Synthesis and characterization of a narrowband $Ca_5(PO_4)_3(OH):Gd^{3+}, Pr^{3+}$ phosphor for medical applications

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Abstract: In this study, we investigate photoluminescent properties of calcium phosphate ($Ca_5(PO_4)_3(OH)$) co-doped with gadolinium (Gd^{3+}) and praseodymium (Pr^{3+}) synthesized using a wet chemistry method. The dried and calcined $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ powder phosphors were characterized using X-ray Diffraction (XRD) and photoluminescence (PL) spectroscopy. The XRD patterns showed a single hexagonal ($Ca_5(PO_4)_3(OH)$) phase. The diffraction peaks became sharper and narrower when the calcination temperature was increased from 700 - 900 °C indicating an increase in the degree of crystallininty. PL excitation measurements showed that the phosphor can be efficiently excited at 221 nm and 274 nm. The PL emission spectrum consisted of two narrow band emission peaks with the major emission at 316 nm and the minor emission at 630 nm, which correspond to radiative transitions of Gd^{3+}. In addition a narrow emission peak at 603 nm corresponding to radiative transition of Pr^{3+} was observed from $Ca_5(PO_4)_3(OH):Pr^{3+}$. The $Ca_5(PO_4)_3(OH):Gd^{3+}$, Pr^{3+} phosphor is evaluated for a possible application as a light source in phototherapy lamps.

1. Introduction

Hydroxylapatite is one of the three occurring mineral forms of apatite (a calcium-phosphate mineral). These minerals are flourapatite ($Ca_5(PO_4)_3F$), chlorapatite ($Ca_5(PO_4)_3Cl$ and hydroxylapatite ($Ca_5(PO_4)_3OH$) [1]. Hydroxylapatite has been found to be an attractive new functional material. It has good optical properties for medical applications in artificial bones, tooth enamel and skin treatment such as psoriasis, vitiligo, atopic dermatitis and others [2]. It is also a good host for rare-earth elements to prepare phosphors that can be used, among other things, in phototherapy lamps. In this study, we investigate the optical properties of hydroxylapatite phosphor co-doped with gadolinium (Gd^{3+}) and praseodymium (Pr^{3+}). Gd^{3+} ion is a well-known quantum cutting or photon cascade emission ion [3]. Gd^{3+} ion has $4f^7$ electronic configuration and the energy gap between the ground state ($^8S_{7/2}$) and the excited state ($^6P_{7/2}$) is 32 000cm^{-1}[4]. The spectral properties of Gd^{3+} have been theoretically and experimentally studied under vacuum ultraviolet (VUV) excitation. 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. Pr^{3+} is a promising candidate for luminescence lamps due to the fact that it exhibits the photon cascade emission. Its electronic structure gives rise to luminescence in the ultra-violet (UV), visible and infrared (IR) wavelength ranges. $Ca_5(PO_4)_3(OH):Gd^{3+}$, Pr^{3+} has been reported to be a good candidate of efficient ultra-violet B (UVB) phosphor excited by VUV–light. The Pr^{3+} and Gd^{3+} ions were selected because Pr^{3+} was found that it transfer energy to Gd^{3+} to enhance the efficiency of the UV emission of the Gd^{3+} [5].The 4f-5d transition of Pr^{3+} directly absorb VUV light and transferred it non-radiatively to Gd^{3+}[6]. In this study, we have applied standard JCPDS file to determine the crystal structure of $Ca_5(PO_4)_3(OH):Gd^{3+}$, Pr^{3+} and also studied the PL properties of $Ca_5(PO_4)_3(OH):Gd^{3+}$, Pr^{3+} under UV light excitation using different concentrations. The intense is required for medical applications.

2. Experimental

2.1 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 ($Ca\ (NO_3)_3{\cdot}4H_2O$) 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 100ml of 0.6M ($Ca\ (NO_3)_3{\cdot}4H_2O$) with addition of 1M $Pr\ (NO_3)_3{\cdot}6H_2O$ and 11M $Gd\ (NO_3)_3{\cdot}5H_2O$ at pH = 7.3 were prepared and all the solutions were stirred vigorously at room temperature. Throughout the mixing process the pH of the system was maintained at a pH = 6.5, and after adding 0.1M NaOH the pH of the solution was maintained at 10.8. The obtained white precipitate was stirred for 12 hours at room temperature. The precipitate was first washed with distilled water and then ethanol to increase the dispersion characteristics, and finally it was dried at 80 °C for 24 hours. The dried powder was ground by using a mortar and pestle and was calcined at 900 °C for 2 hours. Different products were collected due to different concentration of Gd^{3+} and Pr^{3+} used during synthesis.

