# Luminescent properties of $Pr^{3+}$ doped $SrF_2$ prepared by different synthesis techniques.

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**Abstract**.  $Pr^{3+}$  doped Strontium fluoride (SrF<sub>2</sub>) was prepared by hydrothermal and combustion methods. X-ray diffraction patterns indicated that the samples were completely crystallized with a pure face-centred cubic (space group: Fm3m) structure. Both SrF<sub>2</sub>:Pr<sup>3+</sup> samples exhibit blue-red emission centred at 488 nm under a 439 nm excitation wavelength ( $\lambda_{exc}$ ) at room temperature. The emission intensity of Pr<sup>3+</sup> was found to be dependent on the synthesis procedure. The blue-red emission decreased with an increase in the Pr<sup>3+</sup> concentration. This was attributed to the [ ${}^{3}P_{0}$ ,  ${}^{3}H_{4}$ ]  $\rightarrow$  [ ${}^{3}H_{6}$ ,  ${}^{1}D_{2}$ ] and [ ${}^{1}D_{2}$ ,  ${}^{3}H_{4}$ ]  $\rightarrow$  [ ${}^{1}G_{4}$ ,  ${}^{3}F_{3}$ , 4] cross-relaxation process that resulted from the smaller average interionic distances between the dopant ions.

## 1. Introduction

 $Pr^{3+}$  is an interesting ion because it has multiple transitions that allow for detailed studies of both radiative and non-radiative mechanisms.  $Pr^{3+}$  doped materials have been extensively investigated due to its potential use in a variety of applications [1, 2, 3, 4, 5]. For phosphor applications, the 4f – 4f transitions are the most relevant, especially the  ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$  in red emission from  $Pr^{3+}$  doped oxide materials [6, 7]. Fluoride based luminescent materials are also prominent amongst other candidates because they have lesser energy losses due to the non-radiative relaxation processes [8]. Different synthesis methods have been invented to prepare nanostructured fluoride materials that can be used as efficient luminescent materials [9, 10].

Recently, the  $Pr^{3+}$  ion is found to be a promising ion in the lanthanide-based luminescent materials for quantum cutting, which can be used to enhance the solar cell efficiency [1, 11]. The choice of a host material with lower vibrational energy, which can minimize the non-radiative transition, is very important for the quantum cutting procedure. Strontium fluoride (SrF<sub>2</sub>) has a very small cut-off phonon energy (~ 350 cm<sup>-1</sup>) and it was found to be a good host for the quantum cutting application [9]. The hydrothermal method is the most successful synthesis technique for the SrF<sub>2</sub> powders [12, 13, 14].

The  $SrF_2$ :  $Pr^{3+}$  system has been investigated by several researchers [5, 15, 16] and the majority reported the photon emission cascade and energy transfer mechanism in  $SrF_2$  doped with  $Pr^{3+}$  ions

(with the main focus on the  $4f^n - 4f^{n-1}5d$  emission). The 4f - 4f transitions have also been studied, but most of these results have been devoted to the red emission from  $Pr^{3+}$  doped oxide materials [6, 7, 17]. However, the application of  $Pr^{3+}$  in solar cells also requires knowledge of the 4f - 4f transitions. Hence, the information on 4f - 4f transitions are paramount important.

On the other hand, it has been shown that the probability of the multi-phonon relaxation between  ${}^{3}P_{0}$  and  ${}^{1}D_{2}$  levels of  $Pr^{3+}$  significantly decreases as the phonon energy of the host decreased [18]. It has also been observed that the emission intensity of the  ${}^{3}P_{0}$  state of  $Pr^{3+}$  doped host with a small phonon energy decreased with increasing the  $Pr^{3+}$  concentration, which was attributed to the cross-relaxation process [18, 19, 20, 21]. This behaviour normally occurs at the smaller average interionic distances between the  $Pr^{3+}$  ions.

Herein, the luminescent properties of  $Pr^{3+}$  doped  $SrF_2$  phosphor powders prepared by using both the hydrothermal and combustion methods are reported. In addition, the cross-relaxation mechanism from  ${}^{3}P_0$  level is also discussed.

