Synthesis, structure and temperature dependent luminescence of Eu$^{3+}$ doped hydroxyapatite

Xiaobing Luo*, Xiaoxia Luo, Hongwei Wang, Yue Deng, Peixin Yang, Yili Tian

College of Science, Chongqing University of Posts and Telecommunications, Chongqing, 400065, P. R. China
E-mail: luoxb@cqupt.edu.cn

Abstract. A series of Eu$^{3+}$ substituted hydroxyapatite (HA) were prepared by co-precipitation reactions. The phase, fluorescence and temperature dependent luminescence of the phosphors were investigated by X-ray diffraction (XRD) and photoluminescence (PL). It is found that the doped Eu$^{3+}$ ions have entered the hexagonal lattice with no obvious secondary phase were detected by XRD. The $^5D_0 \rightarrow ^7F_0$ transition was clearly split into two even at room temperature. The predominate 573 nm peak illustrates Eu$^{3+}$ ions occupy more Ca(II) sites. The temperature dependent luminescent results show HA:xEu might be applied as one potential optical thermometry material.

1. Introduction
Hydroxyapatite (HA) widely exists in the bones and teeth of animals. Owing to its chemical similarity to natural HA, artificial HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, Ca/P = 1.67) has good biocompatibility and biodegradation. Therefore, artificial is extensively employed in biomedical sector, particularly in dentistry and orthopedics [1], gene vector [2], drug carrier[3], fluorescent labeling [4] and so on. Fluorescent labeling can realize the continuous and nondestructive observations, which is helpful for monitoring the implanted subject, the delivering progression of drug carries. Thus, luminescent HA, which can be obtained by substituting Ca$^{2+}$ ions in the crystal lattice by rare earth ions, is challenging. In fact, because the components of the natural hydroxyapatite are complicated, people have studied the substitution of various cations and anions in the hydroxyapatites [1]. Y. Han et al. have found that Eu-HA nanocrystallines could be used to label Bel-7402 human liver cancer cells [5].

The crystal structure of HA is unique. Two different crystal phases of HA have been observed in previous reports. One is hexagonal with the lattice parameters $a = b = 9.432$ Å, $c = 6.881$ Å and $\gamma = 120^\circ$, the other one is monoclinic with the lattice parameters $a = 9.421$ Å, $b = 2a$, $c = 6.881$ Å and $\gamma = 120^\circ$ [6]. In the case of hexagonal structure with the space group $P6_3/m$, it is possible to identify two sites for calcium ions, i.e., Ca(I) and Ca(II): Ca(I) is called as the columnar Ca, and Ca(II) the screw axis Ca [7]. Ca(I) is in columns parallel to the $c$-axis and are surrounded by 9 oxygen atoms, among which 6 oxygen atoms from PO$_4^{3-}$ groups are at the first nearest neighboring sites, while further 3 oxygen atoms are located at the second nearest neighboring sites. Ca(I) is in high $C_3$ symmetry. However, Ca(II) is seven-coordinated with 6 PO$_4^{3-}$ groups and 1 OH$, forming two equilateral triangles along $c$ axis. Specifically, for Ca(II) site, 6 oxygen atoms are located at the first nearest neighboring sites, while a further one oxygen atom is placed at the second nearest neighboring site Ca(II) is in low $C$, symmetry.

2. Experimental
2.1. Synthesis of Eu$^{3+}$ doped hydroxyapatite.

The nanocrystalline powders of Eu$^{3+}$ doped hexagonal hydroxyapatites (Eu:Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) were synthesized by co-precipitation method. The concentration of Eu$^{3+}$ ions has been set to 1, 3, 5, and 7 mol% in respect to the appropriate Ca$^{2+}$ molar content. The starting materials used for the preparation were Eu$_2$O$_3$, NH$_4$H$_2$PO$_4$ and Eu$_2$O$_3$. According to the molar ratios of (Eu+Ca)/P=1.67, Eu$_2$O$_3$ was dissolved in dilute HNO$_3$ to obtain Eu(NO$_3$)$_3$. The mixture of Ca(NO$_3$)$_2$ aqueous solution and Eu(NO$_3$)$_3$ aqueous solution was poured into the NH$_4$H$_2$PO$_4$ aqueous solution under vigorous stirring. After the pH value was adjusted to about 10 by NH$_3$•H$_2$O, the precipitation was washed by distilled water at least three times and then dried by oven-dried. Finally, the dried precipitation was calcined at 600$^\circ$C for 6h to obtain the samples.

