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Near-infrared spectral downshifting in $Sr_{(3-x)}(VO_4)_2{:}_xNd^{3+}$ phosphor

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Abstract. In this study, the spectral downshifting (DS) from ultraviolet (UV) light to near-infrared (NIR) radiation in $Sr_3(VO_4)_2{:}Nd^{3+}$ phosphor is reported. The prepared materials were characterized by X-ray powder diffraction (XRD) and photoluminescence (PL) properties along with steady state luminescence time decay curves were studied, which confirmed the energy transfer (ET) from $VO_4{}^{3-}$ ions to Nd^{3+} ions. The DS phenomenon by phosphor was observed, which involved emission of NIR photons (1075 and 1064 nm) and visible photons (506 nm) from absorbed UV photons at 349 nm. The theoretical energy transfer efficiency (ETE) was calculated with the help of steady state luminescence time decay curves and the maximum ET efficiency approached up to 41.33%. The crystalline silicon (c-Si) cell has maximum efficiency in NIR region of solar spectrum due to an energy band gap of 1.12 eV. $Sr_3(VO_4)_2{:}Nd^{3+}$ can be potentially used as a NIR DC phosphor for c-Si solar cells.

Keywords. Downshifting; energy transfer; photoluminescence; $Sr_{(3-x)}(VO_4)_2{:}_xNd^{3+}$.

1. Introduction

Luminescent materials with QE more than 100% could be playing a vital role in the field of lighting industry and electronic display systems. Quantum-cutting (QC) through DC is able to split one incident high-energy photon into two (or more) lower energy photons with a QE higher than 100% [1]. The QC process could generate two or more low-energy photons from an absorbed incident high-energy photon. This idea was first predicted by Dexter in 1957 and was demonstrated in $YF_3{:}Pr^{3+}$ phosphor for the excitation of 185 nm with a quantum efficiency of around 140% in 1974 [2–4]. However, QC phosphors through DC have been investigated from last 10 years for their use in the lighting and display industry. Their applications in solar cells have been realized with increased conversion efficiency [5–15]. Even after significant development of the PV industry over the past decades, the efficient and cost-effective conversion of solar energy into electricity through PV cells remains a daunting task [16–18]. A serious problem limiting the photoelectric conversion efficiency of PV or solar cells is their insensitivity to a full solar spectrum. This is attributed to the fact that each PV material responds to a narrow range of solar photons with energy matching with the characteristic band gap of the material. The photons with energy higher than the band gap are absorbed, but the excess energy is not effectively used. It is released as heat and causes thermalization losses [19]. This problem of spectral mismatch, which is responsible for limiting value of conversion efficiency of solar cells, can be overcome by luminescence processes such as downshifting (DS), QC/DC and upconversion (UC) [20].

In recent years, DS materials have attracted considerable attention because of their strong potential to enhance conversion efficiency of solar cells. DS is a process where one UV or visible photon gets converted into photons of near-infrared (NIR) region, where solar response and conversion efficiency of crystalline silicon (c-Si) are maximum as their emission energy is just above the band gap of silicon (Si) ($E_g = 1.12$ eV, $\lambda \sim 1100$ nm). Theoretically, for a Si-based solar cell in conjunction with an ideal DC material layer, conversion efficiency up to 38.6% could be achieved from sunlight, which is a significant improvement over the limiting efficiency of 30.9% for conventional solar cells under the same conditions [21].

To fulfill the requirements of DC/DS, the host materials must have a band gap of more than 3.0 eV; otherwise the material will absorb visible light; the excitation energy must be higher than 6 eV ($\lambda < 200$ nm) so that the high-energy levels ($E > 50000$ cm^{-1}) can be located within the band gap, and the energy of phonons should be as low as possible in order to reduce the probabilities of multi-phonon relaxations between spaced energy levels of rare-earth (RE) ions [22–24].

Among the various host materials, the alkaline earth metal vanadates with general formula $M_3(VO_4)_2$ (M = Ca, Sr, Ba) have been proved to be good candidates for the luminescent hosts, because they can absorb strongly the UV light and then efficiently transfer the energy to RE activator ions due to good match of energy levels in the wide region and strong interaction between states of VO_4^{3-} and RE ions [25,26]. Moreover, the VO_4^{3-} complex ion group in which the central vanadium metal ion is coordinated by four O^{2-} ions in tetrahedral symmetry has been identified as an efficient luminescent centre, similar to other Scheelite-type compounds.
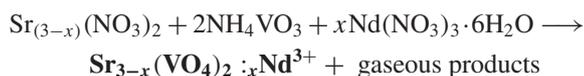
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The characteristic luminescence of VO_4^{3-} ions is commonly observed in other vanadate complexes such as $Mg_3(VO_4)_2$, $LiZnVO_4$ and $NaCaVO_4$ [27,28]. If trivalent rare-earth ions such as Eu^{3+}, Sm^{3+} and Dy^{3+} are introduced into a vanadate host, bright luminescence due to the dopant ions can be observed due to efficient energy transfer (ET) processes from the vanadate ions [29]. The neodymium (Nd^{3+}) ions doped $Sr_3(VO_4)_2$ provides characteristic NIR emission in the range 880–1100 nm, which is suitable to overcome the spectral mismatch problem of c-Si solar cells.

