Surface Characterization and Photoluminescence Properties of Ce$^{3+}$,Eu Co-Doped SrF$_2$ Nanophosphor

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Abstract: SrF$_2$:Eu,Ce$^{3+}$ nanophosphors were successfully synthesized by the hydrothermal method during down-shifting investigations for solar cell applications. The phosphors were characterized by X-ray diffraction (XRD), scanning Auger nanoprobe, time of flight-secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) spectroscopy. XRD showed that the crystallite size calculated with Scherrer’s equation was in the nanometre scale. XPS confirmed the formation of the matrix and the presence of the dopants in the SrF$_2$ host. The PL of the nanophosphor samples were studied using different excitation sources. The phenomenon of energy transfer from Ce$^{3+}$ to Eu$^{2+}$ has been demonstrated.

Keywords: SrF$_2$; cerium; TOF-SIMS; XPS; shake-down; energy transfer

1. Introduction

Strontium fluoride (SrF$_2$) is one of the most widely used optical materials because of its interesting luminescent, optical, and physical properties. It has a wide band gap, low phonon energy, low
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2. Results and Discussion

The refraction index, high radiation resistance, and good mechanical strength [1,2]. The photoluminescence properties of SrF$_2$ doped by Ln$^{3+}$ ions have been extensively investigated in which charge compensation is required when Ln$^{3+}$ ions substitute Sr$^{2+}$ cation. This gives rise to a rich multisite structure. It has therefore been considered as a good phosphor host material that can be doped by a number of lanthanide ions for various luminescent applications [1–4]. SrF$_2$ host material doped with Ce$^{3+}$ lanthanide ions is an example of a phosphor material that is extensively being investigated specifically for light amplification [5,6]. Some of these light amplification studies proposed that the SrF$_2$:Ce$^{3+}$ phosphor material could be a promising scintillator [5]. Shendrik et al. [5] reported efficient scintillation light output of SrF$_2$:Ce$^{3+}$ with high temperature stability suggesting that this material can be applied in well-logging scintillation detectors. They have also reported that the optimal Ce$^{3+}$ doping level for maximum luminescence was 0.3 mol% if prepared by the Stockbarger method. Ce$^{3+}$ ions in SrF$_2$ showed a fully allowed broad band 4f–5d transition [5] and this transition strongly absorbs UV radiation that results in a high absorption coefficient.

In the other hand, several previous studies have described the luminescence of Eu$^{3+}$ doped materials as a good downshifting ion [7–10]. Gao et al. [7] reported luminescence due to transitions from the $^5$D$_0$ excited level to the $^7$F$_J$ levels, where spectral conversion of 325–550 nm light to 570–710 nm light has been demonstrated. In our previous investigation of SrF$_2$:Eu we reported the emissions from both the Eu oxidation states (Eu$^{3+}$ and Eu$^{2+}$) where emission from 400 to 710 nm was observed [10]. X-ray photoelectron spectroscopy (XPS) results confirmed that the samples contained both Eu$^{2+}$ and Eu$^{3+}$ ions. The Eu$^{3+}$ ion doped materials emits narrow emission peaks in the range of the orange-red emission with large Stokes shifts (>150 nm) that originates from the 4f–4f weak absorption transitions [11,12], whereas the 4f–5d absorption transition of the Eu$^{3+}$ ion in SrF$_2$ is situated at the far ultraviolet region, which can be less accessible. In some applications, high or suitable absorption cross-section is needed and this requires a sensitizer with a high absorption coefficient [2,9,13]. Therefore, the presence of the Eu$^{2+}$ and Eu$^{3+}$ ions in the SrF$_2$ host greatly enhanced the emission intensity of Eu$^{3+}$ at high concentrations [10]. In this work, Ce$^{3+}$ singly and co-doped Eu in SrF$_2$ was prepared by using the hydrothermal method. The surface and photoluminescence properties are discussed.

2. Results and Discussion

2.1. Structure Analysis

2.1.1. X-Ray Diffraction (XRD)

Figure 1 shows the XRD patterns of un-doped and doped SrF$_2$ as well as the standard data for SrF$_2$ from card 00-086-2418. Doping with Ce- or Eu ions as well as the co-doped systems result in a small shift to higher angles with comparison to the un-doped sample and the standard data. This can be attributed to the radius difference between Eu (Eu$^{2+}$ is 0.125 nm, Eu$^{3+}$ is 0.107 nm), Ce$^{3+}$ (0.114 nm) and Sr$^{2+}$ (0.126 nm) ions, which confirms that Eu- and Ce ions are successfully incorporated into the SrF$_2$ lattice. It should be mentioned that doping with Eu- and Ce ions (up to 10 mol%) does not change the structure of the SrF$_2$ host in this study. The calculated SrF$_2$ lattice parameter is found to be (5.785 ± 0.005) Å and this agreed well with the reported value of (5.7996 ± 0.0001) Å [14].
The estimated average crystallite size ($S$) for pure and doped SrF$_2$ is calculated by using the diffraction peaks and Scherrer’s equation [15], $S = 0.9\lambda/\beta \cos \theta$. $S$ is the average crystallite size of the SrF$_2$ particles, $\lambda$ is the wavelength of the X-rays (0.154 nm) and $\beta$ is the full-width at half maximum of the X-ray peak at the Bragg angle $\theta$. The average crystallite size of the pure SrF$_2$ was found to be 7.6 nm. The XRD peaks broaden with increasing the dopants ions (see Figure 1). The broadening of the XRD peaks were also observed by other groups [16,17]. H.A.A. Seed Ahmed et al. [16] attributed the XRD peak broadening to impurity broadening. Whereas, F. Wang et al. [17] assigned the XRD peak broadening to reduction in the nanoparticle size of the matrix. In our previous investigation of Eu doped SrF$_2$ samples, we assigned the XRD broadening as a result of a decrease in particle size of the matrix, which agreed well with F. Wang et al. [10]. Therefore, in the current study we can also assign these peaks’ broadening to reduction in particle size of the matrix. The particle size reduced up to 3.9 nm for the SrF$_2$ sample that was doped with 0.7 mol% Ce$^{3+}$ and 10 mol% Eu.

