Enhancement of Pr^{3+} red emission by adding In^{3+} as co-dopant in $CaTiO_3:Pr^{3+}$ phosphor

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Abstract. A single red emission peak of calcium titanate doped with praseodymium ions is observed around 613 nm. Photoluminescence (PL) enhancement of $CaTiO_3:Pr^{3+}$ was obtained by the addition of In^{3+} as a co-dopant. The orthorhombic structure of the phosphor was confirmed by X-ray diffraction spectroscopy, and the PL properties were investigated using a PL spectrometer. The maximum concentration of Pr^{3+} ions that is necessary to obtain the optimal PL intensity was 0.2 mol% and 0.1 mol% for In^{3+} ions.

1. Introduction

The red emitting orthorhombic perovskite (figure 1a) calcium titanate ($CaTiO_3$) doped with trivalent praseodymium (Pr^{3+}) ions, is known to have a single narrow red emission peak at 613 nm coming from the $^1D_2 \rightarrow {}^3H_4$ transition of Pr^{3+}[1,2]. It is promoted by the complete quenching of the $^3P_0$ level (figure 1b) through the intervalence charge transfer state (IVCT) induced by orbital overlapping of Pr^{3+} and Ti^{4+} ions inside the $CaTiO_3$ matrix [1,2].

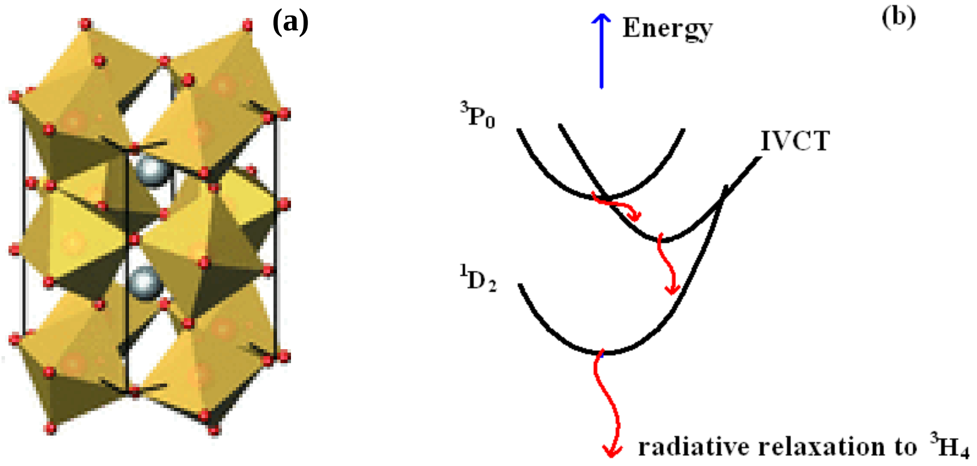

Figure 1: Orthorhombic $CaTiO_3$ crystal structure **(a)** and the IVCT model (b) [7]

This phosphor material has been around for some time, and the challenging goal for researchers is to enhance its emission intensity. This problem has been tackled in various ways, such as preparing $CaTiO_3:Pr^{3+}$ via different synthetic routes, and through charge compensation using different metal cations [3,4,7]. In the present work, we present the enhancement of $CaTiO_3:Pr^{3+}$ through charge compensation, using In^{3+} cations.

2. Experimental

$CaTiO_3$:0.2 Pr^{3+},0.1In^{3+} was obtained by varying different Pr^{3+} concentrations in $CaTiO_3$ ranging from 0.1, 0.2 to 0.5 mol%, to finally obtain an optimal concentration of 0.2 mol% Pr^{3+}. In^{3+} concentration was also varied from 0.05, 0.1, 0.2 and 0.3 mol% to obtain an optimal concentration of 0.1 mol% In^{3+}. These phosphors were prepared by solid state reaction at 1200 °C by directly firing a mixture of $CaCO_3$ and TiO_2 (Anatase phase) for 4h to fabricate $CaTiO_3$. Activation is achieved by adding $PrCl_3$, and charge compensation is achieved by adding $In(NO_3)_3$.

The phase was identified using a Bruker, AXS D8 Advance X-ray diffractometer (XRD). The luminescence properties were investigated using a Varian Carry-Eclipse fluorescent spectrometer for Photoluminescence (PL) measurements.