## 2. Experimental

For the hydrothermal synthesis, analytical grade of  $Sr(NO_3)_2$ ,  $Pr(NO_3)_3.6H_2O$ ,  $NH_4F$ , sodium oleate, oleic acid and ethanol were used without further purification. For a typical synthesis of  $SrF_2:Pr^{3+}$ , ethanol, sodium oleate and oleic acid were added simultaneously to an aqueous solution containing  $Sr(NO_3)_2$  and  $Pr(NO_3)_3.6H_2O$ . After 10 min of stirring the milky colloidal solution was transferred to 125 ml autoclave lined with teflon and heated at 180  $^{\circ}C$  for 24 h. The product was collected by centrifugal and washed with water and ethanol. Finally, the product was dried for 24 h in an oven at 80  $^{\circ}C$ .

In combustion synthesis, an aqueous solution of  $NH_4F$  was added drop wise to a mixture of  $Sr(NO_3)_2$ ,  $Pr(NO_3)_3.6H_2O$  and urea, which was used as fuel. The milky solution was collected after thoroughly stirring. Then, the obtained solution was transferred into a porcelain crucible and placed in a furnace at 500  $^{\circ}C$  until the ignition occurred. Finally, the as-prepared powder was sintered for 2 h at 700  $^{\circ}C$ . The phosphors were characterized by X-ray diffraction (Bruker Advance D8) to identify the crystalline structure of the powder. The luminescence spectra from  $SrF_2:Pr^{3+}$  phosphors were collected using Photoluminescence (PL) spectroscopy (Cary Eclipse fluorescence spectrophotometer).

#### 3. Results and Discussion

The XRD patterns of the  $SrF_2:Pr^{3+}$  of both synthesis methods (hydrothermal and combustion) as well as the standard data for  $SrF_2$  (card No. 00-086-2418) are shown in figure 1. The sharp and strong diffraction peaks indicate that the sample powder is fully crystallized (face-centred cubic with space group: Fm3m). Doping of 0.1 mol% of  $Pr^{3+}$  causes a slight shift to a higher angle with comparison to the standard data (figure 1). This can be attributed to the radius difference between  $Pr^{3+}$  (0.099 nm) and  $Sr^{2+}$  (0.126 nm) ions, which confirms that  $Pr^{3+}$  ions are incorporated into the  $SrF_2$  lattice. The sintering temperature of the as-prepared hydrothermal sample caused a slight variation in the XRD intensities. The reason might be that, the orientation growth of the particles occurs in certain directions. The calculated  $SrF_2$  lattice parameters are (5.7744 ± 0.0054) Å and (5.764 ± 0.0025) Å for the samples prepared by the combustion and hydrothermal methods, respectively, indicating a small reduction in the unit cell in the hydrothermal method case.

The estimated particle sizes were calculated by using the diffraction peaks and Scherrer's equation [22]. These were found to be approximately 38 nm and 56 nm for samples prepared by hydrothermal and combustion methods, respectively. This shows that the hydrothermal method produces smaller particle size.



**Figure1**. XRD pattern of SrF<sub>2</sub>:Pr<sup>3+</sup> 0.1 mol% samples of both methods (a) hydrothermal and (b) combustion.