2.1.2. Auger and TOF SIMS analysis

An Auger profile of Ce and Eu co-doped SrF$_2$ was done to identify the sample’s composition. The Auger spectrum of the SrF$_2$:Ce$^{3+}$,Eu is presented in Figure 2. The Auger peaks at 71, 1515, 1644 and 1713 eV are assigned to Sr while the F peak is situated at 656 eV [18]. The Auger spectrum not only confirmed the formation of the host matrix, but also showed the presence of the dopants. The Eu peaks were at 111, 142, 853 and 985 eV, while the peak at 89 eV corresponds to Ce. In addition C and O were also observed. The C contamination is attributed to adventitious hydrocarbons and the O is considered to be a common impurity in a fluoride compound [19,20]. The presence of the O in the sample did not change the structure of the sample (see Figure 1). Therefore, the O contamination was due to adventitious impurity species in the surface rather than oxygen impurity in the SrF$_2$ matrix.
2.1.3. X-ray Photoelectron Spectroscopy (XPS)

XPS measurements have been done in order to investigate the chemical composition and bonding state of the SrF2:Ce,Eu phosphor powders. A higher dopant concentration (5 mol% for both Eu and Ce) was used in order to obtain a reasonable signal from the dopants. Figure 3 shows the peak fits for the (a) Sr 3d, (b) F 1s, (c) Eu 3d and (d) Ce 3d high resolution XPS peaks. The results also confirmed the presence of the host matrix elements (Sr and F) as well as the dopants (Eu and Ce) to their corresponding binding energies. During the peaks fit procedure, the C 1s peak at 284.8 eV was taken as a reference for all charge shift corrections. This is done because the C 1s peak resulted from hydrocarbon contamination and its binding energy generally remains constant, irrespective to the chemical state of the sample. In addition to that, all the Gaussian percentages were assumed to have a combined Gaussian-Lorentzian shape. The high resolution XPS peak for the Sr 3d showed two individual peaks. These two peaks are assigned to Sr 3d in SrF2 that originate from the spin-orbit splitting 3d_{5/2} (133.5 eV) and 3d_{3/2} (135.3 eV), while the F 1s peak is situated at 684.7 eV. The spin-orbit splitting of Sr 3d is about 1.78 eV, it is in a good agreement with reported value of 1.75 eV [21].

The peak deconvolution for the Eu 3d high resolution XPS peaks are shown in Figure 3c. The 3d level of Eu ion is composed of four peaks. These four peaks can be attributed to Eu^{3+} and Eu^{2+} spin-orbit splitting 3d_{5/2} and 3d_{3/2} core level, respectively [21–24]. The spin-orbit splitting for both oxidation states Eu^{3+} and Eu^{2+} is about 29.96 eV. The Eu 3d results showed good agreement with our previous XPS investigation of SrF2:Eu phosphors powder where Eu composed of its two oxidation states (Eu^{2+} and Eu^{3+}) [10].
The Ce $3d$ high resolution peak is shown in Figure 3d. The strong peaks correspond to the photoemission from the Ce$^{3+}$ $3d$ state. Due to the spin-orbit interaction, the Ce$^{3+}$ $3d$ photoemission peak consisted of two peaks that are assigned to the $3d_{3/2}$ and $3d_{5/2}$ peaks with $4f^1$ final states, with an intensity ratio $I(3d_{5/2})/I(3d_{3/2}) = 3/2$ [22,25,26]. The spin-orbit splitting value ($\approx 18.15$ eV) is in good agreement with the estimated value ($\approx 18.10$ eV). The energy peaks labelled SD are due to the strong Coulomb interaction between photoemission in the $3d$ level and electrons located near the Fermi level. These peaks originate from the screening of the $3d$ level by valence band electrons to the $4f$ states [22]. This is possible due to hybridization of the Ce $4f$ level with the conduction band states [26]. In the photoemission nomenclature, these peaks are a result from what is called, shake-down process [22]. The $3d$ shake-down peaks behave the same as the $3d$ spin-orbit splitting peaks but they are a result from the $3d^{9}4f^2$ final state. Therefore, the SD peaks can be assigned to the $3d_{3/2}$ and $3d_{5/2}$ XPS peaks with $4f^2$ final states and this is in accordance with previous work done in Ce [25,26]. The shoulder peaks marked as A is related to the F KLL Auger electron peak. The XPS peak positions, area distributions and chemical bonding for all the peaks in as-prepared SrF$_2$:Ce,Eu are tabulated in Table 1.
### Table 1. XPS peak position, area distribution and chemical bonding of as-prepared SrF₂:Ce,Eu phosphor powder.

