Luminescent properties of $Ca_5(PO_4)_3OH:Gd^{3+}$, Pr^{3+} phosphor powder

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Abstract. Hydroxylapatite (Ca_5 $(PO_4)_3(OH)$) is a well-known bioceramic material for medical application. It is biocompatible meaning that it has the ability to form chemical bonds with living tissues. Phosphate based inorganic compounds doped with rare earth ions form an important family of phosphors for solid state lighting applications [1]. In this study, we prepared (using co-precipitation method) and investigated the structure, morphology, and photoluminescent properties of ($Ca_5(PO_4)_3(OH)$) co-doped with gadolinium (Gd^{3+}) and praseodymium (Pr^{3+}). The X-ray diffraction (XRD) patterns show a hexagonal phase of $Ca_5(PO_4)_3(OH)$ consistent with the standard JCPDS data file No 73-0293. The XRD peaks were sharp and intense suggesting that the phosphor was highly crystalline. The scanning electron microscopic images show that the powders consist of an agglomeration of spherical particles. The photoluminescent spectrum of $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ phosphor exhibit a narrow emission peak at 313 nm due to the $^6P_{7/2}\rightarrow{}^8S_{7/2}$ transition of the Gd^{3+} ion, and this emission was enhanced by Pr^{3+} co-doping. The photoluminescent properties of the $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ phosphor are evaluated for application in phototherapy lamps.

Introduction

Hydroxylapatite is one of the three occurring mineral forms of apatite (calcium-phosphate mineral). These minerals are flourapatite ($Ca_5(PO_4)_3F$), chlorapatite ($Ca_5(PO_4)_3Cl$ and hydroxylapatite ($Ca_5(PO_4)_3OH$) [2]. Hydroxylapatite has been found to be an attractive new functional material used mainly in medical applications because of its biocompatibility. Today, it is also used as a host for rare-earth elements to prepare phosphors that can be used, among other things, in phototherapy lamps for treatment of different skin diseases and general lighting applications. The dopant Gd^{3+} has been used as a luminescent activator in hydroxylapatite hosts to produce ultraviolet radiation (UVR), specifically in the ultraviolet B (UVB) region of the electromagnetic wave spectrum. In addition, up-conversion emission of Gd^{3+} has also been reported which shows Gd^{3+} emission peaks in the range of ~280 - 320 nm. These spectral characteristics suggest that Gd^{3+} can have a wide range of UV applications. In this study, the enhancement of this UVB emission by co-doping with Pr^{3+} is demonstrated. The enhanced UVB emission will be useful in prolonging the life span of phototherapy lamps used in treatment of various skin diseases.

Experimental

1 Synthesis

$Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ phosphor was synthesized by the reaction of diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), sodium hydroxide (NaOH) and calcium nitrate tetrahydrate ($Ca(NO_3)_34H_2O$) in distilled water. In a typical preparation, 100 ml of 0.4M ($(NH_4)_2HPO_4$) solution with pH= 6.5, 100 ml of 0.1M (NaOH) solution with pH = 13.5, and 100 ml of 0.6M ($Ca(NO_3)_34H_2O$), and 2M $Pr(NO_3)_36H_2O$ and 10M $Gd(NO_3)_3\cdot 5H_2O$ solutions, both at pH = 7.3, were prepared and all the combined solutions were stirred vigorously at room temperature. Throughout the mixing process the pH of the system was maintained at pH = 6.5, and after adding 0.1M NaOH the pH of the solution increased to 10.8 and the white precipitate was formed. The precipitate was stirred for 12 hours at room temperature, was washed with distilled water and then with ethanol to increase the dispersion characteristics, and was finally dried at 80 °C for 24 hours. The dried powder was ground by using a mortar and pestle and calcined at 900 °C for 2 hours. $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ powder phosphors with different concentrations of Gd^{3+} and Pr^{3+} were prepared.