2.2 Characterization

The crystalline structure was analyzed using an X-ray Diffraction (XRD), Bruker AXS D8 Advance diffractometer using Cukα radiation (λ = 1.5406 Å). An accelerating voltage was set at 40 kV and current at 40 mA. 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. Photoluminescence (PL) measurements were carried out at room temperature using a Varian Cary Eclipse fluorescence spectrophotometer coupled with a monochromatized xenon lamp with an output power of (60-75W).

3. Results and discussion

Figure 1 shows the XRD patterns of $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ powder and the peaks of the diffractogram confirms that the products had a high degree of crystallinity. Diffraction peaks of ($Ca_5(PO_4)_3(OH)$, $Ca_5(PO_4)_3(OH):Pr^{3+}$, $Ca_5(PO_4)_3(OH):Gd^{3+}$ and $Ca_5(PO_4)_3(OH):Gd^{3+},Pr^{3+}$ all correspond to the single hexagonal phase of $Ca_5(PO_4)_3(OH)$ referenced in the JCPDS file No. 73-0293. There are impurities detected around 2θ=28 and 31 on $Ca_5(PO_4)_3(OH):Gd^{3+}$ and $Ca_5\ (PO_4)_3(OH):Gd^{3+},Pr^{3+}$ powders. These peaks correspond to Gd^{3+} diffraction patterns [7] and they are also confirmed by JCPDS file No. 02-0864. The XRD patterns shows that the sample was well annealed at 900 ^{0}C. The average particle size was calculated from the full width at half maxima of the diffraction peaks by Scherer equation (1) and the crystallite size of the powder was ~ 70-90 nm for the samples calcined at 900 °C.

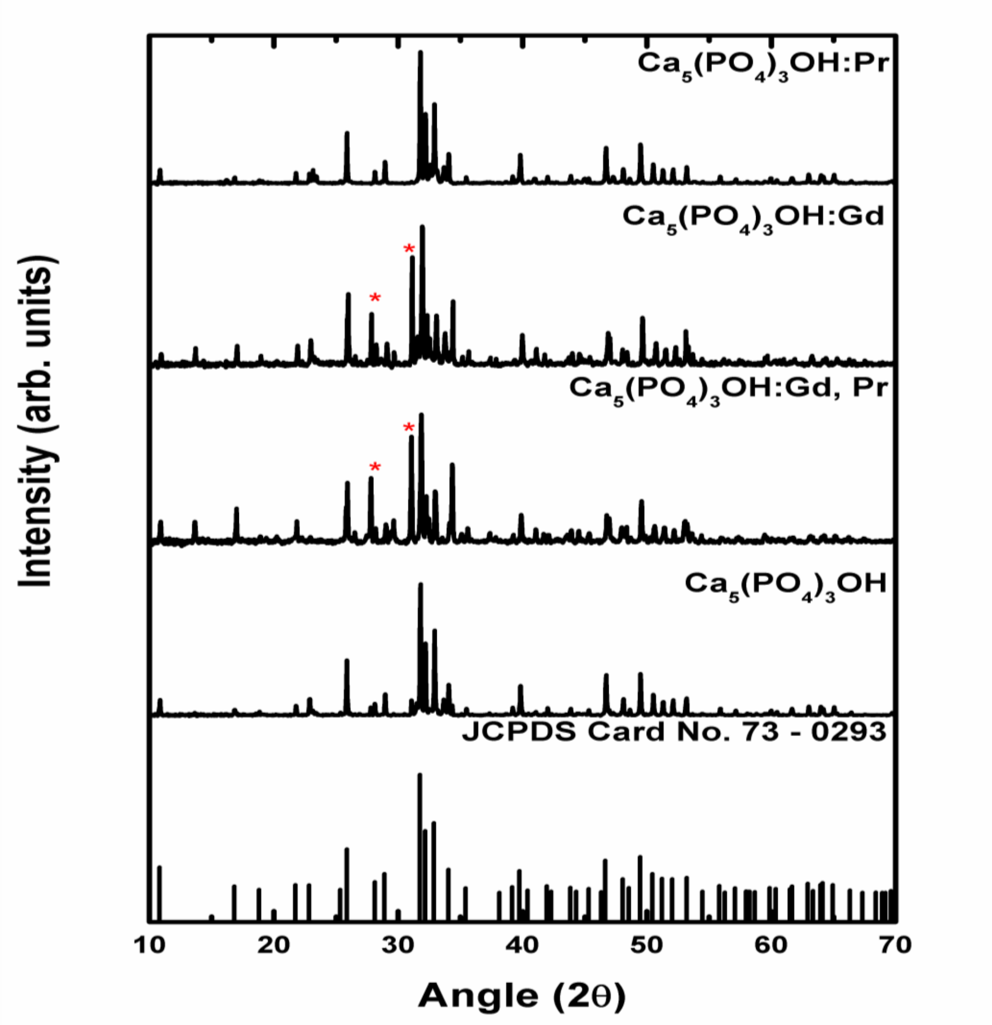

Figure 1: XRD patterns of $Ca_5\ (PO_4)_3(OH):Gd^{3+}$, Pr^{3+} powder and JCPDS match (card no. 73-0293)