| Element | B.E (±0.1 eV) | Area distribution | Interpretation                        |
|---------|---------------|-------------------|---------------------------------------|
| F1s     | 684.7         | 2688              | F in SrF₂                              |
| Sr3d    | 133.5         | 1986              | Sr 3d<sub>5/2</sub> in SrF₂            |
|         | 135.3         | 1311              | Sr 3d<sub>3/2</sub> in SrF₂            |
| Eu3d    | 1123.3        | 1613              | Eu<sup>2+</sup> 3d<sub>5/2</sub> in fluoride |
|         | 1133.05       | 1372              | Eu<sup>3+</sup> 3d<sub>5/2</sub> in fluoride |
|         | 1153.2        | 1064              | Eu<sup>2+</sup> 3d<sub>3/2</sub> in fluoride |
| Ce3d    | 1163.0        | 905               | Eu<sup>3+</sup> 3d<sub>3/2</sub> in fluoride |
|         | 880.3         | 1296              | Shake-down satellite                   |
|         | 884.8         | 5141              | Ce<sup>3+</sup> 3d<sub>5/2</sub> in fluoride |
|         | 898.5         | 855               | Shake-down satellite                   |
|         | 903.0         | 3393              | Ce<sup>3+</sup> 3d<sub>3/2</sub> in fluoride |
|         | 876.1         | 1592              | F KLL<sub>1</sub>L<sub>1</sub> Auger electron peak |

#### 2.2. Photoluminescence Spectroscopy

##### 2.2.1. SrF₂:Ce<sup>3+</sup>

The emission and excitation spectra of the Ce<sup>3+</sup> singly doped SrF₂ nanophosphor are shown in Figure 4. The excitation spectrum consists of a prominent peak that is centred at 295 nm. This peak has been previously assigned to Ce<sup>3+</sup>:4f–5d excitation transition in SrF₂ [27]. By exciting the samples by 295 nm, a broad band emission peak is observed, which is attributed to the inter-configuration 5d<sup>1</sup>–4f<sup>4</sup> allowed transition of Ce<sup>3+</sup> ions. The inset graph in Figure 4 shows the emission intensity variation as a function of the Ce<sup>3+</sup> concentration. The maximum luminescence intensity occurred for the sample doped with 0.7 mol% and a further increase in concentration resulted in a decrease in Ce<sup>3+</sup> emission intensity. A previous study done by R. Shendrik et al. [5] on the SrF₂:Ce<sup>3+</sup> sample reported that Ce<sup>3+</sup> has a broad emission band that consist of two emission peaks (Ce<sup>3+</sup> 5d to 4f ground state (²F<sub>7/2</sub> and ²F<sub>5/2</sub>)) and the maximum intensity was observed at a Ce<sup>3+</sup> dopant concentration of 0.3 mol%. In this study, the peaks were broadened and they fully overlapped, which might be the reason that only one broad peak was observed.

##### 2.2.2. SrF₂:Ce,Eu

Figure 5a shows the PL emission spectra of SrF₂:Eu obtained by using the He-Cd laser PL system with a 325 nm excitation wavelength. The spectra clearly consist of a broad emission band that is centred at 416 nm with narrow bands in the range of 550–710 nm. The broad emission band is assigned to the inter-configuration 4f<sup>6</sup>5d<sup>1</sup>–4f<sup>7</sup> allowed transition of Eu<sup>2+</sup> [11,12] and the narrow emission bands to the Eu<sup>3+</sup> emission originating from the 4f–4f transition [28]. The Eu<sup>3+</sup> emission consists of orange–red emission bands that is attributed to the ⁵D<sub>0</sub>→⁷F<sub>J</sub> transitions (J = 1, 2, 3, 4). This implies that the SrF₂:Eu samples consist of both Eu oxidation states (Eu<sup>2+</sup> and Eu<sup>3+</sup>), with their emission ranging from 400 to 710 nm [10]. The Eu<sup>3+</sup> emission bands increased with an increase in the Eu dopant concentration in the SrF₂ matrix. This can also be seen in Figure 5b, where the emission of Eu<sup>3+</sup>
excited by 394 nm is portrayed. The PL emission intensity increased slightly at the lower concentrations but then increased dramatically at 10 mol%. The presence of both Eu oxidation states therefore strongly enhanced the emission intensity of the Eu$^{3+}$ ions. Detailed investigations on the luminescence phenomenon of Eu$^{3+}$ and Eu$^{2+}$ have previously been studied by various workers [10,29–31].