2 Characterization

The crystalline structure was analyzed by X-ray Diffraction (XRD), using Bruker AXS D8 Advance diffractometer and the samples were irradiated with Cukα radiation (λ = 1.5406 Å). The crystallite size (D) was calculated from XRD peaks using Scherrer equation:

$$D = 0.89\lambda / \beta \cos\theta \qquad (1)$$

where λ is the wavelength of the used Cu Kα radiation, β is the full width at the maximum of the $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ line and θ is the diffraction angle. The particle morphology was analyzed using Scanning Electron microscope (SEM). The photoluminescent (PL) was used to determine the luminescent properties of the samples in air at room temperature.

Results and discussion

Figure 1 (a) shows the XRD pattern of $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ phosphor powder. The samples were all annealed at 900 °C in air. The diffraction peaks from $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ are consistent with the hexagonal phase of $Ca_5(PO_4)_3$ referenced in the standard JCPDS Card Number 73-0293. The narrow and sharp diffraction peaks suggest that our materials were highly crystalline. Figure 1 (b) shows the XRD patterns of $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ phosphor powders calcined at 600, 700, 800, 900 and 1000 °C for 2 hours. The spectra show that the crystallinity of the powder was improved with an increasing temperature. The strongest peaks that were used to estimate the crystallite size by Scherrer's equation were (2θ = 25.95°, 31.89°, 46.77°, and 49.55°). The average crystallite size of the phosphor powders calcined at the different temperatures was in the range of ~22 - 65 nm.

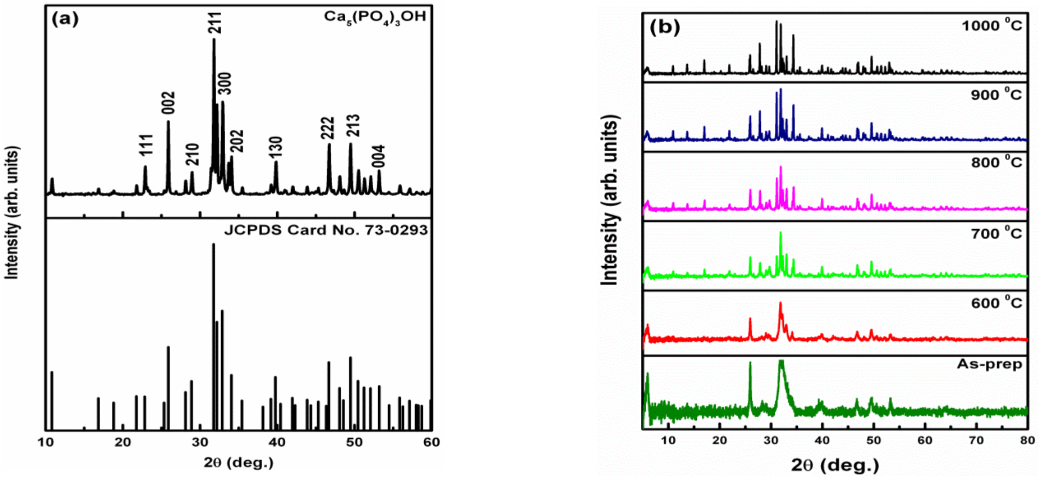

Figure 1 (a) XRD patterns of $Ca_5(PO_4)_3(OH)$ powder calcined at 900 °C (and standard JCPDS Card No. 73-0293), and (b) $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ powders calcined at different temperatures.

Figure 2 shows the SEM image of $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ powder calcined at 900 °C for 2 hours in air. The image shows that the particles are agglomerated together with isolated particles appearing spherical in shape. A qualitative analysis of the chemical composition performed by EDS confirmed all the elements (Ca, P, O, Gd^{3+} and Pr^{3+}).

