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Enhanced Pr\textsuperscript{3+} photoluminescence by energy transfer in SrF\textsubscript{2}:Eu\textsuperscript{2+}, Pr\textsuperscript{3+} phosphor

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Efficient energy transfer was demonstrated in the SrF\textsubscript{2}:Eu\textsuperscript{2+}, Pr\textsuperscript{3+} phosphor synthesized by the co-precipitation method. Results obtained with X-ray diffraction (XRD), scanning electron microscopy (SEM), x-ray spectroscopy (XPS), photoluminescence (PL) and decay curves proposed the UV-Vis energy transfer process. The energy transfer process between the Eu\textsuperscript{2+} and Pr\textsuperscript{3+} ions in SrF\textsubscript{2} was investigated to evaluate the potential of the Eu\textsuperscript{2+} ion as a sensitizer for the Pr\textsuperscript{3+} ion. The results proposed that Eu\textsuperscript{2+} could be a good sensitizer for absorbing the UV photons and efficiently enhancing the Pr\textsuperscript{3+} emission intensity. The energy transfer process was effective until concentration quenching for the Pr\textsuperscript{3+} ions occurred. The concentration quenching was attributed to cross-relaxation between the Pr\textsuperscript{3+} ions. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4941833]

I. INTRODUCTION

Phosphor materials prepared by doping inorganic hosts with lanthanide ions have brought much attention due to their various applications.\textsuperscript{1–3} One of these applications is the use of lanthanide ions to boost the efficiency of the Si solar cells.\textsuperscript{3–5} Pr\textsuperscript{3+}\textendash{}Yb\textsuperscript{3+} down-conversion couple doped inorganic host have been extensively investigated for solar cell application.\textsuperscript{6,7} SrF\textsubscript{2}: Pr\textsuperscript{3+}\textendash{}Yb\textsuperscript{3+} reported as one of the best down-conversion phosphor materials.\textsuperscript{6,7} In SrF\textsubscript{2}: Pr\textsuperscript{3+}\textendash{}Yb\textsuperscript{3+} absorption of a blue photon results in feeding two Yb\textsuperscript{3+} ions, which gives rise to the emission of two near infrared photons with an efficiency close to 200%. The weak absorption cross-section of the 4f-4f transition of the Pr\textsuperscript{3+} ion is, however, an obstacle to investigate such a promising efficiency enhancement. One suggestion to investigate is to add a third sensitizer.\textsuperscript{4,8} Eu\textsuperscript{2+} could be used as a sensitizer because it shows a fully allowed 4f-5d transition.\textsuperscript{9,10} This transition strongly depends on the crystal field of the matrix. The efficient energy transfer between a sensitizer and a donor can only occur when the emission band of the sensitizer overlap with the excitation band of the donor. For examples, in CaS host the emission band of Eu\textsuperscript{2+} appears at longer wavelength (yellow emission),\textsuperscript{11} which makes it not suitable to sensitize \textsuperscript{3}P\textsubscript{j} levels of Pr\textsuperscript{3+}. Eu\textsuperscript{2+} has been successfully used as a sensitizer to feed Pr\textsuperscript{3+} in different host for various applications.\textsuperscript{12,13} W. Xu et al demonstrated efficient energy transfer from Eu\textsuperscript{2+} to Pr\textsuperscript{3+} in chalcohalide glasses.\textsuperscript{12} For solar cell application, Y. Chen et al.\textsuperscript{13} demonstrated efficient energy transfer between the Eu\textsuperscript{2+} and Pr\textsuperscript{3+} couple in LiSrPO\textsubscript{4} powder that resulted in NIR emission from \textsuperscript{1}D\textsubscript{2} and \textsuperscript{1}G\textsubscript{4} levels of Pr\textsuperscript{3+}. We have recently shown that Eu\textsuperscript{2+} doped SrF\textsubscript{2} host emits a blue colour centred at 416 nm.\textsuperscript{10} Pr\textsuperscript{3+} is capable of emitting when excited at blue region,\textsuperscript{14} which overlaps the emission wavelength range of Eu\textsuperscript{2+}. Thus, the sensitization of Eu\textsuperscript{2+} on Pr\textsuperscript{3+} in SrF\textsubscript{2} is very likely to occur.