\[\text{Figure 4.} \text{ Excitation and emission spectra of the SrF}_2: \text{Ce}^{3+}(0.7 \text{ mol}) \text{ nanophosphor. The inset shows the 5d–4f transition’s emission intensity as a function of Ce}^{3+} \text{ concentration.}\]

\[\text{Figure 5.} \text{ Photoluminescence spectra of SrF}_2:x\text{Eu excited by (a) using the He-Cd laser system with 325 nm excitation wavelength and (b) the Cary Eclipse with a wavelength of 394 nm.}\]

Figure 6a depicts the PL emission of Ce$^{3+\text{(0.7%)}}$ co-doped SrF$_2$:xEu (where $x = 0.2\%, 0.6\%, 5\%$ and 10%) excited with the He-Cd laser system with a 325 nm wavelength. The spectra also consisted of both the Eu$^{2+}$ and Eu$^{3+}$ emissions. A shoulder peak (marked with a dollar sign ($\$\)) at a lower wavelength only appeared for the smaller dopant concentrations (0.2 and 0.6 mol%). This shoulder ($\$\) is assigned to the 4f–5d emission of Ce$^{3+}$, which is completely quenched at the higher Eu
concentration. With an increasing concentration of the Eu ions the relative PL emission intensity of the Eu\(^{2+}\) gradually decreased and the Eu\(^{3+}\) emission intensity increased. The emission intensity of the Eu\(^{3+}\) has dramatically increased at the high Eu doping concentration. This can clearly be seen in Figure 6b where the Eu\(^{3+}\) emission intensity plotted as function of Eu concentration for the Eu co-doped Ce\(^{3+}\) system. It can be noticed that Ce\(^{3+}\) co-doped SrF\(_2\):Eu greatly enhanced the Eu\(^{3+}\) ions emission intensity at high Eu concentration. The increase of the Eu\(^{3+}\) emission intensity with an increase in the Eu concentration can be attributed to an increase in the Eu\(^{3+}/\)Eu\(^{2+}\) ratio in the presence of the Ce\(^{3+}\) ions.

In the SrF\(_2\) crystal, the Sr\(^{2+}\) ion is located at the body centre of a cube of eight F\(^{-}\) ions. The trivalent Ln\(^{3+}\) ions normally replace the Sr\(^{2+}\) cation. The extra charge of the Ln\(^{3+}\) ions is compensated by F\(^{-}\) anion charges situated elsewhere in an interstitial site. With increasing Ln\(^{3+}\) concentration, some kind of structural deformation occurs, the Ln\(^{3+}\)-F dipoles couple to dimers, trimers and higher aggregates. The interstitial F\(^{-}\) ions and vacancies on the normal F\(^{-}\) site compose cuboctahedral clusters [32]. However, at low Eu concentration (less than Ce\(^{3+}\) concentration), the clusters are not completely formed. Besides, compare with the size of the Eu\(^{3+}\) (0.107 nm), the size of the Eu\(^{2+}\) (0.125 nm) is much closer to the size of the Sr\(^{2+}\) (0.126 nm), and hence the reduction of Eu\(^{3+}\) to Eu\(^{2+}\) ions is favored because it could reduce the lattice distortion of the doped SrF\(_2\) crystal [33]. At high Eu concentration (bigger than the Ce\(^{3+}\) concentration), the dimensions of the Eu\(^{3+}\) ions cluster increased and hence the ratio of Eu\(^{3+}\)/Eu\(^{2+}\) increased. The increase of the Eu\(^{3+}\) ions therefore increased the Eu\(^{3+}\) emission intensity.

The PL emission spectra of the SrF\(_2\):Ce\(^{3+}\),Eu nanophosphor excited by the 295 nm excitation wavelength are plotted in Figure 7a. The broad emission band that is centered at a wavelength of 330 nm is a characteristic of the Ce\(^{3+}\) ion which is in agreement with the emission spectra for Ce\(^{3+}\) in Figure 4. The additional broad peak beside the Ce\(^{3+}\) emission that was centered at 416 nm is assigned to the Eu\(^{2+}\) ions in SrF\(_2\) (clearly shown in the inset graph of Figure 7a). The Eu\(^{2+}\) emission slightly increased before it decreased with increasing Eu concentration. In Figure 7a the emission spectrum of