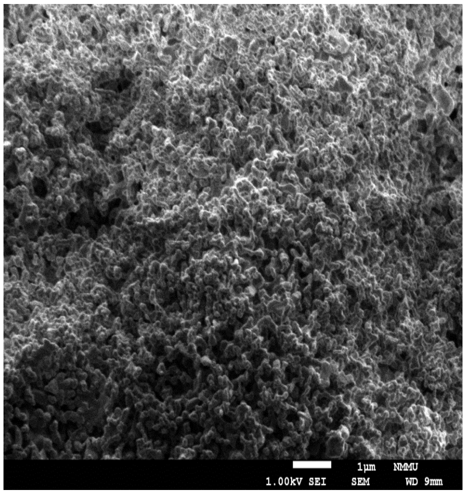

Figure 2: SEM images of $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ phosphor powder.

Figure 3 (a) shows the optical absorption spectra of pure $Ca_5(PO_4)_3(OH)$, $Ca_5(PO_4)_3(OH):Gd^{3+}$, $Ca_5(PO_4)_3(OH):Pr^{3+}$ and $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ powders. The host has a strong absorption bands with main absorption at 207 nm and minor absorption at 300 nm. The $Ca_5(PO_4)_3(OH):Gd^{3+}$ follow the same trend as that of the host. The peaks at 207 nm and 300 nm are respectively assigned to band to band absorption and intrinsic defects in the material [6, 7]. $Ca_5(PO_4)_3(OH):Pr^{3+}$ and $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ systems shows two absorption bands at 446, 471, 483 nm assigned to $^3H_4 \rightarrow {}^3P_{j\ (j\ =\ 0,\ 1,\ 2)}$ and 593 nm assigned to $^3H_4 \rightarrow {}^1D_2$ transitions of Pr^{3+} [8,9]. The inset on $Ca_5(PO_4)_3(OH):Pr^{3+}$ system show the enlargement of the absorption bands at range of 445 to 630 nm. Figure 3 (b) shows the plot of $(\alpha h\upsilon)^2$ vs photon energy ($h\upsilon$), where α is the absorption coefficient. The optical band gap was determined by extrapolating the linear portion of the curve or tail [10] and the estimated value of the band gap energy was found to be 5.2 eV.

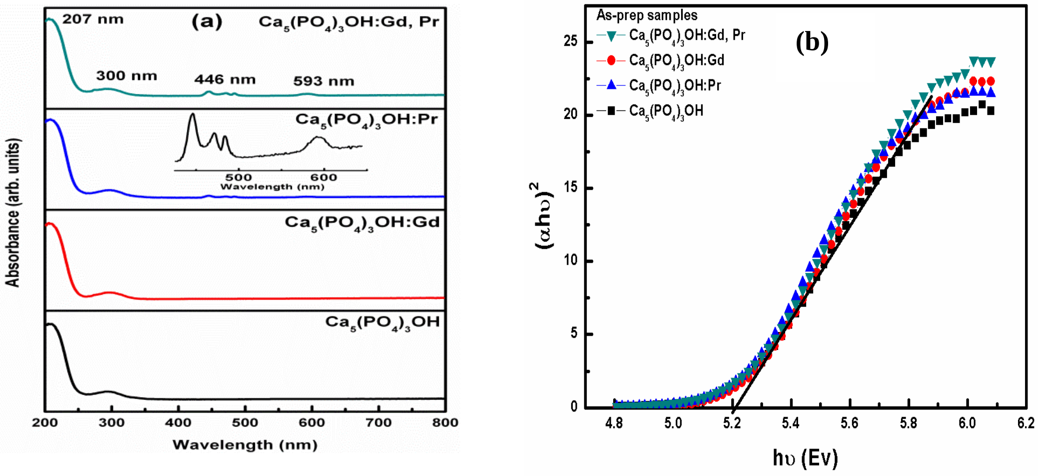

Figure 3: (a) Optical absorption spectra and (b) $(\alpha h\upsilon)^2$ vs photon energy ($h\upsilon$) plot of $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$