SrF\textsubscript{2} stands out as an excellent host for various lanthanide ions due to its wide transparency window in visible spectrum and further reduced multiphonon relaxation rates as compared to other hosts such as YPO\textsubscript{4} and CaMoO\textsubscript{4}.\textsuperscript{15–17} The YPO\textsubscript{4} and CaMoO\textsubscript{4} hosts have relatively high

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multi phonon relaxation but they can be prepared at a very low temperature.\textsuperscript{17,18} In SrF\textsubscript{2} crystals, lanthanide ions form clusters in SrF\textsubscript{2} as a result of the need for charge compensation when divalent Sr\textsuperscript{2+} is substituted by trivalent Pr\textsuperscript{3+}.\textsuperscript{7} The clustering might enhance the probability that Pr\textsuperscript{3+}-ion is in close proximity to the Eu\textsuperscript{2+} neighbours, which is very likely to improve the energy transfer between the two ions. In this work, the possibility of using the Eu\textsuperscript{2+} ion as a sensitizer for the Pr\textsuperscript{3+} ion in the SrF\textsubscript{2} system are presented. This work therefore serves as a requirement in preparation for the quantum cutting effect in the Pr\textsuperscript{3+}-Yb\textsuperscript{3+} couple in the SrF\textsubscript{2} host.

II. EXPERIMENTAL SETUP

For the co-precipitation process, analytical grade of Sr(NO\textsubscript{3})\textsubscript{2}, Pr(NO\textsubscript{3})\textsubscript{3}, 6H\textsubscript{2}O, Eu(NO\textsubscript{3})\textsubscript{3}, 6H\textsubscript{2}O and NH\textsubscript{4}F were used without further purification. Sodium hydroxide was used to adjust the pH of the system, which were 8.5 in this study. For a typical synthesis of SrF\textsubscript{2}:Eu\textsuperscript{2+}, Pr\textsuperscript{3+}, 30 mmol of NH\textsubscript{4}F and 0.1 mol/mL of sodium hydroxide were added drop-wise to an aqueous solution containing Sr(NO\textsubscript{3})\textsubscript{2} and Pr(NO\textsubscript{3})\textsubscript{3}, 6H\textsubscript{2}O and Eu(NO\textsubscript{3})\textsubscript{3}, 5H\textsubscript{2}O in a period of about 30 min. After one hour of stirring, the mixture was left for 5 hours. Then the product was collected by using a centrifugal and washed with water and ethanol. Finally, the product was dried for 48 hours in an oven at 80 \(^\circ\text{C}\). The samples were annealed under a reducing atmosphere (Ar 95%/H\textsubscript{2} 5%) for 2 hours in order to reduce Eu\textsuperscript{3+} into Eu\textsuperscript{2+} ions.

The phosphors were characterized by X-ray diffraction (XRD) (Bruker Advance D8 diffractometer with Cu K\textsubscript{α} radiation (\(\lambda = 0.154 \text{ nm}\)) to identify the crystalline structure of the powder. The morphology and elemental composition of the materials were analysed using JEOL JSM-7800F high field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive x-ray spectrometer (EDS). High resolution x-ray photoelectron spectroscopy (XPS) was obtained with a PHI 5000 Versaprobe system. A low energy Ar\textsuperscript{+} ion gun and low energy neutralizer electron gun were used to minimize charging on the surface. A 100 \(\mu\text{m}\) diameter monochromatic Al K\textsubscript{α} x-ray beam (\(hν = 1486.6 \text{ eV}\)) generated by a 25 W, 15 kV electron beam was used to analyze the different binding energy peaks. The pass energy was set to 11 eV giving an analyzer resolution of \(\leq 0.5 \text{ eV}\). Multipack version 8.2 software was utilized to analyze the spectra to identify the chemical compounds and their electronic states using Gaussian–Lorentz fits. Diffuse reflection spectra were measured using a Lambda 950 UV–vis spectrophotometer with spectralon as the reference material. Photoluminescence spectra (PL) were collected using a Cary Eclipse fluorescence spectrophotometer equipped with a xenon lamp. Luminescence decay curves of Eu\textsuperscript{2+} were recorded under pulsed excitation (HORIBA scientific) with 375LH NanoLED diode with a 375 nm excitation wavelength. While, the luminescence decay curves of Pr\textsuperscript{3+} were measured under pulsed excitation using a diode pumped YAG laser with a 335 nm excitation wavelength, power of 1.3 milliwatt and a SR430 Multichannel scalar photomultiplier (Linköping, Sweden). All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