**Figure 6.** (a) PL spectra of SrF\(_2\):Ce\(^{3+}\) (0.7 mol%), xEu excited with the laser system with a 325 nm excitation wavelength and (b) 394 nm using the xenon lamp.
the SrF$_2$:Eu without Ce excited at 295 nm is also shown. It clearly shows no Eu$^{2+}$ emission has occurred. The presence of Eu$^{2+}$ emission under 295 nm excitation, in the co-doped samples, is therefore evidence of an energy transfer process from Ce$^{3+}$ to Eu$^{2+}$. This process can occur in such material since the emission of Ce$^{3+}$ overlaps the excitation spectra of Eu$^{2+}$ (Figure 7b; SrF$_2$:Ce$^{3+}$ (0.7 mol%), Eu (0.6 mol%)). Such spectral overlap is a necessary condition for the occurrence of the energy transfer from Ce$^{3+}$ to Eu$^{2+}$. An efficient energy transfer from Ce$^{3+}$ to Eu$^{2+}$ in a fluoride crystal was previously demonstrated even for a very low concentration [34]. More evidence of energy transfer between Ce$^{3+}$ and Eu$^{2+}$ is shown in Figure 7c where the room temperature luminescence excitation spectra of SrF$_2$:Ce$^{3+}$ (0.7 mol%), Eu (0.6 mol%) nanophosphors are plotted. The excitation spectrum of Eu$^{2+}$ (dotted line) not only consists of the Eu$^{2+}$:4f$^7$→4f$^6$5d excitation transition but also the Ce$^{3+}$ excitation band (clearly seen in the inset of the Figure 7c). All these results confirm the existence of energy transfer from Ce$^{3+}$ to the Eu$^{2+}$ ion.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** (a) PL emission spectra of Ce$^{3+}$ and Eu$^{2+}$ from SrF$_2$:Ce$^{3+}$ (0.7 mol%) with different Eu doping concentration as well as from Eu$^{2+}$ in SrF$_2$:Eu excited by an excitation wavelength of 295 nm; (b) Spectral overlap between Ce$^{3+}$ emission and Eu$^{2+}$ excitation and (c) excitation spectra of SrF$_2$:Ce$^{3+}$ (0.7 mol%), Eu (0.6 mol%) nanophosphors measured at an emission wavelength of 416 nm. The inset in (a) is the enlarge spectrum of the Eu$^{2+}$ emission ions and the inset in (c) is the enlarge Ce$^{3+}$ excitation from SrF$_2$:Ce$^{3+}$ (0.7 mol%), Eu (5.0 mol%).
Results obtained from the luminescence decay curves for Ce\(^{3+}\) emission also contributed further to the energy transfer process. The decay time of the donor ions does not change in the presence and absence of the acceptor ions if the radiative energy is dominant \[35\]. In the situation of non-radiative energy transfer the decay time of the donor ions gradually decreases with an increase in the acceptor concentration. The PL decay curves of Ce\(^{3+}\) with various Eu concentration are shown in Figure 8. The decay curve of the Ce\(^{3+}\) ions gradually decreased with an increase in the Eu concentration. The luminescence decay curve of Ce\(^{3+}\) singly doped SrF\(_2\) nanoparticles can well be fitted into a single-exponential function, shown in the inset of Figure 8, whereas the decay curve of the entire co-doped concentrations were fitted with a bi-exponential decay model \[35,36\]:

\[
I(t) = A_1 \exp\left(-t/\tau_1\right) + A_2 \exp\left(-t/\tau_2\right)
\]

\(I(t)\) is the luminescence intensity at time \(t\); \(A_1\) and \(A_2\) are constants; and \(\tau_1\) and \(\tau_2\) are the short- and long-decay components, respectively. The average lifetime constant (\(\bar{\tau}\)) can be calculated from the following equation:

\[
\bar{\tau} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}
\]

**Figure 8.** The decay lifetime of Ce\(^{3+}\) ions in the SrF\(_2\) host with an increase in Eu concentration. The inset graph shows the decay curve of 0.7% Ce\(^{3+}\) in SrF\(_2\) fitted to a single-exponential fitting function.

The lifetime of the Ce\(^{3+}\) doped SrF\(_2\) is determined to be 77.15 ns. This value is in good agreement with the reported value of Ce\(^{3+}\) in SrF\(_2\) \[27\]. In the Eu ions co-doped system, the average lifetime of the donor ion (Ce\(^{3+}\)) decreased up to 8.2 ns at 10 mol% Eu concentration. This results confirm that the excitation energy of Ce\(^{3+}\) ions was transferred to the Eu\(^{2+}\) ions. The lifetime results for the Ce\(^{3+}\) ions in the SrF\(_2\) host strongly suggest that the energy transfer from Ce\(^{3+}\) to Eu\(^{2+}\) was non-radiative. The energy transfer efficiency from Ce\(^{3+}\) to Eu is defined by the following expression:

\[
\eta_{ET} = 1 - \tau/\tau_0
\]
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where $\tau$ and $\tau_0$ are the average lifetime of Ce$^{3+}$ in the presence and absence of the Eu ions, respectively. The corresponding lifetime and energy transfer efficiencies are tabulated in Table 2. From Table 2, the energy transfer of Ce$^{3+}$ increased gradually with an increase in the Eu concentration. The maximum energy transfer efficiency is about 89.4% for the sample doped with 0.7 mol% Ce$^{3+}$ and 10 mol% Eu. An efficient energy transfer has occurred from Ce$^{3+}$ to Eu$^{2+}$. The emission of Eu$^{2+}$ has slightly increased before it decreased with increasing Eu concentration due to the decrease of the Eu$^{2+}$ ratio in the SrF$_2$ host. In our previous investigation of SrF$_2$:Eu the Eu$^{2+}$ ion was, however, found to be unstable when irradiated by a YAG laser. The Eu$^{2+}$ ion’s PL emission intensity rapidly decreased with time and this result made the SrF$_2$:Eu nanophosphor an unsuitable candidate for several applications, such as white light-emitting diodes and wavelength conversion films for silicon photovoltaic cells [10].