Figure 2 shows the PL emission and excitation spectra of $Ca_5\ (PO_4)_3(OH):Gd^{3+}$ calcined at 900 °C. The excitation spectrums were recorded when monitoring emissions at 610 nm. The excitation peaks at 221 and 274 nm are due to the $^8S_{7/2}\rightarrow{}^6G_j$ and $^8S_{7/2}\rightarrow{}^6I_j$ transitions of Gd^{3+} [8]. The PL emission of Gd^{3+} consists of two narrow band peaks with a major emission at 610 nm and minor emission at 316 nm corresponding to the $^6P_{7/2}\rightarrow{}^8S_{7/2}$ and $^8G_{7/2}\rightarrow{}^8P_{5/2}$ transitions of Gd^{3+} respectively [9]. From the UV-visible spectroscopic characteristics and luminescence properties of $Ca_5(PO_4)_3(OH):Gd^{3+}$ it was found that the quantum cutting by energy transfer from Gd^{3+} improve the red emission of Gd^{3+} ion under UV excitation but only part of the excitation energy in the excited ^6P_j states can be transferred to its red emission and nonradiative energy transfer efficiency from ^6P_j to ^6G_j. The fact that Gd^{3+} excited by $^8S_{7/2}\rightarrow{}^6G_j$ transition emits a red photon due to $^6G_{7/2}\rightarrow{}^6P_{5/2}$ transition and an UV photon due to $^6P_{7/2}\rightarrow{}^8S_{7/2}$ transition confirms the occurrence of quantum cutting of Gd^{3+} in the sample [8]. We have also varied Gd^{3+} concentrations to determine the best concentration that gives optimum PL emission intensity. Gd^{3+} emission shows concentration quenching for concentrations above 10 mol % with an emission wavelength (λ_{emi} = 610 nm) this is shown in the inset of figure 2.

