven-fold coordination (Ca(2) site), and Ca$^{2+}$ 1.18 Å and Eu$^{3+}$ 1.12 Å for a nine-fold coordination (Ca(1) site$^{37}$). So the Eu$^{3+}$ ion is slightly smaller than Ca$^{2+}$ cation. The x refined values for the as-prepared series are in very good agreement with the targeted 2x % values.
With increasing the heat treatment temperature, the $x$ refined values are decreasing for two reasons: 1/ because less europium cations are located into the CaFAp structure and 2/ because of the increasing amount of the secondary monazite phase. The two calcium sites behave differently with the heat treatment. The as-prepared samples present europium cation in both the Ca(1) and Ca(2) calcium site in an almost equivalent proportion (see Figure s5). The increase in the heat treatment induces the progressive departure of Eu$^{3+}$ from the Ca(1) site; the latter is free of substitution for the 1000°C series. On the other hand, the Eu$^{3+}$ substitution level in the Ca(2) site is not temperature dependant. The doping-emptying of the Ca(1) site explains the decrease of the $x$ refined value with the increase of temperature. The different behaviour of the two Ca(1) and Ca(2) sites can be attributed to the two dense and low-density columns in the CaFAp structure. Dense columns are built around the Ca(1) sites in a relatively rigid organisation. Contrary, the low-density columns are built around the Ca(2) sites and they are more flexible because of the presence of fluoride anions in the Ca$^{2+}$ neighbouring. The F$^-$ location can be shifted (well-known in the case of hydroxyl anion in CaHAp structure) to accommodate the slight ionic radius difference between Ca$^{2+}$ and Eu$^{3+}$. Three observations can be made on the variation of the coherent domain size:

- For the undoped samples, the coherent domain size is directly related to the thermal treatment. An increase of crystallinity is observed for an increase in the treatment temperature.
- The Eu-doping affects strongly the crystallinity of the sample. The coherent domain size sharply decreases as soon as small amount of europium is present.
- For the Eu$^{3+}$-doped samples, only the 1000°C treatment allows to induce an increase of the coherent domain size. The three as-prepared, 500°C and 800°C series show quite similar coherent domain size.

The projection of the fluorapatite unit cells, the coordination polyhedra of Ca$^{2+}$ cations and coordination polyhedra of fluorine ions are shown in Figure 3.
Figure 2. Representative result of the Rietveld analysis for the Ca$_{9.85}$Eu$_{0.1}$(PO$_4$)$_6$F$_2$ obtained at 500°C (red – fitted diffraction; blue – differential pattern, column – reference phase peak position).

Figure 3. Projection of the Ca$_{10}$(PO$_4$)$_6$F$_2$ unit cell with indication of the Ca(1) and Ca(2) as well as the closest crystallographic surrounding of F$^{-}$ anion (polyhedra and connectivity).
3.1.1. Calcium sites description

The calcium atoms are aligned along the hexagonal axis (forming dense column with the Ca(1) site and sparser column with the Ca(2) site) and are surrounded by phosphate groups \(6 \text{ PO}_4\) around Ca(1) and \(5 \text{ PO}_4\) around Ca(2)) forming channels in which are located the fluoride anions. All phosphates are equivalents (1 single P site) and oxygen atoms are described by three positions (O(1), O(2) and O(3)). The Ca(1) site is 9-fold coordinated: 3 \text{ PO}_4\) approaching an edge (2 oxygen atoms) and 3 \text{ PO}_4\) approaching a corner (1 single oxygen atom). The Ca(2) site is 7-fold coordinated (pseudo pentagonal based bipyramid): 1 \text{ PO}_4\) approaching an edge, 4 \text{ PO}_4\) approaching a corner and one fluoride neighbouring anion. The presence of the fluoride anion (which can move quite easily along the hexagonal axis) brings flexibility to this Ca(2) site which can accommodate more easily a cationic substitution mechanism.