2.2. Characterization

The powder X-ray diffraction (XRD) measurement was recorded by an X-Ray Diffractometer (Persee, XD-2) with Cu-K$\alpha$ ($\lambda$ = 1.5406 Å) at 36 KV and 20 mA. The scan rate was 2$^\circ$/min and the scan range was between 10$^\circ$ and 60$^\circ$. The UV-visible reflectance spectrum was obtained on a Ф130 mm integrating sphere attachment in a double-beam spectrometer (Cary 530). BaSO$_4$ was employed as the reference for 100% reflectance. The phosphorescence excitation (PLE), phosphorescence (PL) spectra and the fluorescence decay were recorded by a fluorescence spectrophotometer (Edinburgh, FLS920) equipped with a 450 W xenon lamp or a pulsed xenon lamp as the light source, and a Shimadzu R9287 photomultiplier as the detector. The samples were mounted in one home-made temperature controller to obtain the temperature-dependent excitation and emission spectra.

3. Results and discussion

3.1. Phase formation

The XRD patterns of different Eu$^{3+}$- doped HA phosphors were shown in Figure 1. As shown, all the diffraction peaks are weak and the baselines are noisy, which might illustrate that the crystallization of the prepared Eu$^{3+}$ doped HA is not perfect. But it is similar with the reported results where the samples were synthesized by hydrothermal method [8], thermal decomposition method, or ultrasound assisted precipitation method [9]. On the other hand, the position and the relative intensity of the diffraction peaks of each sample are in agreement with the hexagonal HA in P6$_3$/m space group with the JCPDS No. 74-0566. No significant signal related to other phases was detected, which indicated that Eu$^{3+}$ ions had successfully doped into HA crystals. As stated above, the doped Eu$^{3+}$ ions could have two different sites since Eu$^{3+}$ ions substituted Ca$^{2+}$ ions in the lattice.

![Figure 1. XRD powder diffraction patterns of Eu$^{3+}$ doped HA phosphors.](image)

3.2. Diffuse reflectance spectroscopy

The diffuse reflectance spectra of powders are often used to investigate the absorption properties of the samples. Figure 2 shows the diffuse reflectance spectra of HA: xEu (x = 1%, 3%, 5% and 7%). From the figure, it is see that all the profiles present high and constant reflectance (above 90% s) at wavelength longer than 600 nm, which illustrate there is no absorption in 600-800 nm spectra range. The weak sharp
absorption peaks due to Eu$^{3+}$ ions at 394, 466, and 531 nm were observed. The assignments of the f-f transitions are noted in the figure. One intense wide band centered at about 305 nm could be attributed to the charge transfer band of Eu-O, which is consistent with the documented data [10].

3.3. Luminescence of HA:Eu at room temperature

Figure 3 shows the PL and PLE spectra of one representative sample HA: 5% Eu. Both the sharp structured intra-configurational f-f transition of Eu$^{3+}$ ions and the broad charge transfer band of Eu-O are observed in the PLE spectra. The assignments of the peaks are marked in the figure. From the excitation spectrum, it is seen that the Eu doped HA has strong excitation property. In the emission spectra, the transition from the excited state of $^5D_0$ to the ladder energy levels of $^7F_J$ ($J = 0, 1, 2, 3, 4$) are clearly observed. The emission intensity under the excitation of 391 nm (the characteristic transition of Eu$^{3+}$: $^7F_6 \rightarrow ^5L_6$) is much higher than that of 284 nm (the charge transfer band of Eu-O) as expected.