The XRD patterns of the SrF\textsubscript{2}:Eu\textsuperscript{2+}, Pr\textsuperscript{3+} phosphor powder as well as the standard data for SrF\textsubscript{2} (card No. 00-086-2418) are shown in figure 1. The doped samples crystallized into the face centred cubic phase with the Fm3m space group and a lattice parameter of 5.794 \(\pm 0.0054 \text{ nm}\). Bragg’s law was used to determine the inter planar spacing d (which considered to be an experimental value because it depends on 20 measured experimentally)

\[ nλ = 2d\sin\theta \]

where \(n\) is an integer determined by the order given, \(λ\) is the wavelength of the x-rays, \(d\) is the spacing between the planes in the atomic lattice, and \(θ\) is the angle between the incident ray and the scattering planes. The lattice constant was obtained using the standard formula for the cubic system as all lattice parameters are the same, this is

\[ 1/d^2 = (h^2 + k^2 + l^2)/a^2 \]
where $a$ is the lattice spacing of the cubic crystal, and $h$, $k$, and $l$ are the Miller indices of the Bragg plane.

It can also be seen that all observed peaks match well with the reference data, which indicates that there was no obvious influence of the dopants on the crystalline structure of the host.

SEM images were obtained in order to investigate the surface morphology of the phosphors. Figure 2(a) shows the SEM image of SrF$_2$ co-doped with 1.5 mol% and 4 mol% concentrations of Eu$^{2+}$ and Pr$^{3+}$ respectively. The image shows that the powder consisted of agglomerated spherical particles with a diameter bigger than 100 nm. Figure 2(b) depicts the elemental analysis of the samples using EDS. Representative peaks associated to F, Eu, Pr and Sr elements are clearly identified. The EDS result confirmed the presence of Sr, F, Eu and Pr in the sample powder. EDS can however not differentiate between the oxidation states of the elements.

Eu can occur in the divalent (Eu$^{2+}$) and in the trivalent (Eu$^{3+}$) states, while Pr can occur in the trivalent (Pr$^{3+}$) and tetravalent (Pr$^{4+}$) states. Both the oxidation states of Eu are optically active and were detected in the SrF$_2$ host in a study previously done by the authors and it was reported in investigations done by other researchers. In the Pr ions only the Pr$^{3+}$ oxidation state is optically active, while the Pr$^{4+}$ state acts as quenching center on the materials. The XPS technique is a suitable technique to investigate the oxidation states of the lanthanide ions in compounds. XPS analysis was therefore performed to investigate the conversion of the Eu$^{3+}$ to Eu$^{2+}$ ions as well as the optically active Pr$^{3+}$ ions of Pr. All the Gaussian percentages were assumed to have a combined Gaussian-Lorentzian shape during the deconvolution of the peaks. The high resolution XPS peaks of Eu 3d and Pr 3d are shown in figure 3. The high resolution XPS peaks of Pr 3d consists of two spin-orbit splitting peaks of 3d$_{5/2}$ and 3d$_{3/2}$. Peak deconvolution showed the two main peaks, $m$ and $m'$, the satellite peaks, $s$ and $s'$, and an extra peak that exist only as the 3d$_{3/2}$ component, $t'$. The $s$ and $s'$ satellite structures are known to occur from strong mixing of the two final states of 3d$^9$4f$^2$ and 3d$^9$4f$^3$, while the $t'$ structure was claimed to be caused by the multiplet effect. All these peaks are characteristics of the Pr$^{3+}$ ions.