3.1.2. IR and Raman spectra

The infrared spectra were recorded for the Ca\(_{9.85}\)Eu\(_{0.1}\)(PO\(_4\))\(_6\)F\(_2\) heat treated at 600°, 800°, 1000°C and the Raman spectra were recorded for the Ca\(_{10-3x}\)Eu\(_{2x}\)(PO\(_4\))\(_6\)F\(_2\), where \(2x = 0.5, 1, 2, 3\) mol% of Eu\(^{3+}\) ions, to analyse in detail structural properties of synthesised materials. The results are shown in Figures 4 and 5. In the IR spectra, characteristic active vibrational transitions of the \text{PO}_4\(^{3-}\) groups are clearly visible: the doubly degenerated \(v_2\) bending at 473 cm\(^{-1}\), the triply degenerated \(v_4\) vibration at 562.1 and 598.3 cm\(^{-1}\), the \(v_1\) non-degenerated symmetric stretching at 963.7 cm\(^{-1}\), the triply degenerated antisymmetric stretching at 1018.7 and 1092.5 cm\(^{-1}\). The peaks connected with vibration transitions of OH\(^-\) groups at about 3500 cm\(^{-1}\) and 630 cm\(^{-1}\) are not observed. Moreover, additional peak at 745.7 cm\(^{-1}\) was observed that could be assigned to the F-OH-F configuration and may be transferred by one to another with relatively low energy\(^{12}\). A small difference in location between particular peaks are noticeable which could be related with fluoride ions departure from fluorapatite structure after increasing the annealing temperature and therefore, with changes in internal structure of obtained materials. The Raman spectra consist of three overlapping peaks located at 1052.7, 1042.1 and 1034.4 cm\(^{-1}\) connected with asymmetric stretching \((v_3)\) of the PO\(_4\)^{3-} group\(^{38}\). These peaks are located at almost the same Raman shift which indicate that europium(III) ions concentration does not affected strongly the fluorapatite structure.
**Figure 4.** IR spectra of the $\text{Ca}_{9.85}\text{Eu}_{0.1}(\text{PO}_4)_6\text{F}_2$ prepared by microwave assisted hydrothermal synthesis and heat-treated at different temperatures.

**Figure 5.** Raman spectra of the $\text{Ca}_{(10-3x)}\text{Eu}_{2x}(\text{PO}_4)_6\text{F}_2$ prepared by microwave assisted hydrothermal synthesis and heat-treated at 600°C/3h.
The morphology of the calcium fluorapatite doped with 1 mol% of Eu$^{3+}$ and heat treated at 500°C was studied via TEM and Selected Area Electron Diffraction (SAED) techniques. As can be seen in Figure 6, nanoparticles are crystalline with a low level of aggregation. The particles are elongated in one direction and have grown up in rectangular prism nanorods. The preparation of pure phase fluorapatite was additionally confirmed by SAED analysis. Moreover, the nanoparticles of the Ca$_{9.85}$Eu$_{0.1}$(PO$_4$)$_6$F$_2$ annealed at 500°C were counted in length and width diameters according to TEM measurements that correspond very well with the Rietveld calculations.

**Figure 6.** Representative TEM images and SAED image of the Ca$_{9.85}$Eu$_{0.1}$(PO$_4$)$_6$F$_2$ prepared by microwave stimulated hydrothermal synthesis and annealed at 500°C/3h.
Figure 7. Histogram of the grain size distribution (length and width diameters) of the Ca$_{9.85}$Eu$_{0.1}$(PO$_4$)$_6$F$_2$ prepared by microwave stimulated hydrothermal synthesis and annealed at 500°C/3h.