3. Results and Discussion

3.1. Structure

The phase formation of the synthesized $CaTiO_3:Pr^{3+}$ phosphors co-doped with different In^{3+} ions are shown in the XRD patterns (figure 2), which match the well known orthorhombic perovskite structure of $CaTiO_3$ phase described by the JCPDS card no. 22-0153. According to these patterns, full phases were formed for each material and the incorporated In^{3+} ions into the matrixes had negligible effect.

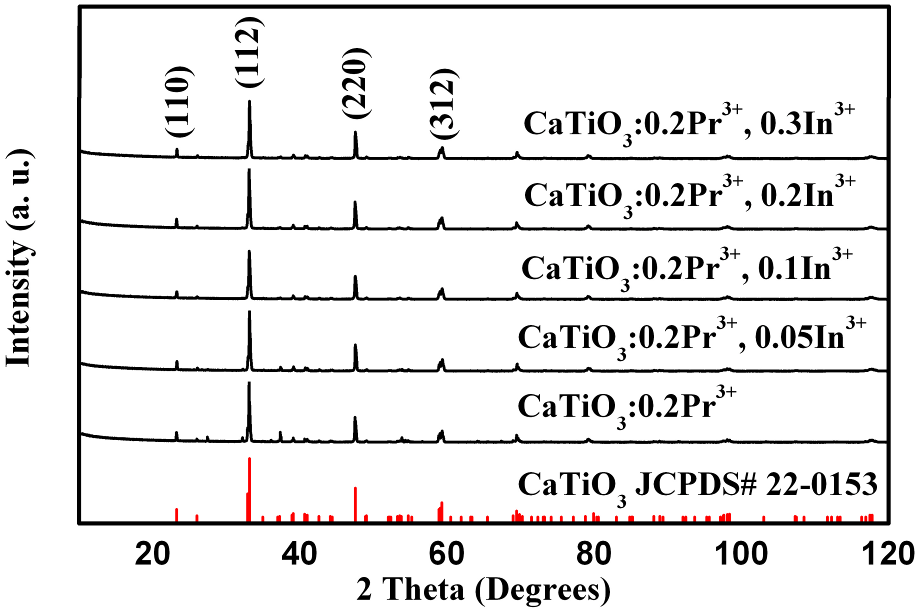

Figure 2: XRD pattern of $CaTiO_3:Pr^{3+}$ with different In^{3+} concentrations as indicated.

3.2. Pr $^{3+}$emission enhancement

Substitution of the trivalent Pr^{3+} ions in the site of the divalent Ca^{2+} ions brings about charge imbalance, by generating more positive charge in the system. This forces the matrix to compensate for such by generating positive O vacancies, and negative Ti and Ca vacancies that act as luminescence quenching centers. At higher Pr^{3+} concentrations there are more negative vacancies being formed and the distance between neighboring Pr^{3+} ions becomes smaller. This leads to more quenching centers than at lower concentration, and the shortened distance between neighboring Pr^{3+} increases the chances of the two Pr^{3+} ions to trap an electron between them. The trapped carrier between Pr^{3+} ions will then non-radiatively de-excite to ground state because of phonon interaction. Figure 3 a&b, show spectra of $CaTiO_3$ doped with different Pr^{3+} concentrations, and were measured using a medium photon multiplier (PMT) voltage. The optimal concentration is obtained as 0.2 mol%, and for concentrations higher than 0.2 mol% the luminescence decreases. This is attributed to concentration quenching [3,4].