It is interesting to noted that the transition of $^5D_0 \rightarrow ^7F_0$ is clearly to be slipped into two sharp peaks even at room temperature under the excitation of 391 and 284 nm. It is known that $^5D_0 \rightarrow ^7F_0$, transition of Eu$^{3+}$ ions is generally parity forbidden, but when Eu$^{3+}$ ions are located in $C_p$, $C_n$ and $C_{nv}$ sites, the parity forbidden will be partially permitted and thus a $^5D_0 \rightarrow ^7F_0$ transition can be observed. Furthermore, the number of $^5D_0 \rightarrow ^7F_0$ transition peaks will correspond to the number of lattice site in the luminescent materials. The observation of the split of $^5D_0 \rightarrow ^7F_0$ transition illustrates two lattice sites of Eu$^{3+}$ ions in the lattice, which is in good agreement with the crystal structure. Furthermore, the two peaks in $^5D_0 \rightarrow ^7F_0$ transition located at 573 and 576 nm recorded in this work corresponds to Ca(II) and Ca(I) sites respectively. In addition, the intensity of 573 nm is much higher than that of 576 nm (see the black curve excited by 284 nm in Figure 3), which hints that there are more Eu$^{3+}$ ions occupy Ca(II) sites than Ca(I) sites in the lattice. The result is consistent with the previous study of site preference of rare earth doped in hydroxyapatite [11]. At the same time, it is found in the emission spectrum excited by 284 nm that the overall intensity of $^5D_0 \rightarrow ^7F_0$ is as high as that of $^5D_0 \rightarrow ^7F_2$, which is quite interesting.
displays the excitation and emission spectra of HA:xEu (x = 1%, 3%, 5% and 7%) samples at room temperature. It is found out that the emission intensity of these series of samples increases at first until the doping concentration of Eu\(^{3+}\) is 5\%, the intensity reaches a maximum and it decreases with the concentration. But the shape of the spectrum profiles does not show obvious change with the doping concentration in this work. The relative emission intensity of \(^5\text{D}_0 \rightarrow ^7\text{F}_0\) \text{Ca(II)} at 573 nm and that of \(^5\text{D}_0 \rightarrow ^7\text{F}_0\) \text{Ca(I)} at 576 nm does not change either, which illustrates that the energy migration as reported in ref. [5] does not occur.

**Figure 4.** PLE (a) and PL(b) spectra of HA:xEu at room temperature.

3.4. Temperature dependent excitation and emission spectra of HA:5%Eu

From the above results it is known that the HA:5%Eu phosphor presents the maximum emission intensity among the HA:xEu (x = 1-7\%) samples. Figure 5 and Figure 6 present the temperature dependent excitation and emission spectra along with the fitting results of this optimal sample. It could be found that the intensity declines rapidly when temperature increases from 25 K to 275 K both in excitation and emission spectra as expected, because the non-radiative transition increases with temperature. Figure 5 (a) shows the 3-dimentional excitation spectra of this representative sample HA:5%Eu at different temperatures, and Figure 5(b) are the data fitting results based on temperature dependent excitation spectra, from which it is seen that the excitation intensity ratio between Eu\(^{3+}\) f-f transition at 391 nm and that of the charge transfer band at 284 nm, the relative sensitivity and the excitation at 391 nm exhibit linear relationship with the temperature.

**Figure 5.** (a) The 3-dimentional PLE spectra of HA:5%Eu at different temperatures. (b) The intensity ratio between Eu\(^{3+}\) f-f transition at 391 nm and that of CTB at 284 nm as a function of temperature.
Figure 6. (a) The PL spectra of HA:5%Eu at various temperatures. (b) Temperature dependence of emission @616 nm 587 nm.

Figure 6 (a) is the emission spectra of HA:5%Eu phosphor at various temperatures. Figure 6 (b) shows the temperature dependence of the emission intensity of 616 nm /587 nm. Similar with the results obtained from excitation spectra, the linear relationship is observed.