3.2. Optical properties

Above terminal concentration of 3 mol% Eu$^{3+}$ in fluorapatite lattice, phases separation were detected and appearance of extra EuPO$_4$ crystal phase was noticed. Because of this, only samples in the 0.5 – 3 mol% concentration range and in the 500 – 1000°C temperature range were characterized via the PL emission and excitation spectra, as shown in Figures 8, 9 and 10. The representative excitation/emission spectra recorded at 618 nm emission line corresponding to the maximum intensity of the $^5D_0 \rightarrow ^7F_2$ electric dipole transition and representative emission spectra obtained under pulsed 266 nm excitation at 300 K for CaFAp doped with 1 mol% Eu$^{3+}$ ions are presented in Figure 8. The excitation spectra consist of an allowed, strong and broad band localized in the ultraviolet range of electromagnetic radiation relative with ligand-to-metal charge transfer (C–T) Eu$^{3+} \leftrightarrow$O$^{2-}$ of PO$_4$$^{3-}$ group as well as of series forbidden, weak and narrow lines connected with the intraconfigurational f–f transitions. The maximum of CT transition is located at 40 000 cm$^{-1}$ (250 nm) and could be strongly affected by extrinsic crystal field. On the other hand, the narrow lines observed at
33 613 cm\(^{-1}\) (297 nm) were assigned to \(7F_0 \rightarrow 5F_{(4,3,2,1)}^4P_0\) transitions; at 31 397 cm\(^{-1}\) (318.5 nm) to \(7F_0 \rightarrow 5H_{(6,5,4,7,3)}^5\); at 27 662 cm\(^{-1}\) (361.5 nm) to \(7F_0 \rightarrow 5D_4\); at 26 178 cm\(^{-1}\) (382 nm) to \(5L_7^7F_0 \rightarrow 5G_{(2,3)}^5L_7^5\); at 25 381 cm\(^{-1}\) (394 nm) to \(7F_0 \rightarrow 5L_6^5\); at 21 528 cm\(^{-1}\) (464.5 nm) to \(7F_0 \rightarrow 5D_2\); at 18 762 cm\(^{-1}\) (533 nm) to \(7F_0 \rightarrow 5D_1\) and at 16 949 cm\(^{-1}\) (590 nm) to \(7F_0 \rightarrow 5D_0\).

The positions of maxima of \(f-f\) transitions are independent on the host lattice structure and remains almost constant due to a good isolation of the \(f\) shells by the external orbitals as well as low electron-lattice coupling\(^{19,26}\).

![Figure 8](image)

**Figure 8.** Representative excitation spectra (red line) and emission spectra (blue line) of the \(\text{Ca}_{9.85}\text{Eu}_{0.1}(\text{PO}_4)_6\text{F}_2\) nanoparticles annealed at 800°C.

The room-temperature emission spectra of the \(\text{Ca}_{(10-3x)}\text{Eu}_{2x}(\text{PO}_4)_6\text{F}_2\) nanopowders were acquired in the spectral range from 17 500 nm to 14 000 cm\(^{-1}\) under pulsed 266 nm excitation as a function of optically active ions concentrations \((2x = 0.5 - 3 \text{ mol\%})\) for three calcination temperatures \((600°, 800°, 1000°C)\) and as a function of annealing temperature \((\text{as-prepared} - 1000°C)\). All the spectra were normalized to the \(5D_0 \rightarrow 7F_1\) magnetic dipole transition due to low dependence of host lattice to its intensity\(^{39,40}\) (see Figure 9). As can be seen, classic emission spectra of \(\text{Eu}^{3+}\) ions consisting of five peaks located nearly 17 343 cm\(^{-1}\) (576 nm), 16 903 cm\(^{-1}\) (591.6 nm), 16 174 cm\(^{-1}\) (618 nm), 15 276 cm\(^{-1}\) (654.6 nm) and 14 313 cm\(^{-1}\) (699 nm) can be observed. These peaks are related with \(f-f\) transitions inside the \(f\) shell.
of Eu$^{3+}$ ions: $^5D_0 \to ^7F_0$, $^5D_0 \to ^7F_1$, $^5D_0 \to ^7F_2$, $^5D_0 \to ^7F_3$ and $^5D_0 \to ^7F_4$ respectively. The most efficient emission was observed for the hypersensitive $^5D_0 \to ^7F_2$ electron transition. The europium ion is often used as a structural and luminescence probe owing to its sensitivity to the even slight changes in its local surrounding. To accomplish this target, the $^5D_0 \to ^7F_{0,1,2}$ transitions were analyzed. Since, the $^7F_0$ ground state and the $^5D_0$ first excited state are non-degenerated under any symmetry, study of the $^7F_0 - ^5D_0$ transition can give straightforward information about the existence of the total crystallographic sites substituted by europium(III) ions in the matrix. Moreover, the presence of this transition confirms the low symmetry environment of the Eu$^{3+}$ built into the host lattice$^{19}$. The $^5D_0 \to ^7F_2$ electric dipole transition is enormously sensitive even to minor changes in the local environment of the Eu$^{3+}$ ions whereas the $^5D_0 \to ^7F_1$ magnetic dipole transition remains nearly independent on the symmetry and matrix. In this matter, the magnetic dipole transition can be considered as an internal reference. If the Eu$^{3+}$ ion is in position with the center of symmetry, only the magnetic transition is permitted. On the other hand, the electric dipole transition is dominant$^{39-41}$. The relative emission intensities ratio ($R$) is defined as follows:

$$R = \frac{\int^5D_0 \to ^7F_2}{\int^5D_0 \to ^7F_1}.$$ (2)