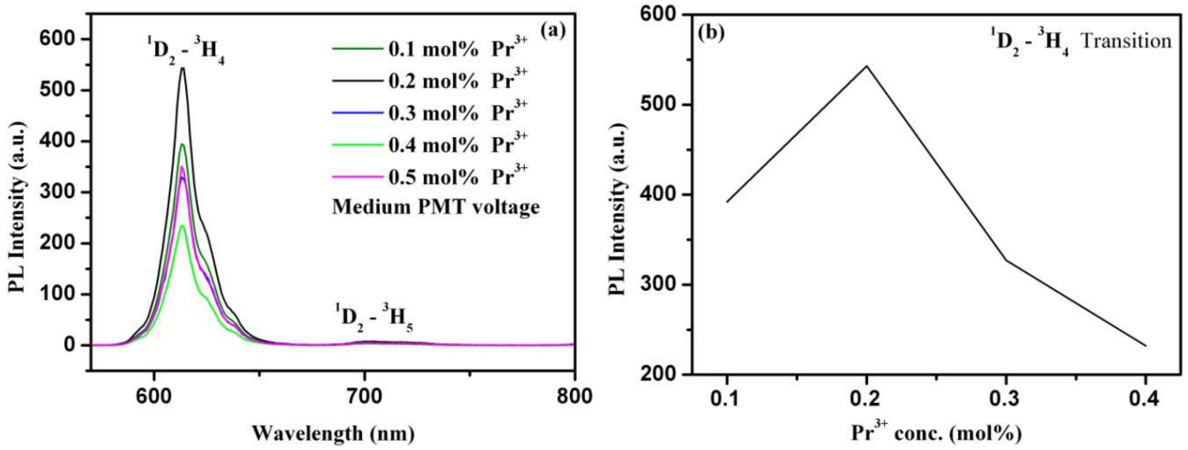

Figure 3: (a) PL spectra of $CaTiO_3$ doped with different Pr^{3+} concentration and (b) PL maximum intensity as a function of Pr^{3+} concentration.

The 613 nm single red emission of Pr^{3+} ions doped in $CaTiO_3$ (figure 3a & 4a) is related to the intervalence charge transfer state (IVCT) that provides an efficient quenching channel for the non – radiative depopulation of the ^3P_o level by a cross over to the $^1D_2$ level at room temperature and this results into the observed single red emission from the $^1D_2 \rightarrow {}^3H_4$ transition [5].

3.3. *Charge compensation*

$CaTiO_3$ self compensates the charge imbalance by generating negatively charged calcium vacancies, by reducing Ti^{4+} to Ti^{3+} and also by generating positively charged oxygen vacancies. The Ti^{3+} titanium state induces the d → d transition that acts by re-absorbing the population of electrons from the excited states of Pr^{3+}, which later de-excite non-radiatively to the valence band and thereby acting as a luminescence quenching center. Addition of charge compensators to $CaTiO_3:Pr^{3+}$ acts by promoting energy transfer to the excited states of Pr^{3+} from the host material. Hence addition of In^{3+} cations enhances the PL intensity (figure 4 a&b) of $CaTiO_3:Pr^{3+}$ [1,4,5,6,8,9]. The spectra of In^{3+} co-doped $CaTiO_3:Pr^{3+}$ (figure 4a) were measured using a low photon multiplier (PMT) voltage.

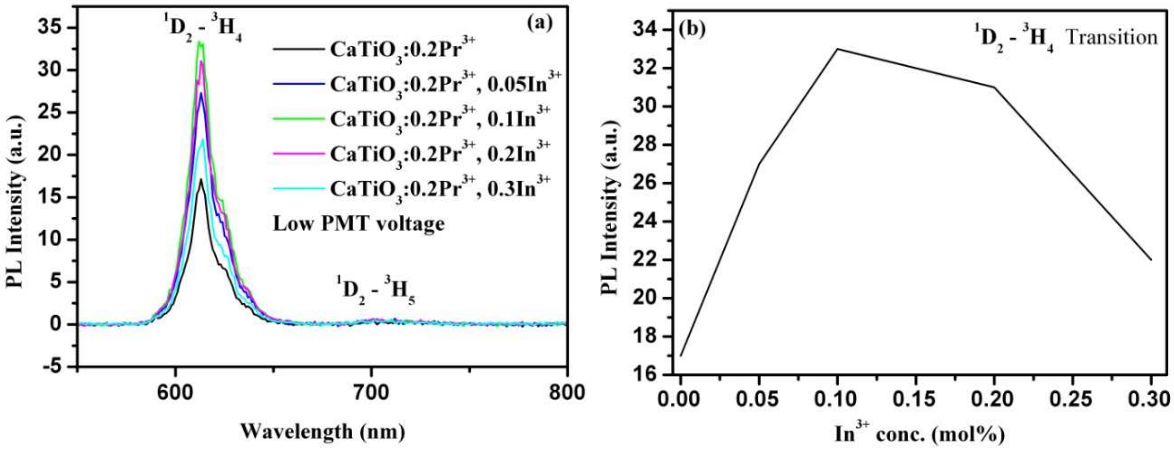

Figure 4: (a) PL spectra of $CaTiO_3$:0.2Pr^{3+} doped with different In^{3+} concentration and (b) PL intensity as a function of In^{3+} concentration.

4. Conclusion

$CaTiO_3$:Pr^{3+}, In^{3+} with a single red narrow emission peak at 613 nm was synthesized using solid state reaction at 1200 ^oC for 4h. Addition of In^{3+} in $CaTiO_3$:0.2Pr^{3+} showed significant enhancement in the emission of the phosphor. The optimal doping mole percentage of In^{3+} was found to be 0.1 mol%.

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