Figure 4 (a) shows the PL (i) excitation and (ii) emission spectra of $Ca_5(PO_4)_3OH:Gd, Pr^{3+}$ calcined at 900 °C. The excitation peaks at 222 nm and 274 nm are attributed to host absorption and $^8S_{7/2} \rightarrow {}^6I_j$ transition of Gd^{3+} respectively [11, 12]. The PL emission of $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$ consists of narrow band emission at 313 nm corresponding to $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} [13]. The incorporation of Pr^{3+} was shown to improve the host absorption at 222 nm and this in turn improved the 313 nm emission of the Gd^{3+}. The mechanism by which Pr^{3+} enhances the host absorption is not known yet, but this study is in progress and the mechanism will be reported in our future publications. The energy absorbed by the host is transferred to Gd^{3+} which inturn enhances the UVB emission at 313 nm. The inset of figure 4 (a) shows that the maximum PL intensity was obtained when concentrations of Gd^{3+} and Pr^{3+} were 10 and 2 mol% respectively, suggesting that the excitation energy from the host to Gd^{3+} was transferred efficiently at this combination. Figure 4 (b) shows the emission and excitation spectra of $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$ calcined at different temperatures (600 - 1000 °C). The PL intensity increased with an increasing temperature. All the peaks (excitation and emission) are at the same positions as those shown in figure 4 (a) suggesting that calcining at different temperatures did not affect the excitation and radiative transition of the $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$.

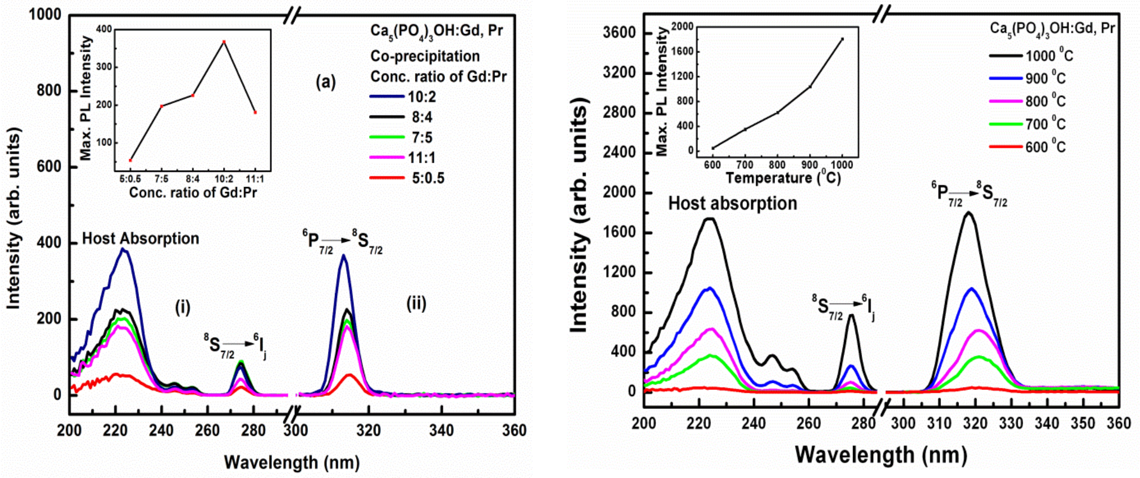

Figure 4. (a) PL excitation and emission spectra of Ca$_5$(PO$_4$)$_3$OH:Gd^{3+},Pr^{3+} and (b) calcined at different temperatures.

Conclusion

In summary, Ca$_5$(PO$_4$)$_3$(OH):Gd^{3+},Pr^{3} phosphor was successfully synthesized via the co-precipitation method. The Ca$_5$(PO$_4$)$_3$(OH):Gd^{3+}system exhibited a narrowband UVB emission at 313 nm. This emission was enhanced by co-doping with Pr^{3+} and also by calcining at different temperatures.

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