Through this simple equation it is possible to notice little changes in the local environment of Eu$^{3+}$ ions. The ratio between integral intensity of these transitions is used for the assessment of the europium(III) ions coordination polyhedron asymmetry. This entails that the bigger the ratio between these transitions, the less centrosymmetric local surrounding around Eu$^{3+}$ is. The influence of calcination temperature and Eu$^{3+}$ ions concentration on $R$ value is presented in Table 2.

Considering the crystallographic data of calcium fluorapatite, Eu$^{3+}$ dopant can theoretically be incorporated at both Ca(1) and Ca(2) crystallographic positions. The Ca(1) position with $C_3$ symmetry is coordinated by nine oxygen ions of PO$_4^{3-}$ group and the Ca(2) position with $C_s$ symmetry is coordinated by six oxygen ions of PO$_4^{3-}$ group and one fluorine ion. It is worth to emphasize that only Ca$^{2+}$ ions located at $C_s$ crystallographic site is directly bonded with fluorine ion and one fluorine ion is surrounded by three Ca(2) ions (see Figure 3). The substitution of europium(III) ions into calcium sites needs a charge compensation mechanism, describes as$^{16,17}$.
$\text{Ca}^{2+} + \text{F}^- \leftrightarrow \text{Eu}^{3+} + \text{O}^{2-}, \ (3)$

or

$3\text{Ca}^{2+} \leftrightarrow 2\text{Eu}^{3+} + \text{V}, \ (4)$

The first mechanism seems to be more probable for apatite and it is possible only for Ca(2) site in $C_s$ symmetry, because only this ions is surrounded by one fluorine atom, which could be easily substituted during wet synthesis by oxygen ion coming from water. The second mechanism can lead to substitution of two Ca(2) ions which belongs to the same triangle built from calcium ions or to different triangles known as cis-symmetry and trans-symmetry arrangements of substituted Eu$^{3+}$ ions along the channel structures from these triangles. In the literature it is well-known that three lines for the 0-0 transition are present in apatite compounds$^{42,43}$.

Figure 9. Emission spectra of the Ca$_{10.3x}$Eu$_{2x}$(PO$_4$)$_6$F$_2$ nanoparticles annealed at 600°C (left upper), 800°C (right upper), 1000°C (left bottom) and the Ca$_{9.85}$Eu$_{0.1}$(PO$_4$)$_6$F$_2$ depending on annealed temperature (right bottom).

Taking into account the CaFAp:Eu$^{3+}$ calcined at 600°C/3h (see Figure 9), the $^5D_0 \rightarrow ^7F_0$ transition consists of two maxima located at 17 343 cm$^{-1}$ (576.6 nm – Ca(2) site with $C_s$
symmetry) and 17 269 cm$^{-1}$ (579.1 nm – Ca(1) site with $C_3$ symmetry), which corresponds well with two possibilities of europium(III) ions substitution into fluorapatite matrix. The intensity of the $^5D_0 \rightarrow ^7F_2$ transition in the ratio to the $^5D_0 \rightarrow ^7F_1$ is decreasing with increase of lanthanide ions concentration, which means the drop of distortion of europium polyhedra in the host lattice (see Table 2). The charge and ionic radii incompatibility between calcium(II) and europium(III) ions is sufficient (Ca$^{2+}$ (CN$_9$) – 1.18 Å, Eu$^{3+}$ (CN$_9$) – 1.12 Å, Ca$^{2+}$ (CN$_7$) – 1.06 Å, Eu$^{3+}$ (CN$_7$) – 1.01 Å)$^{37}$, but it could be compensated by escaping of fluorine ions caused by high temperature treatment. It is clearly visible that with increase of europium(III) ions concentration, the emission intensity from $C_s$ symmetry is decreasing. In crystal lattice, the fluorine vacancies are created and the surrounding of Eu$^{3+}$ ions is changed, hence the appearance of extra 0-0 lines could also be related with formation of new crystal sites. In pursuance of the $2J + 1$ principle, a maximum of three sublevels should exist at $C_s$ symmetry for the $^5D_0 \rightarrow ^7F_1$ transition and five in the case of the $^5D_0 \rightarrow ^7F_2$ transition. Whereas, a maximum of two Stark components should be present at $C_3$ symmetry for $^5D_0 \rightarrow ^7F_1$ and three for $^5D_0 \rightarrow ^7F_2$ transition$^{16}$.