Figure 3(b) shows the peak deconvolution for the Eu 3d high resolution XPS peaks. The Eu 3d peak consists of two peaks that originated from the spin-orbit splitting, 3d$_{5/2}$ and 3d$_{3/2}$. Peak deconvolution showed the two main peaks, $m$ and $m'$, the satellite peaks, $s$ and $s'$, and an extra peak that exist only as the 3d$_{3/2}$ component, $t'$. In our previous XPS investigation of as-prepared SrF$_2$:Eu phosphors powders the Eu also showed both the two oxidation states, Eu$^{2+}$ and Eu$^{3+}$. In figure 3(b), the peaks labelled as Eu$^{3+}$ 3d$_{5/2}$ and Eu$^{3+}$ 3d$_{3/2}$ state that can hardly be seen are the main peaks of the Eu$^{3+}$ oxidation state. This result confirms that the conversion process of Eu$^{3+}$ to Eu$^{2+}$ occurred.

Figure 4 shows the excitation and emission spectra of the singly doped Pr$^{3+}$ ions whose charge was compensated locally by the F ions. The excitation spectrum of SrF$_2$:Pr$^{3+}$ (dotted line) was obtained by monitoring the emission centred at 488 nm ($^3P_0$→$^3H_4$ transition). The observed excitation bands correspond to the transitions of $^3H_4$→$^3P_j$ ($j = 0, 1, 2$) and $^1I_6$. All these bands
occurred within the 4f–4f transitions of the Pr^{3+} ion. Upon excitation with 439 nm (into 3P_j), depopulation from higher energy bands occurred to the metastable 3P_0 energy band. The emission bands centred at 488, 524, 605, 638, 715 and 730 nm were due to the 3P_0→3H_j, 3P_0→3H_5, 3P_0→3H_6, 3P_0→3F_2, 3P_0→3F_3, and 3P_0→3F_4 transitions, respectively. All the observed emission peaks originated mostly from the 3P_0 energy level. This demonstrates that the dominant transition in SrF_2 is the 3P_0 transition.

The excitation and emission spectra of Eu^{2+} in SrF_2 crystal are shown in figure 5. The spectra clearly consist of broad excitation and emission bands centred at 332 and 416 nm, respectively. It is well known that such broad excitation and emission bands are mainly originating from the inter-configuration 4f^65d→4f^7 allowed transition of Eu^{2+} ion. The inset graph in figure 5 shows the emission intensity variation as a function of Eu^{2+} concentration. The maximum luminescence intensity occurred for the sample doped with 1.5 mol% and a further increase in concentration resulted in a decrease in Eu^{2+} emission intensity.

Figure 6 compares the excitation and emission spectra of Pr^{3+} and Eu^{2+} singly doped SrF_2. It is worth noting that the emission band of Eu^{2+} overlaps with the excitation band of the 3P_j (j = 0, 1, 2) Pr^{3+} ion. This result is strong evidence to show that the Eu^{2+} ion should be a good sensitizer for the Pr^{3+} ion under 332 nm excitation. To study the energy transfer efficiency for the Eu^{2+}-Pr^{3+} couple a series of powder samples were prepared with 1.5 mol% of Eu^{2+} and various Pr^{3+} (0, 1, 2, 3, 5, 7 and 10 mol%) concentrations. In figure 7, the emission spectra of Eu^{2+} (4f^65d→4f^7 transition) and Pr^{3+}:4f-4f transition with varied Pr^{3+} concentrations are shown under identical conditions. The emission spectra of Pr^{3+} co-doped SrF_2, figure 7(b), shows the characteristic 3P_0 emission line of
FIG. 3. XPS High resolution peaks for the (a) Pr 3d and (b) Eu 3d ions in the SrF$_2$:1.5 mol% Eu, 4 mol% Pr$^{3+}$ phosphor powder.