Table 2. Lifetime of the 5d–4f transition of Ce$^{3+}$ (330 nm) and the Ce$^{3+}$-Eu energy transfer efficiency ($\eta_{ET}$) in SrF$_2$ matrix.

| Eu concentration (mol%) | $\tau$ (ns) | $\eta_{ET}$ (%) |
|-------------------------|-------------|-----------------|
| 0                       | 77.15       | 0               |
| 1                       | 46.3        | 40              |
| 2                       | 31.9        | 58.6            |
| 5                       | 16.05       | 79.2            |
| 10                      | 8.2         | 89.4            |

3. Experimental Section

Doped and un-doped SrF$_2$ phosphor samples were synthesised by the hydrothermal method. For the hydrothermal process, all chemical reagents were of analytical grade and were used without further purification. For a typical synthesis, 1 mmol of Sr(NO$_3$)$_2$ was first dissolved in 30 mL distilled water, followed by 5 mmol of C$_{10}$H$_{14}$N$_2$O$_8$·2H$_2$O (Na$_2$EDTA, ethylenediamine tetraacetic acid disodium salt) and 2 mmol of NaBF$_4$ under constant stirring. After further magnetic stirring for 10 min the solution was transferred into a 125 mL autoclave lined with Teflon, heated at 160 °C for one hour and naturally cooled down to room temperature [37]. The product was collected by centrifugal and washed with water and ethanol. Finally, the product was dried for 10 h in an oven at 60 °C. Ce$^{3+}$ and Eu co-doped SrF$_2$ samples were prepared by the same hydrothermal technique. Eu(NO$_3$)$_3$(H$_2$O)$_5$ and Ce(NO$_3$)$_3$(H$_2$O)$_6$ were used as sources for the Eu and Ce dopants, respectively.

The phosphors were characterized by X-ray diffraction (XRD) (Bruker AXS GmbH, Karlsruhe, Germany) (Bruker Advance D8 diffractometer with Cu K$_\alpha$ radiation ($\lambda = 0.154$ nm)) to identify the crystalline structure of the powder. Auger spectra were collected with a PHI 700 Scanning Auger Nanoprobe (ULVAC-PHI Inc, Chanhassen, MN, USA) equipped with a scanning Auger microscope (SAM). The field emission electron gun used for the SAM analyses was set at: 2.34 A filament current; 4.35 kV extractor voltage and 381.4 µA extractor current. With these settings a 25 kV, 10 nA electron beam was obtained for the Auger analyses. The electron beam diameter was about 10 nm. An IonTof time of flight secondary ion mass spectrometer (TOF-SIMS) instrument (ION-TOF GmbH, Muenster, Germany) equipped with a Bi primary ion source was used to characterize the nanophosphor materials for their chemical composition and dopants distribution. In spectroscopy mode, the system equipped with a DC current of 30 nA and a pulsed current of 1 pA at 30 kV with a heating current of 2.95 A and
emission current of 0.8 μA was used. High resolution X-ray photoelectron spectroscopy (XPS) was obtained with a PHI 5000 VersaProbe system (ULVAC-PHI Inc, Chanhassan, MN, USA). A low energy Ar⁺ ion gun and low energy neutralizer electron gun were used to minimize charging on the surface. A 100 μm diameter monochromatic Al Kα 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 \( \leq 0.5 \text{ eV} \). Multipack version 8.2 software (ULVAC-PHI Inc, Chanhassan, MN, USA) was utilized to analyze the spectra to identify the chemical compounds and their electronic states using Gaussian-Lorentz fits. Photoluminescence spectra (PL) were collected using a Cary Eclipse fluorescence spectrophotometer (Varian Ltd, Mulgrave Victoria, Australia) equipped with a xenon lamp and also with a He-Cd laser PL system with a 325 nm excitation wavelength. Luminescence decay curves were recorded by using a NanoLED with a 335 nm excitation wavelength and repetition rate of 1 MHz. All measurements were performed at room temperature.

4. Conclusions

As-prepared SrF₂:Eu,Ce nanophosphors were successfully synthesised with the hydrothermal technique. The average crystallite size that was calculated by using Scherrer’s equation was found to be 7.6 nm for the host sample. Dopant ions were intended to decrease the particle size of the host. The Auger spectra confirmed the presence of Sr, F, Eu and Ce elements in the host matrix. Photoluminescence properties of Ce³⁺ and Eu co-doped SrF₂ nano-phosphor have been investigated. A possible efficient energy transfer from Ce³⁺ to Eu²⁺ ions was demonstrated. From the PL decay curves the energy transfer efficiency was calculated to be 89.4% for the SrF₂: 0.7 mol% Ce³⁺, 10 mol% Eu sample.

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Author Contributions

Hendrik C. Swart is the leader of the research group and supervisor of the PhD students and he helped with the data interpretation and writing of the paper. Elizabeth Coetsee is also one of the supervisors of the PhD students and she helped with the editing of the paper. Luyanda Noto helped with the TOF-SIMS analysis and discussion and Mubarak Y. A. Yagoub was mainly responsible for the planning, experimental part as well as writing the main part of the paper, the decay measurements were done with the help of Peber Bergman in his laboratory.