In the case of CaFAp:Eu$^{3+}$ annealed at 800°C/3h, it is possible to distinguish five $^5D_0 \rightarrow ^7F_0$ lines located at 17 484 cm$^{-1}$ (571.9 nm), 17 441 cm$^{-1}$ (573.4 nm), 17 342 cm$^{-1}$ (576.6 nm), 17 324 cm$^{-1}$ (577.2 nm) and 17 269 cm$^{-1}$ (579.1 nm). It could be related with phase separation under high temperature treatment to extra EuPO$_4$ phase. Furthermore, the 0-0 transition of Eu$^{3+}$ ions demonstrated abnormal strong intensity (800°C, 1000°C), which was connected with rising of covalent nature of the Eu-O bonding known in apatites$^{44}$.

The case of materials annealed at 1000°C/3h is very similar to samples heat treated at 800°C/3h, but one can favour extra transitions located at 17 291 cm$^{-1}$ (578.3 nm), 17 323 cm$^{-1}$ (577.3 nm), 17 342 cm$^{-1}$ (576.6 nm), 17 418 cm$^{-1}$ (574.1 nm), 17 442 cm$^{-1}$ (573.3), 17 484 cm$^{-1}$ (572 nm). With increasing of annealing temperature, a higher amount of fluorine ions was removed enabling a creation of an extra Ca$_3$(PO$_4$)$_2$ phase with five available crystallographic sites for Eu$^{3+}$ (see Figure S1). Thereupon, the new 0-0 transitions were appearing. The asymmetry parameter $R$ dropped progressively with an increase of europium(III) ions concentration for samples heat-treated at 800°C. Thereby, the local environment of Eu$^{3+}$ got less distorted with increase of optical ions concentration. Inverse situation was observed in the case of 1000°C. The $R$ value increased with an increase of heat-treatment temperature, that means an increase of the distortion of europium polyhedra.
Nevertheless, temperature dependent emission of the CaFAp:1% Eu$^{3+}$ is the most interesting result. For as-prepared sample one can observe only two 0-0 lines and the transition of Eu$^{3+}$ located at $C_2$ position was more intense than at $C_5$ crystallographic site. But in the case of sample heat-treated at 500°C/3h, the intensity of both 0-0 transitions was almost identical. After further elevating the annealing temperature to 600°C/3h and to 700°C/3h, the most intense 0-0 transition was observed from $C_s$ symmetry of Eu$^{3+}$ ions into fluorapatite structure. In samples annealed at 800°C/3h, 900°C/3h and 1000°C/3h, one can observe five 0-0 lines and the most intense line comes from radiative transition of Eu$^{3+}$ ions located at $C_s$ symmetry. This behavior is well known in the literature and is connected with thermal diffusion of europium ions$^{45,46}$. The $R$ value was increasing with increase of annealing temperature from 1.96 for as-prepared material to 6.04 for material heat treated at 1000°C (see Table 1). Moreover, it was demonstrated that the fraction of the $^5D_0 \rightarrow ^7F_4$ transition with respect to the whole emission spectrum decrease with increasing of annealing temperatures. The electronegativity of the Eu$^{3+}$ cations does not change due to the same concentration of Eu$^{3+}$ in samples annealed at different temperatures$^{47}$. However, it can be seen significant increasing in the intensity of the $^5D_0 \rightarrow ^7F_2$, so-called “hypersensitive transition” that leads to the conclusion that the local symmetry of the Eu$^{3+}$ ion in fluorapatites get more distorted with increasing of heat-treatment temperature.
Figure 10. Representative emission spectra of the Ca\textsubscript{9.85}Eu\textsubscript{0.1}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2} nanoparticles annealed 800°C measured at different temperatures.