Pr$^{3+}$ that correlates well with the emission spectra for the Pr$^{3+}$ ion singly doped sample, as was shown in figure 4. From figure 7(a) it can be seen that the Eu$^{2+}$ emission (4f$^6$5d $\rightarrow$ 4f$^7$ transition) decreased significantly with the increased Pr$^{3+}$ concentration. The Pr$^{3+}$ emissions were enhanced steadily with an increase P$_2$ concentration. This is shown in the inset of figure 7(b) where the emission spectra of Pr$^{3+}$ (3P$_0$ $\rightarrow$ 1H$_4$ transition) are plotted as a function of Pr$^{3+}$ concentration. The increase in Pr$^{3+}$ concentration resulted in a concentration quenching effect that occurs at higher doping concentrations (around 2 mol%). This can be attributed to the cross-relaxation caused by the interactions between the nearby Pr$^{3+}$ ions. Due to the nature of the Pr$^{3+}$ energy levels the concentration quenching between the Pr$^{3+}$ ions in fluoride and oxide hosts occurred at relatively low Pr$^{3+}$ concentration (maximum 0.4 mol%).

The optimal intensity obtained for the Pr$^{3+}$ doped SrF$_2$ crystal was 0.4 and 0.2 mol% when prepared by hydrothermal and combustion synthesis techniques, respectively. The Eu$^{2+}$ co-doped SrF$_2$:Pr$^{3+}$ in the current study enhanced the Pr$^{3+}$ optimal intensity and hence improved the Pr$^{3+}$: 4f-4f absorption strength. A good estimation of this enhancement is obtained by calculating the ratio of the integrated emission intensity of Eu$^{2+}$ luminescence (between 388 and 550 nm) for a sample without Pr$^{3+}$ to the integrated Pr$^{3+}$ luminescence (between 460-800 nm) for a sample
co-doped with Eu\(^{2+}\) and Pr\(^{3+}\). The highest value was for samples doped with 2 mol\% Pr\(^{3+}\), which also indicates that the Pr\(^{3+}\) emission intensity was quenched as a result of concentration quenching due to cross-relaxation between the Pr\(^{3+}\) ions.

Figure 7(c) portrays a comparison between the PL spectra of the SrF\(_2\):Eu\(^{2+}\) (1.5 mol\%), Pr\(^{3+}\) (0.3 mol\%) and 0.3 mol\% Pr\(^{3+}\) singly doped in SrF\(_2\) excited by 332 and 439 nm, respectively. The emission bands of Pr\(^{3+}\) in SrF\(_2\) were clearly observed in both spectra. All the Pr\(^{3+}\) emission bands were significantly enhanced in the co-doped sample. The biggest enhancement is for the 488 nm band (\(^3\)P\(_0\)→\(^3\)H\(_4\) transition). A comparison between the total calculated intensity emissions revealed that the Pr bands in the co-doped sample have been enhanced by nearly six times. Figure 7(c) also includes the emission spectrum of the SrF\(_2\):Pr\(^{3+}\) (0.3 mol\%) without Eu\(^{2+}\) excited at 332 nm. It clearly shows that Eu\(^{2+}\) well enhanced the emission of Pr\(^{3+}\) in the co-doped sample. All these results demonstrate that efficient energy transfer occurred from the Eu\(^{2+}\) to the Pr\(^{3+}\) ions.

More evidence for the energy transfer between the Eu\(^{2+}\) and Pr\(^{3+}\) ions are reported in figure 8, where the photoluminescence excitation (PLE) spectra of the Pr\(^{3+}\) singly doped and co-doped with Eu\(^{2+}\) in SrF\(_2\) crystal are plotted. Three excitation bands at 439, 468 and 484 nm were detected for the Pr\(^{3+}\) singly doped SrF\(_2\) phosphor when the Pr\(^{3+}\) emission wavelength of 488 nm was monitored. These peaks are due to the absorption transition of \(^3\)H\(_4\)→\(^3\)P\(_2\), \(^3\)H\(_4\)→\(^3\)P\(_0\) and \(^1\)I\(_6\), and \(^3\)H\(_4\)→\(^3\)P\(_0\), respectively. These excitation bands were slightly weakened in the co-doped phosphor.
FIG. 6. Spectral overlap between Eu\(^{2+}\) emission and Pr\(^{3+}\) excitation in the SrF\(_2\) crystal structure.