Conflicts of Interest

The authors declare no conflict of interest.
References

1. Ivanovskikh, K.V.; Pustovarov, V.A.; Krim, M.; Shulgin, B.V. Time-resolved vacuum ultraviolet spectroscopy of Er$^{3+}$ ions in the SrF$_2$ crystal. *J. Appl. Spectrosc.* **2005**, *72*, 564–568.

2. Van der Ende, B.M.; Aarts, L.; Meijerink, A. Near-infrared quantum cutting for photovoltaics. *Adv. Mater.* **2009**, *21*, 3073–3077.

3. Ivanovskikh, K.; Pustovarov, V.; Smirnov, A.; Shulgin, B. Inter- and intraconfigurational luminescence of trivalent rare earth ions doped into strontium fluoride crystals under vacuum ultraviolet excitation. *Phys. Stat. Soli C* **2007**, *4*, 889–892.

4. Kristianpoller, N.; Weiss, D.; Chen, R. Optical and dosimetric properties of variously doped SrF$_2$ crystals. *Radiat. Meas.* **2004**, *38*, 719–722.

5. Shendrik, R.; Radzhabov, E.A.; Nepomnyashchikh, A.I. Scintillation properties of pure and Ce$^{3+}$-doped SrF$_2$ crystals. *Radiat. Meas.* **2013**, *56*, 58–61.

6. Shendrik, R.; Radzhabov, E. Emission in CaF$_2$, BaF$_2$, SrF$_2$. *IEEE Trans. Nucl. Sci.* **2009**, *57*, 1295–1299.

7. Gao, D.; Zheng, H.; Zhang, X.; Fu, Z.; Zhang, Z.; Tian, Y.; Cui, M. Efficient fluorescence emission and photon conversion of LaOF:Eu$^{3+}$ nanocrystals. *Appl. Phys. Lett.* **2011**, *98*, 011907–011909.

8. Chung, P.; Chung, H.; Holloway, P.H. Phosphor coatings to enhance Si photovoltaic cell performance. *J. Vac. Sci. Technol. A* **2007**, *25*, 61–66.

9. Huang, X.Y.; Wang, J.X.; Yu, D.C.; Ye, S.; Zhang, Q.Y.; Sun, X.W. Spectral conversion for solar cell efficiency enhancement using YVO$_4$:Bi$^{3+}$,Ln$^{3+}$ (Ln = Dy, Er, Ho, Eu, Sm, and Yb) phosphors. *J. Appl. Phys.* **2011**, *109*, 113526–113532.

10. Yagoub, M.Y.A.; Swart, H.C.; Noto, L.L.; O'Connell, J.H.; Lee, M.E.; Coetsee, E. The effects of Eu-concentrations on the luminescent properties of SrF$_2$:Eu nanophosphor. *J. Lumin.* **2014**, *156*, 150–156.

11. Li, Y.C.; Chang, Y.H.; Lin, Y.F.; Chang, Y.S.; Lin, Y.J. Synthesis and luminescent properties of Ln$^{3+}$ (Eu$^{3+}$, Sm$^{3+}$, Dy$^{3+}$)-doped lanthanum aluminum germanate LaAlGe$_2$O$_7$ phosphors. *J. Alloys Compd.* **2007**, *439*, 367–375.

12. Jin, Y.; Qin, W.; Zhang, J. Preparation and optical properties of SrF$_2$: Eu$^{3+}$ nanospheres. *J. Fluor. Chem.* **2008**, *129*, 515–518.

13. Huang, X.; Han, S.; Huang, W.; Liu, X. Enhancing solar cell efficiency: The search for luminescent materials as spectral converters. *Chem. Soc. Rev.* **2013**, *42*, 173–201.

14. Rakov, N.; Guimaraes, R.B.; Franceschini, D.F.; Maciel, G.S. Er:SiF$_2$ luminescent powders prepared by combustion synthesis. *Mater. Chem. Phys.* **2012**, *135*, 317–321.

15. Oprea, C.; Ciupina, V.; Prodan, G. Investigation of nanocrystals using TEM micrographs and electron diffraction technique. *Rom. J. Phys.* **2008**, *53*, 223–230.

16. Seed Ahmed, H.A.A.; Ntwaeborwa, O.M.; Kroon, R.E. The energy transfer mechanism in Ce,Tb co-doped LaF$_3$ nanoparticles. *Curr. Appl. Phys.* **2013**, *13*, 1264–1268.

17. Wang, F.; Han, Y.; Lim, C.S.; Lu, Y.; Wang, J.; Xu, J.; Chen, H.; Zhang, C.; Hong, M.; Liu, X. Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping. *Nature* **2010**, *463*, 1061–1065.
18. Childs, K.D.; Carlson, B.A.; LaVanier, L.A.; Moulder, J.F.; Paul, D.F.; Stickle, W.F.; Watson, D.G. *Handbook of Auger Electron Spectroscopy*, 3rd ed.; Physical Electronics: Eden Peairie, MN, USA, 1995.