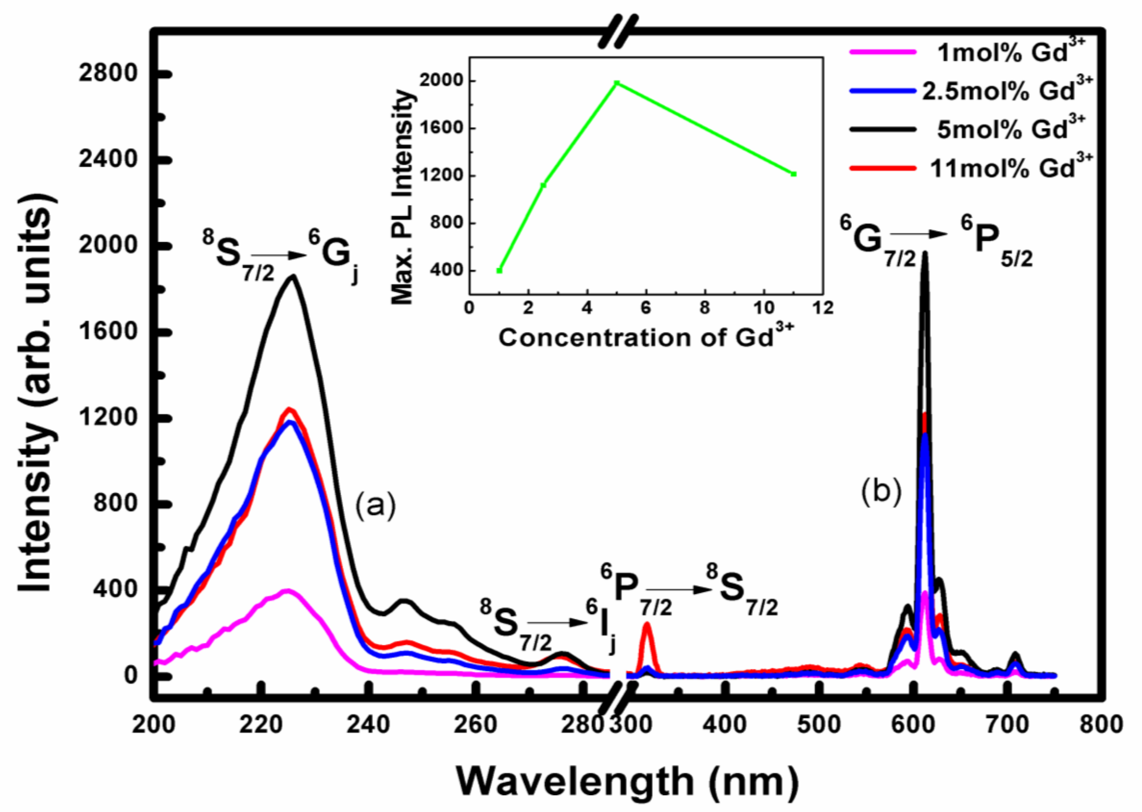

Fig 2. PL (a) excitation and (b) emission spectra of $Ca_5(PO_4)_3OH:Gd^{3+}$

Figure 3 shows the PL emission and excitation spectra of $Ca_5(PO_4)_3OH:Pr^{3+}$ calcined at 900 ^{0}C. The excitation at 447 nm (λ_{emi} = 603 nm) and 483 nm (λ_{emi} = 603 nm) are assigned to $^3H_4 \rightarrow {}^3P_2$ and $^3H_4 \rightarrow {}^3P_0$ transitions of Pr^{3+} respectively. The PL emission consists of a narrow peak at 603 nm corresponding to $^3P_0 \rightarrow {}^3H_4$ transition of Pr^{3+}. From the UV-visible spectroscopic characteristics and luminescence properties of Pr^{3+}, it was found that Pr^{3+} can exhibit different excitation bands in the UV-visible region (300~ 500 nm) [10]. We also varied the concentrations of Pr^{3+} to determine the optimum concentration for improved PL emission intensity. The inset in the figure shows that as we increase the concentration of Pr^{3+}, the PL intensity decreases and this can be attributed to concentration quenching effects.

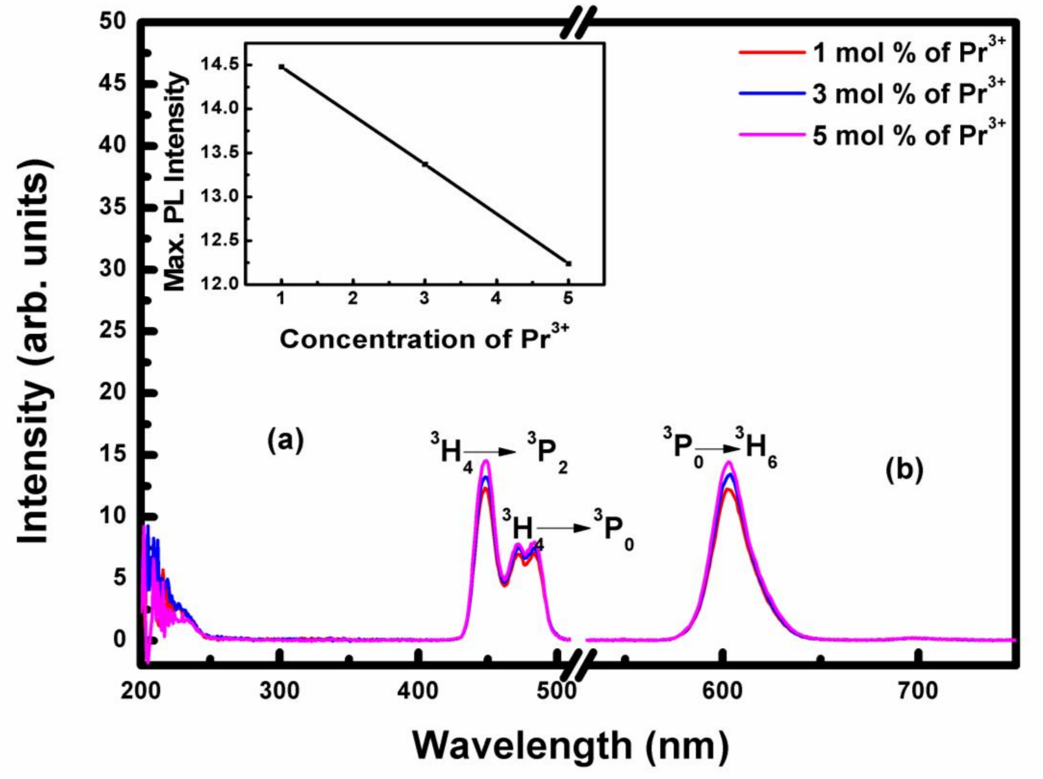

Fig 3. PL (a) excitation and (b) emission spectra of $Ca_5(PO_4)_3OH:Pr^{3+}$.