The co-doped system showed a much broader excitation band, which was attributed to the Eu\(^{2+}\): 4f\(^7\) → 4f\(^6\)5d absorption transition. The Eu\(^{2+}\) co-doping phosphor enhances the excitation cross-section of the system compared to that of the Pr\(^{3+}\) singly doped phosphor. This could be due to the stronger 4f\(^7\) → 4f\(^6\)5d transition, which confirms therefore most of the energy, will be absorbed by the Eu\(^{2+}\) ions, resulting in the weakened Pr\(^{3+}\) excitation peaks.\(^{12}\) It might also be one of the reasons that lead to the Pr\(^{3+}\) emission enhancement in the co-doped samples.

Luminescence decay curves that were measured for the Eu\(^{2+}\) emission 5d energy level contributed further towards the energy transfer efficiency process with different Pr\(^{3+}\) ion concentrations. In general, the decay time of the sensitizer ions does not change in the presence and absence of the donor ions if the radiative energy is dominant.\(^{30}\) Whereas, in the case of non-radiative energy transfer the decay time of sensitizer ions gradually decreases with increasing the donor concentration. In figure 9(a), the decay curves are shown for SrF\(_2\):Eu\(^{2+}\) (1.5 mol\%) co-doped with 0, 1, 2, 5, 7 and 10 mol\% Pr\(^{3+}\). The decay time for the singly doped Eu\(^{2+}\) was 435 ns. This decay time was due to radiative decay from the 4f\(^6\)5d\(^1\) (T\(_{2g}\)) level, which is in agreement with reported values for the decay time of Eu\(^{2+}\) emission.\(^{31}\) Co-doping with Pr\(^{3+}\) induced faster decay, which can be attributed to the energy transfer from Eu\(^{2+}\) to Pr\(^{3+}\). An estimation for the energy transfer efficiency can be obtained from \(\eta_{ET} = 1 - \tau_x/\tau_0\) as outline in reference.\(^{30,32}\) Here, \(\tau_x\) and \(\tau_0\) are the corresponding lifetimes of Eu\(^{2+}\) in the presence and absent of Pr\(^{3+}\), respectively. The corresponding energy transfer efficiency were 28, 39, 59, 65 and 79\% for samples with 1, 2, 5, 7 and 10 mol\% Pr\(^{3+}\), respectively. This shows that the Eu\(^{2+}\)–Pr\(^{3+}\) energy transfer was efficient at high Pr\(^{3+}\) concentrations, but that the Pr\(^{3+}\) emission was quenched due to concentration quenching. The luminescence decay curves of Pr\(^{3+}\) revealed further details into the concentration quenching between Pr\(^{3+}\) ions. In figure 9(b), the decay curves for Pr\(^{3+}\) in the co-doped samples with 0.3, 1, 2, 5 and 10 mol\% Pr\(^{3+}\) are depicted. It can be seen that the decay curve for 0.3 and 1 mol\% are identical and nearly single exponential decay, which demonstrates that there is no interaction between the Pr\(^{3+}\) ions in these doping concentrations. The Pr\(^{3+}\) ion started to interact at around 2 mol\% and that can be seen in the decay curve for 2 mol\%, which has a little bit faster decay. Higher concentrations, however, demonstrated that the concentration quenching of Pr\(^{3+}\) emission intensity occurred due to the cross-relaxation between the Pr\(^{3+}\) ions. The afterglow emission is attributed to the trapping and gradual release of the electrons by the electron trapping centers to the luminescence centers, from where the observed emission originates. The existence of the electron trapping centers in these materials is attributed to the existence of the positively charged vacancies with an energy that resides within the bandgap of the electronic structure of the phosphor. The vacancies are formed within the material as intrinsic defects. Eu\(^{2+}\) doped in some inorganic hosts (such as CaAl\(_2\)O\(_4\)) has afterglow phenomena. Because
FIG. 7. (a) Emission spectra of the 1.5 mol% Eu$^{2+}$ in SrF$_2$ with varied Pr$^{3+}$ concentration, (b) emission spectra of Pr$^{3+}$ co-doped samples with increasing Pr$^{3+}$ concentration and (c) a comparison between Pr$^{3+}$ singly doped (α) and co-doped (β) ions in SrF$_2$. The inset graph in (b) is a variation of Pr$^{3+}$ ($^3P_0$→$^3H_4$) emission intensity as a function of the Pr$^{3+}$ concentration for SrF$_2$ containing 1.5 mol% Eu$^{2+}$.