4. Summary
The Eu$^{3+}$ doped hydroxyapatite HA:xEu (x =0, 1%, 3%, 5% and 7%) were synthesized by co-precipitation reactions. XRD and PL were employed to investigate the phase, fluorescence and temperature dependent luminescence of the samples. It is found that the doped Eu$^{3+}$ ions have successfully entered the hexagonal lattice. The powders could be pumped both by the charge transfer band (CTB) of Eu-O and the characteristic transition of Eu$^{3+}$. It presents red emission under the excitation of 391 nm (Eu$^{3+}$ characteristic transition) and orange emission under the excitation of 284 nm (CTB of Eu-O). The splitting of $^5D_0 \rightarrow ^7F_0$ transition illustrates the substituted Eu$^{3+}$ ions occupy two different sites, and Ca(II) sites were dominate in this study. The optimal doping concentration of Eu$^{3+}$ is determined to be 5%. The temperature dependent luminescence shows the samples might be served as one potential optical thermometry material.

5. References
[1] I. Cacciotti, Cationic and Anionic substitutions in hydroxyapatite, Handbook of Bioceramics and Biocomposites,( DOI )10.1007/978-3-319-09230-0-7-1.  
[2] H. Nie, C.H. Wang, Fabrication and characterization of PLG/Hap composite scaffolds for delivery of BMP-2 plasmid DNA(J. Control. Release) 120 (2007) 111-121.  
[3] P. Yang, Z. Quan, C. Li, X. Kang, H. Lian J. Lin, Bioactive, luminescent and mesoporous europium-doped hydroxyapatite as a drug carrier (Biomater). 29 (2008) 4341-4347.  
[4] R. Singh, H. S. Nalwa, Medical applications of nanoparticles in biological imagine, cell labeling, antimicrobial agents, and anticancer nanodrugs(J. Biomed. Nanotech)7 (2011) 489-503.  
[5] Y. Han, X. Wang, H. Dai, S. Li, Synthesis and luminescence of Eu$^{3+}$ doped hydroxyapatite nanocrystallines: Effects of calcinations and Eu$^{3+}$ content(Lumin ) 135 (2013) 281-287.  
[6] A. S. Posner, A. Perloff, A. F. Diorio, Refinement of the hydroxyapatite structure( Acta Crystallogr)11(1958)308-309.  
[7] M. H. Uddin, T. Matsumoto, M. Okazaki, A. Nakahira, T. Sohmura, Biomimetic fabrication of apatite related biomaterials. In: Mukherjee A (ed) Biomimetics learning from nature( Intech, Rijeka) 2010, pp 289-303  
[8] S. Huang, J. Zhu, K. Zhou, Effects of Eu$^{3+}$ ions on the morphology and luminescence properties of hydroxyapatite nanoparticles synthesized by one-step hydrothermal method (Mater. Res. Bull) 47 (2012) 24-28.  
[9] Y. Han, X. Wang, H. Dai, S. Li, Synthesis and luminescence of Eu$^{3+}$ doped hydroxyapatite nanocrystallines: effects of calcinations and Eu$^{3+}$ content(J. Lumin,)135 (2013) 281-287.
A. K. Parchur, R. S. Ningthoujam, *Behavior of electric and magnetic dipole transitions of Eu$^{3+}$, $^5D_0 \rightarrow ^7F_0$ and Eu-O charge transfer band in Li$^+$ co-doped YPO$_4$:Eu$^{3+}$* (RSC Advances) 2 (2012) 10859.

M. E. Fleet, X. Liu, Y. Pan, *Site preference of rare earth elements in hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$* (J. Solid State Chem.) 149 (2000) 391-398.

Acknowledgement

The project was funded by National Natural Science Foundation of China (11674044, 11604037), Natural Science Foundation Project of Chongqing (CSTC2015jcyjA50005), Chongqing Key Laboratory Improvement Plan (cstc2014pt-sy40001) and University Innovation Team Construction Plan Funding Project of Chongqing (CXTDG201602009).