Figure 4 shows the emission and excitation spectra of $Ca_5(PO_4)_3OH$:Gd, Pr^{3+} calcined at 900 ^{0}C. The excitation peaks at 221 nm and 274 nm (λ_{emi}=316 nm) are assigned to $^8S_{7/2}\rightarrow{}^6G_j$ and $^8S_{7/2}\rightarrow{}^6I_j$ transitions of Gd^{3+} respectively. The PL emission of $Ca_5(PO_4)_3OH:Gd^{3+},Pr^{3+}$ consists of two narrow band peaks with a major emission at 316 nm and minor emission at 630 nm corresponding to $^6P_{7/2}\rightarrow{}^8S_{7/2}$ and $^6G_{7/2}\rightarrow{}^6P_{5/2}$ transitions of Gd^{3+}. In this study Pr^{3+} acts as a sensitizer, the electrons are excited from ground state to the excited state of Pr^{3+} and eventually the excitation energy is transferred to Gd^{3+} resulting in enhanced PL emission of the peak at 316 nm. Energy is probably transferred from the ^6G_j or ^6I_j state of Pr^{3+} to the ^6Pj state of Gd^{3+}. As shown in the inset, the maximum PL intensity and probably the efficient energy transfer were obtained when concentrations of Gd^{3+} and Pr^{3+} are 10 and 2 mol% respectively.

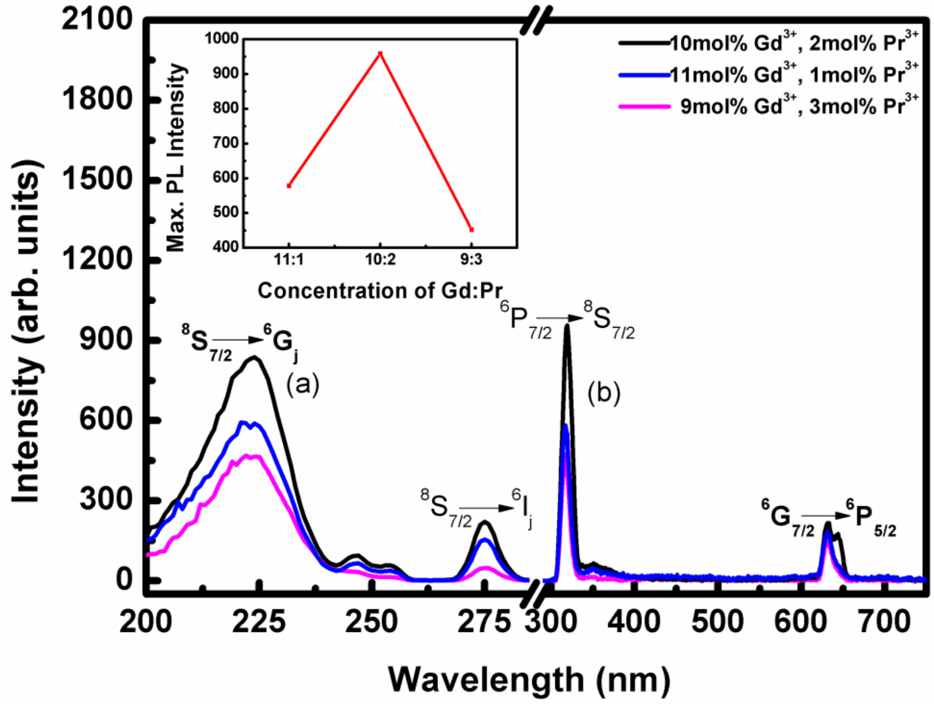

Fig 4. PL (a) excitation and (b) emission spectra of Ca$_5$(PO$_4$)$_3$OH:Gd^{3+}, Pr^{3+} .

4. Conclusion

In summary, Ca$_5$(PO$_4$)$_3$(OH):Gd^{3+},Pr^3 phosphor was successfully synthesized via wet chemical method. Gd^{3+} exhibited a narrowband red emission at 610 nm in the Ca$_5$(PO$_4$)$_3$(OH):Gd^{3+}system and it exhibited a dual emission in the UV (316 nm) and in the visible region (610 nm) in the Ca$_5$(PO$_4$)$_3$(OH):Gd^{3+},Pr^{3+} phosphor. The UV emission was more intense than the red emission. In addition, the UV emission was enhanced by energy transfer from Pr^{3+}.

5. Acknowledgement

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6. References

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