Ca$^{2+}$ vacancies are present in CaAl$_2$O$_4$:Eu$^{2+}$. Holes are trapped and transported to emission centers via Ca$^{2+}$ vacancies and then recombined with electrons. The doped Pr$^{3+}$ brings about the defects Pr$_{Ca}$ and Ca$^{2+}$ vacancies, among which the Ca$^{2+}$ vacancy captures energy and transfers it to emission centers of Eu$^{2+}$, improving the afterglow properties of CaAl$_2$O$_4$:Eu$^{2+}$. In SrF$_2$ an electron trapped at an F-vacancy because when it is doped by Ln$^{3+}$ the charge was compensated locally.
**FIG. 8.** PLE spectra of the SrF$_2$:0.3 mol% Pr$^{3+}$ and SrF$_2$:1.5 mol% Eu$^{2+}$, 2.0 mol% Pr$^{3+}$ samples.

**FIG. 9.** Decay curves of (a) Eu$^{2+}$ 5d (monitoring 416 nm emission) under 355 nm excitation and (b) Pr$^{3+}$ $^3P_0\rightarrow^1H_4$ (monitoring 488 nm emission) under 375 nm excitation.
FIG. 10. Simplified energy level diagram of Eu$^{2+}$ and Pr$^{3+}$ showing a possible energy transfer between Eu$^{2+}$ and Pr$^{3+}$ ions and a possible cross-relaxation mechanism between the Pr$^{3+}$ ions.

by the F ions. Thus, in SrF$_2$ host the trap center is at a relatively high energy. Upon excitation of SrF$_2$:Eu$^{2+}$ phosphor with a blue photon, direct Eu$^{2+}$ excitation occurs and Eu$^{2+}$ emits a broadband emission originating from the fully 5d-4f allowed transition, which is characterized by fast emission rates. This is called fluorescence. Thus, the short lifetime is for Eu$^{2+}$ ions not from the afterglow phenomena.