Figure 2(a), (b) and (c) show the excitation and emission spectra of the SrF<sub>2</sub> doped with different concentration of  $Pr^{3+}$  ions that were prepared by the combustion and the hydrothermal methods. Upon 439 nm excitation (into the <sup>1</sup>I<sub>6</sub> and <sup>3</sup>P<sub>j</sub>, j = 0, 1, 2), depopulation from the <sup>1</sup>I<sub>6</sub> and <sup>3</sup>P<sub>1, 2</sub> energy bands occurs to the metastable <sup>3</sup>P<sub>0</sub> energy band. Both samples exhibit blue–red emission from the <sup>3</sup>P<sub>0</sub> level. There are at least six luminescent bands that correspond to relaxation from the <sup>3</sup>P<sub>0</sub> emission energy band. These six bands are centered at 488, 524, 605, 638, 715 and 730 nm, which are assigned to the <sup>3</sup>P<sub>0</sub> $\rightarrow$ <sup>3</sup>H<sub>4</sub>, <sup>3</sup>P<sub>0</sub> $\rightarrow$ <sup>3</sup>H<sub>5</sub>, <sup>3</sup>P<sub>0</sub> $\rightarrow$ <sup>3</sup>F<sub>2</sub>, <sup>3</sup>P<sub>0</sub> $\rightarrow$ <sup>3</sup>F<sub>3</sub> and <sup>3</sup>P<sub>0</sub> $\rightarrow$ <sup>3</sup>F<sub>4</sub> transitions, respectively [11]. The band with weak intensity at around 690 nm is assigned to the <sup>1</sup>D<sub>2</sub> $\rightarrow$ <sup>3</sup>H<sub>5</sub> transition. This demonstrates that the dominant transition is the <sup>3</sup>P<sub>0</sub> transition. There is also a small peak marked with (**S**) around 879 nm (figure 1(b) and (c)), which is assigned to the <sup>3</sup>P<sub>0</sub> $\rightarrow$ <sup>1</sup>G<sub>4</sub> transitions [11], but in this work, we observed that its position changes with the excitation wavelength, which is exactly twice of the excitation wavelength ( $\lambda_{exc}$ ). The second order observation of the Pr<sup>3+</sup> system has also been previously reported on Pr<sup>3+</sup> doped YF<sub>3</sub>[2].

Figure 2(d) shows the Commission Internationale de l'Eclairage (CIE) coordinates plot for the  $SrF_2:Pr^{3+}$  phosphor prepared by (A) the hydrothermal (0.4 mol%) and (B) the combustion techniques with 0.2 mol% of the dopant. The corresponding coordinates are at (X = 0.25, Y = 0.45) and (X = 0.30, Y = 0.40), respectively. This shows that the cyan color for the hydrothermal method is removed in the  $Pr^{3+}$  emission during the combustion method. This can be ascribed to the emission intensity difference between these two methods.



**Figure 2.** Excitation and emission spectra of  $SrF_2:Pr^{3+}$  at different synthesis methods; (a) excitation spectrum, (b) emission spectrum for combustion method, (c) emission spectrum for hydrothermal method and (d) CIE chromaticity diagram for the  $SrF_2:Pr^{3+}$  under  $\lambda_{exc} = 439$  nm ((A) hydrothermal (X = 0.25, Y = 0.45) and (B) combustion (X = 0.30, Y = 0.40)). The inset graphs in (b) and (c) show the variation of the  $Pr^{3+}$  emission intensity as a function of the  $Pr^{3+}$  concentration.

The inset graphs in figure 2 show the  ${}^{3}P_{0} \rightarrow {}^{3}H_{4}$  emission intensity variation as a function of  $Pr^{3+}$  concentration. It is worth mentioning that all the samples were carefully synthesized and measured under the same condition for each preparation method so that the  $Pr^{3+}$  ion emission intensity can be compared. In the combustion method, the PL intensity of the  ${}^{3}P_{0}$  emission increased from 0.05 to 0.2 mol%  $Pr^{3+}$  concentration, whereas in the hydrothermal method it increased from 0.1 to 0.4 mol%  $Pr^{3+}$  concentrations. It then started to decrease systematically as the  $Pr^{3+}$  concentration increased (figure 2). A comparison of the  ${}^{3}P_{0} \rightarrow {}^{3}H_{4}$  emission intensity in both methods shows the hydrothermal synthesis has a higher optimal concentration, which demonstrates that the hydrothermal synthesis gives rise to higher absorption strength. This difference in the intensity optimization can be associated to the dissimilarity of the synthesis procedure, which confirms that the emission intensity is strongly