In order to get deeper insight into fluorapatite structure, emission spectra of the Ca\textsubscript{9.85}Eu\textsubscript{0.1}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2} annealed at 600° and 800°C per 3 h were measured at three different temperatures (10, 77 and 300 K, see Figure 10). All emission spectra were normalized to the \( ^{5}D_{0} \rightarrow ^{7}F_{1} \) transition. As can be clearly seen, it is easier to isolate particular Stark components at 10 K than at higher temperature of measurement. It is visible that with decreasing of measurement temperature the intensity of electric dipole transition was decreasing. It is possible to distinguish four 0-0 lines located at 17 266 cm\textsuperscript{-1} (579.2 nm), 17 341 cm\textsuperscript{-1} (576.7 nm) and 17 438 cm\textsuperscript{-1} (573.5 nm) and 17 482 cm\textsuperscript{-1} (572 nm) for all measurement temperatures. An extra 0-0 line was observed, what could be connected with creation of additional EuPO\textsubscript{4} phase as well as with departure of fluorine ions and creation of different Eu\textsuperscript{3+} surrounding.

The simplified Judd-Ofelt theory was used to determine the \( \Omega_{2} \) and \( \Omega_{4} \) intensity parameters based on proceeding given in references\textsuperscript{19,48,49}. Calculations were collected in Table 2. The value of the \( \Omega_{2} \) parameter decreases while increasing the Eu\textsuperscript{3+} ions concentration for materials heat-treated at 600°C and 800°C, whereas it remains
unpredictable for materials at 1000°C. The $\Omega_2$ value increases with increasing of heat-treatment temperature. The $R$ parameter change yields almost the same trend as $\Omega_2$ and also indicates the rise of distortion of europium polyhedra as well as it could be related with increase of the Eu$^{3+}$-O$^{2-}$ bond covalency. The $\Omega_4$ parameter can deliver some information about changes in the electron density around Eu$^{3+}$ ions. The magnitude of this parameter falls with increase of europium(III) ions concentration for sample annealing at 600°C until 2 mol% then decreases. In the case of sample annealed at 800°C and 1000°C, this parameter behaves variously. The $\Omega_4$ value increases with increase of heat-treatment temperature until 700 °C and then decreases excepted of sample annealed at 1000°C. Moreover, the changes in the $^5D_0 \rightarrow ^7F_2$/$^5D_0 \rightarrow ^7F_4$ ratio with increasing of annealing temperature are caused by deformation of the fluorapatite structure as well as perturbation of the Eu$^{3+}$ sites in the matrix. The high intensity of the $^5D_0 \rightarrow ^7F_4$ transition is a consequence of increasing of $\Omega_4$ parameters connected with covalence of Eu-O bonding in a highly polarized chemical environment made by the geometric distortion of the europium polyhedron. It leads to an increase in the intensity of the $^5D_0 \rightarrow ^7F_0$ and the $^5D_0 \rightarrow ^7F_4$ transitions in the emission spectrum, in contrast to the $^5D_0 \rightarrow ^7F_2$ transition. The general trend in theoretical Quantum Efficiency (QE) was observed that this parameter is decreasing with increase of europium(III) ions concentration. The highest values of QE are observed for the CaFAp doped with 0.5 mol% Eu$^{3+}$ annealed at 600 °C (~90%) and for the CaFAp doped with 1 mol% Eu$^{3+}$ heat-treated at 700°C (~93%). These materials are the most suitable for bioapplications due to nanometric size as well as good luminescence properties.

Table 2. Decay rates of radiative ($\lambda$rad), non-radiative ($\lambda$nrad) and total ($\lambda$tot) processes of $^5D_0 \rightarrow ^7F_J$ transitions, emission lifetimes ($\tau$), intensity parameters ($\Omega_2$, $\Omega_4$), quantum efficiency ($\eta$) and asymmetry ratio ($R$) of the Ca$_{(10-3x)}$Eu$_{2x}$(PO$_4$)$_6$F$_2$ as function of Eu$^{3+}$ concentration and calcination temperature.