19. Kroon, R.E.; Swart, H.C.; Ntwaeaborwa, O.M.; Seed Ahmed, H.A.A. Ce decay curves in Ce, Tb co-doped LaF3 and the energy transfer mechanism. *Phys. B* 2014, 439, 83–87.

20. Van Wijngaarden, J.T.; Scheidelaar, S.; Vlugt, T.J.H.; Reid, M.F.; Meijerink, A. Energy transfer mechanism for downconversion in the (Pr3+, Yb3+) couple. *Phys. Rev. B* 2010, 81, 155112–155117.

21. Vasquez, R.P. SrF2 by XPS. *Surf. Sci. Spectr.* 1992, 1, 24–30.

22. Vercaemst, R.; Poelman, D.; van Meirhaeghe, R.L.; Fiermans, L.; Laflere, W.H.; Cardon, F. An XPS study of the dopants’ valence states and the composition of CaS1−xSe:x:Eu and SrSi1−xSe:x:Ce thin film electroluminescent devices. *J. Lumin.* 1995, 63, 19–30.

23. Lu, D.; Sugano, M.; Sun, X.Y.; Su, W. X-ray photoelectron spectroscopy study on Ba1−xEu2TiO3. *Appl. Surf. Sci.* 2005, 242, 318–325.

24. Zhang, J.; Yang, M.; Jin, H.; Wang, X.; Zhao, X.; Liu, X.; Peng, L. Self-assembly of LaBO3:Eu twin microspheres synthesized by a facile hydrothermal process and their tunable luminescence properties. *Mater. Res. Bull.* 2012, 47, 247–252.

25. Lässer, R.; Fuggle, J.C.; Beyss, M.; Campagna, M. X-ray photoemission from Ce core levels of CePd3, CeSe, CeAl2 and CeCu2Si2. *Phys. B C* 1980, 102, 360–366.

26. Gamza, M.; Slebarski, A.; Rosner, H. Electronic structure of Ce5Rh4Sn10 from XPS and band structure calculations. *Eur. Phys. J. B* 2008, 63, 1–9.

27. Zhang, C.; Hou, Z.; Chai, R.; Cheng, Z.; Xu, Z.; Li, C.; Huang, L.; Lin, J. Mesoporous SrF2 and SrF2:Ln3+ (Ln = Ce, Tb, Yb, Er) Hierarchical microspheres: Hydrothermal synthesis, growing mechanism, and luminescent properties. *J. Phys. Chem. C* 2010, 114, 6928–6936.

28. Dorenbos, P. Energy of the first 4f7 → 4f65d transition of Eu2+ in inorganic compounds. *J. Lumin.* 2003, 104, 239–260.

29. Dorenbos, P. Valence stability of lanthanide ions in inorganic compounds. *Chem. Mater.* 2005, 17, 6452–6456.

30. Baran, A.; Barzowska, J.; Grinberg, M.; Mahlik, S.; Szczodrakwski, K.; Zorenko, Y. Binding energy of Eu3+ and Eu5+ ions in β-Ca2SiO4 doped with europium. *Opt. Mater.* 2013, 35, 2017–2114.

31. Biswas, K.; Sontakke, A.D.; Sen, R.; Annapurna, K. Luminescence properties of dual valence Eu doped nano-crystalline BaF2 embedded glass-ceramics and observation of Eu2+→Eu3+ energy transfer. *J. Fluoresc.* 2012, 22, 745–752.

32. Pandey, C.; Dhopte, S.M.; Muthal, P.L.; Kondawar, V.K.; Moharil, S.V. Eu3+↔Eu2+ redox reactions in bulk and nano CaF2:Eu. *Radiat. Eff. Defects Solids* 2007, 162, 651–658.

33. Wang, X.; Wu, N.; Shimizu, M.; Sakakura, M.; Shimotsuma, Y.; Miura, K.; Zhou, S.; Qiu, J.; Hirao, K. Space selective reduction of europium ions via SrF2 crystals induced by high repetition rate femtosecond laser. *J. Ceram. Soc. Jpn.* 2011, 119, 939–941.

34. Caldino, U.G.; Gruz, C.D.; Monoz, G.H.; Rubio, J.O. Ce3+↔Eu2+ energy transfer in CaF2. *Solid State Commun.* 1989, 4, 347–351.

35. Zhou, J.; Xia, Z.; You, H.; Shen, K.; Yang, M.; Liao, L. Synthesis and tunable luminescence properties of Eu2+ and Tb3+-activated Na2Ca5(PO4)3F phosphors based on energy. *J. Lumin.* 2013, 135, 20–25.
36. Katsumata, T.; Nabae, T.; Sasajima, K.; Komuro, S.; Morikawa, T. Effects of composition on the long phosphorescent SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ Phosphor Crystals. *J. Electrochem. Soc.* **1997**, *144*, L243–L245.

37. Peng, J.; Hou, S.; Liu, X.; Feng, J.; Yu, X.; Xing, Y.; Su, Z. Hydrothermal synthesis and luminescence properties of hierarchical SrF$_2$ and SrF$_2$:Ln$^{3+}$ (Ln = Er, Nd, Yb, Eu, Tb) micro/nanocomposite architectures. *Mater. Res. Bull.* **2012**, *47*, 328–332.

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