dependent on the synthesis procedure [11]. The recent solid state synthesis of  $SrF_2:Pr^{3+}$  reported that the optimal concentration of  $Pr^{3+}$  was found to be 0.1 mol% [11]. However, the increase in the PL intensity reflects the increase of the luminescent centers of  $Pr^{3+}$  with increasing the  $Pr^{3+}$  concentration [17], whereas, the decrease in the  ${}^{3}P_{0}\rightarrow{}^{3}H_{4}$  emission intensity indicates the quenching of the luminescence intensity. In fact, the quenching of  ${}^{3}P_{0}$  emission intensity can occur through three different processes: (1) relaxation by multi-phonon emission to the  ${}^{1}D_{2}$  level, (2) cross-relaxation between  $Pr^{3+}$  pairs and (3) energy transfer to the killer sites [20, 23], where the latter two rely on the  $Pr^{3+}$  concentration in the host lattice. As it is mentioned earlier the probability of the multi-phonon process significantly reduces as the phonon energy of the host decreases [18]. However, the energy difference between  ${}^{3}P_{0}$  and  ${}^{1}D_{2}$  is around 3500 cm<sup>-1</sup> and the energy cut-off of the  $SrF_{2}$  is about 350 cm<sup>-1</sup>, therefore, ten phonons are required to bridge the energy gap. Hence, the multi-phonon relaxation processes for the  ${}^{3}P_{0}$  and  ${}^{1}D_{2}$  levels can be considered negligible. Therefore, the  ${}^{3}P_{0}$  emission quenching might occur due to the cross-relaxation mechanism between the  $Pr^{3+}$  pairs. This kind of non-radiative mechanism depends on the distance that separates the neighboring  $Pr^{3+}$  ions.



A possible cross-relaxation mechanism that may occur in the  $Pr^{3+}$  ions is schematically shown in figure 3. The  $[{}^{3}P_{0}, {}^{3}H_{4}] \rightarrow [{}^{3}H_{6}, {}^{1}D_{2}]$  cross-relaxation process is already suggested for similar system such as  $Pr^{3+}$ -doped yttrium aluminum garnet (YAG) and gadolinium gallium garnet (GGG) [18, 24]. The  ${}^{1}D_{2}$  level can be populated, which in turn could be easily depopulated via the  $[{}^{1}D_{2}, {}^{3}H_{4}] \rightarrow [{}^{1}G_{4}, {}^{3}F_{3, 4}]$  pathway [18]. Hence, one can conclude that the weak peak around 690 nm is a result of  $[{}^{3}P_{0}, {}^{3}H_{4}] \rightarrow [{}^{3}H_{6}, {}^{1}D_{2}]$  cross-relaxation process. The decrease in the emission intensity of  $Pr^{3+}$  doped materials has been reported by various researchers [19, 20, 21]. Chen et al. [25] reported that an increase in  ${}^{3}P_{0}$  and  ${}^{1}D_{2}$  emission intensity was observed with increasing the  $Pr^{3+}$  concentration up to 0.3 mol %. The total fluorescence quenching was observed for the  ${}^{1}D_{2}$  state at 10 mol% [25]. R. Naccache et al. [18] found that the average  $Pr^{3+} - Pr^{3+}$  distance in GGG crystalline samples dramatically decreased as the  $Pr^{3+}$  concentration increased. Consequently, the cross-relaxation process

is more likely to occur in the most concentrated nano-crystals. Such information could be important for the optimization of the  $Pr^{3+}$  concentration in nano-crystalline materials for certain applications.

# 4. Conclusion

The SrF<sub>2</sub>:  $Pr^{3+}$  powder was prepared by hydrothermal and combustion methods. The XRD patterns showed strong and sharp diffraction peaks for both samples, which indicate that the powders were completely crystallize with a pure face-centred cubic (space group: Fm3m) structure. In comparison between these two methods, the calculated particle sizes showed smaller particles for the hydrothermal technique. It was found that both samples exhibit blue–red emission under 439 nm from 4f – 4f excitation at 425 to 500 nm. It was also showed that the  ${}^{3}P_{0} \rightarrow {}^{3}H_{4}$  emission intensity quenching might be due to the cross-relaxation process.

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