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<th>$\lambda$tot (s$^{-1}$)</th>
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<th>$\Omega_2$ ($10^{-20}$ cm$^2$)</th>
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### 3.3. Decay times

The luminescence kinetics were recorded at room temperature for obtained samples in the 0.5 – 3 mol% concentration range as a function of the dopant concentration and in the 500 – 1000°C temperature range as a function of the annealing temperature corresponding to the $^5D_0 \rightarrow ^7F_2$ transition excited by 266 nm and monitored at 618 nm. The collected luminescence decay curves normalized to the signal intensity are shown in Figure 11. Since, the decay profiles are not a single exponential and an explanation of the physical meaning of the multi-exponential fitting is complicated, the value of lifetimes were calculated as the effective emission decays using the following equation:

$$
\tau_m = \frac{\int_0^{t_{\text{max}}} I(t)dt}{\int_0^{t_{\text{max}}} I(t)dt} = \frac{\int_0^{t_{\text{max}}} I(t)dt}{\int_0^{t_{\text{max}}} I(t)dt}, \quad (5)
$$

where $I(t)$ is the luminescence intensity at time $t$ corrected for the background and the integrals are evaluated on a range $0 < t < t_{\text{max}}$, where $t_{\text{max}} > > \tau_m$. 

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<td>207.59</td>
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Figure 11. Luminescence decay profiles of annealed at 600°C (left upper), 800°C (right upper), 1000°C (left bottom) and the Ca$_{9.85}$Eu$_{0.1}$(PO$_4$)$_6$F$_2$ depending on annealed temperature (right bottom).

The decay profiles and the lifetime values of materials annealed at 600°C are all similar around 3 ms. Slight changes observed between values are within the margin of error (5% of decay time value). The lifetime values of samples annealed at 800°C and 1000°C are around 2.8 ms and 1.9 ms, respectively and they behave in similar way to the above case. In the case of the CaFAp doped with 1 mol% Eu$^{3+}$ and heat treated at different temperatures, firstly average decay time increased while increasing the temperature from 2.7 ms for as-prepared sample to 3.3 ms for sample calcinated at 700°C. Then, the average lifetime decreases down to 1.8 ms for sample calcinated at 1000°C. If one carefully compares these results with emission spectra, one can notice that with increase of annealing temperature, the intensity of the $0$-$0$ line of Eu$^{3+}$ in $C_s$ symmetry increases and results in an increase of the lifetime. But this is observed only below 700°C, then despite increasing of the $0$-$0$ line intensity of Eu$^{3+}$ in $C_s$ site, the decay time decreased. It could be connected with preferential building of Eu$^{3+}$ ions into $C_s$ symmetry than $C_3$ symmetry with increase of heat-treatment temperature (see Figure 9) as a result of thermal diffusion of Eu$^{3+}$ ions.
The fluorapatites possess defects in crystal structure created by dopant and departure of fluorine ions caused by heat-treatment. This could be responsible for the overall lifetime of Eu$^{3+}$ ion due to the contribution of the increasing non-radiative process.

4. Conclusions

The aim of this work was to study the structural and luminescence properties of the Ca$_{10-3x}$Eu$_{2x}$(PO$_4$)$_6$F$_2$ doped with Eu$^{3+}$ ions (2x = 0.5 – 3 mol%) obtained by microwave stimulated method and post heat-treated at temperature range from 500 to 1000°C per 3 h. The successful substitution of Eu$^{3+}$ ions into fluorapatite in entire concentration scope as well as hexagonal structure of prepared materials were confirmed by the powder XRD technique. At upper terminal Eu$^{3+}$ ions concentration, the extra EuPO$_4$ appeared due to charge and ionic radii incompatibility between Ca$^{2+}$ and Eu$^{3+}$ ions. The nanometric size of the fluorapatite activated by Eu$^{3+}$ ions was confirmed by Rietveld refinement and TEM microscopy for all samples heat treated below 1000°C. The structural and spectroscopic properties have shown that optically active dopant were incorporated into both calcium crystallographic sites. Three 0-0 lines are visible on emission spectra derived from Eu(1) site as well as from cis- and trans-symmetry of Eu(2) site. Additional 0-0 peaks could be related with phase separation and with escaping of fluorine ions influenced by high annealing temperature. The highly intense 0-0 transitions were observed for materials heat treated above 800°C which was connected with an increase of covalent character of Eu-O bonding.

5. Acknowledgements

This work was supported by the National Science Centre project titled ‘Nanomaterials for fluorescence lifetimes bio-imaging (NFLBio)’ (no. UMO-2012/06/M/ST5/00048). The authors are grateful for the help with XRD measurements to M.Sc. E. Bukowska, for TEM images to Ph.D. M. Malecka and for IR and Raman measurements to M.Sc. A. Ciupa as well as Ph.D. L. Marciniak and Ph.D. R. Pazik for help with spectroscopic measurements.
6. References