A detailed energy transfer processes from Eu$^{2+}$ to Pr$^{3+}$ and the possible cross-relaxation mechanism that may occur between the Pr$^{3+}$ ions are schematically shown in figure 10. Upon 332 nm excitation, the absorbed UV photon energy by Eu$^{2+}$ is likely transferred to excited states of Pr$^{3+}$ ($^1$I$_6$ and $^3$P$_j$, $j = 0, 1, 2$) through resonant energy transfer from Eu$^{2+}$ (4f$^5$5d) to Pr$^{3+}$ ($^3$P$_2$). The other energy transfer pathway is due to the cross-relaxation process between the Eu$^{2+}$ to Pr$^{3+}$ energy levels: [4f$^5$5d,$^3$I$_6$] $\rightarrow$ [4f$^6$S$_{7/2}$,$^3$P$_2$]. These two energy transfer pathways result in the enhanced Pr$^{3+}$ emission via the $^3$P$_2$ $\rightarrow$ $^1$I$_6$ and $^3$P$_j$ ($j = 0, 1$) non-radiative process. This process has also been reported recently by W. Xu et. al.$^{22}$ for GeS$_2$-GeS$_2$-CsCl chalocohalide glasses co-doped with Pr$^{3+}$ and Eu$^{2+}$. However, we propose two cross-relaxation processes that are mostly responsible to reduce the $^3$P$_0$ emission intensity of Pr$^{3+}$ ions in the SrF$_2$ matrix. The first cross-relaxation possibility is [$^3$P$_0$,$^3$I$_6$] $\rightarrow$ [$^3$H$_{6/2}$,$^1$D$_2$] as indicated in figure 10 (pathway 1). The [$^3$P$_0$,$^3$I$_6$] $\rightarrow$ [$^3$H$_{6/2}$,$^1$D$_2$] cross-relaxation process is a suggestion taken from literature for Pr$^{3+}$-doped yttrium aluminium garnet (YAG) and gadolinium gallium garnet (GGG).$^{33,34}$ Another de-activating pathway within a Pr-Pr pair is the [$^3$P$_0$,$^3$I$_6$] $\rightarrow$ [$^1$G$_4$,$^1$G$_4$] cross-relaxation process as is shown in figure 10 (pathway 2). This pathway was also a suggestion taken from literature for a Pr$^{3+}$ doped KYb(WO$_4$)$_2$ crystal.$^{35}$ The present results showed efficient energy transfer from Eu$^{2+}$ to Pr$^{3+}$. The $^3$P$_0$ emission intensity has increased and then decreased. The decreased intensity of Pr$^{3+}$ emission bands at higher Pr$^{3+}$ concentration was due to the cross-relaxation process between Pr$^{3+}$ ions. A. Guille et. al.$^8$ demonstrated energy transfer between the Ce$^{3+}$-Pr$^{3+}$ couple in CaYAlO$_4$ powders and thin film. The energy transfer followed by a cross relaxation process that involves the 4f levels of the Ce$^{3+}$ ion, lead to the sensitization of the $^1$D$_2$ level of the Pr$^{3+}$ ion. The process was explained by the fact that the Ce$^{3+}$ donor has two 4f ground states ($^2$F$_{5/2}$ and $^2$F$_{7/2}$) separated with the same energy as the energy level of Pr$^{3+}$ ($^3$P$_0$ and $^3$D$_2$). As a result, the cross-relaxation Ce$^{3+}$:{$^2$F$_{5/2}$$\rightarrow$$^2$F$_{7/2}$} $\rightarrow$ Pr$^{3+}$ : {$^3$P$_0$$\rightarrow$$^3$D$_2$} populates the $^1$D$_2$ level of the Pr$^{3+}$ ion. They conclude that the energy transfer process from this level to the Yb$^{3+}$ ion is possible but it would not lead to the quantum cutting process. This reduces their potential for application in solar cell. In this study it was shown that the energy transfer from the Eu$^{2+}$ to Pr$^{3+}$ ions sensitized the transition from the $^3$P$_0$ level of the Pr$^{3+}$ ion where the quantum cutting process towards the Yb$^{3+}$ ion via resonance and cross-relaxation energy transfer is likely to occur. Therefore, Eu$^{2+}$ can be used as an efficient sensitizer to feed the Pr$^{3+}$ ions and...
therefore it might improve the NIR absorption of the Pr$^{3+}$–Yb$^{3+}$ couple in SrF$_2$ for solar cell application. Further investigations on the Pr$^{3+}$–Yb$^{3+}$ couple in SrF$_2$ will therefore be done in our future research study.

**IV. CONCLUSION**

It was successfully demonstrated that efficient energy transfer occurred from the 5d band of the Eu$^{2+}$ ions toward the 3$P_1$ levels of the Pr$^{3+}$ ion. The energy transfer was likely to be followed by a cross-relaxation process between the Pr$^{3+}$ ions. The Eu$^{2+}$ ions could be an efficient sensitizer to the Pr$^{3+}$ ions and hence increased the excitation cross-section of the Pr$^{3+}$ ions. This might then result in a quantum cutting process for the Pr$^{3+}$–Yb$^{3+}$ couple in the SrF$_2$ crystal.

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