The solid-state reaction method has been the most widely and intensively used method for the preparation of phosphors, including fluorides and oxides, because it is comparatively simple and very suitable for mass production. The mechanism of solid-state reactions is diffusion control reaction and hence repeated grinding and repeated heating are required [30–33]. Inspired from the above discussion, the present work is planned to study PL properties of $Sr_{3-x}(VO_4)_2{:}_xNd^{3+}$ prepared by solid-state reaction method. To the best of our knowledge, this is the first report on DC in $Sr_3(VO_4)_2$ doped with Nd^{3+} ion.

2. Experimental

Qian *et al* and Zhu *et al* had reported the synthesis of [35,39] $Sr_3(VO_4)_2$ but it required sintering time of more than 12 h. The conventional solid-state route was employed for the synthesis of $Sr_{3-x}(VO_4)_2{:}_xNd^{3+}$ ($x = 0, 1, 2$ and 4%). The precursors $Sr_3(NO_3)_2$ (99.0%), NH_4VO_3 (99.9%) and $Nd(NO_3)_3{\cdot}6H_2O$ (99.9%) were used as initiative materials. The chemicals were weighed in proper stoichiometric ratio based on the composition and were homogeneously mixed in a china basin. The materials were finally sintered at 1000°C for 8 h in a microwave furnace.

The proposed chemical composition and molar ratio of the ingredients used are shown below.

$$Sr_{(3-x)}(NO_3)_2 + 2NH_4VO_3 + xNd(NO_3)_3{\cdot}6H_2O \longrightarrow$$
$$\mathbf{Sr_{3-x}(VO_4)_2}{:}_x\mathbf{Nd^{3+}} + \text{gaseous products}$$

The crystal structure of the phosphor powders was characterized by X-ray diffraction analysis using a Rigaku miniflex II X-ray diffractometer with scan speed of 6.000° min^{-1} and Cu Kα ($\lambda = 0.15406$ nm) radiation in the range 10° to 90°. The PL emission and PL excitation spectra were recorded on a (Hitachi F-7000) fluorescence spectrophotometer at room temperature and NIR PL emission and PL excitation spectra were recorded with an FLS980 photoluminescence spectrometer. All the measurements were carried out at room temperature.

3. Results and discussion

3.1 *Structural properties*

The formation of $Sr_3(VO_4)_2$ in the crystalline phase prepared by conventional solid-state reaction method was confirmed
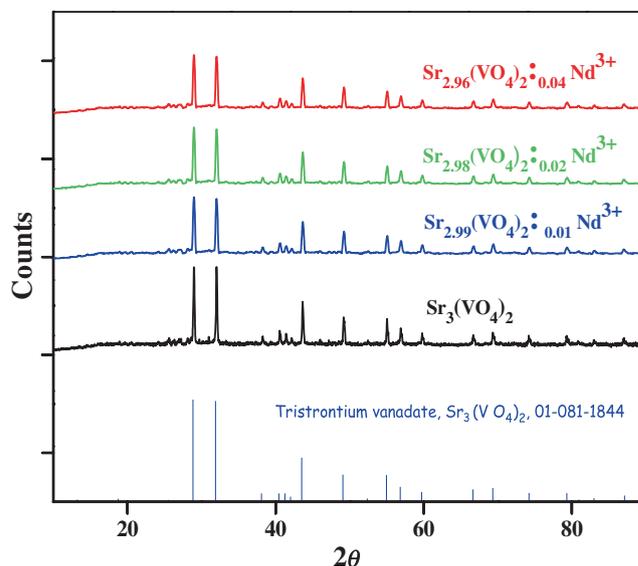

Figure 1. XRD pattern of $Sr_{3-x}(VO_4)_2{:}_xNd^{3+}$ ($x = 0.00, 1, 2$ and 4%) as prepared by solid-state reaction method.

by XRD pattern as shown in figure 1. The XRD pattern for $Sr_{3-x}(VO_4)_2{:}_xNd^{3+}$ ($x = 0\%, 1\%, 2\%$ and 4%) agreed well with the standard data from ICDD file (01-081-1844). The prepared sample crystallized in the trigonal phase and high-intensity peaks were observed at 28.78, 31.83, 43.44, 48.99, 54.85 and 56.70 corresponding to (0 1 5), (1 1 0), (2 0 5), (1 0 1), (1 2 5) and (3 0 0), respectively. The XRD also showed that the prepared material is completely crystalline and was in a single phase, where $a = b = 5.619$ Å and $c = 20.10$ Å. The space group for $Sr_3(VO_4)_2$ is R-3m(166). Moreover, from analysis of the XRD pattern it is understood that the introduction of activator Nd^{3+} ion does not influence the crystal structure of the $Sr_3(VO_4)_2$ sample, because both Nd^{3+} and Sr^{2+} ions have similar ionic radius (Nd^{3+}: 0.983 Å, Sr^{2+}: 1.18 Å for six-fold coordination) and the neodymium ion enters the lattice substitution ally in strontium sites [36]. The average crystallite size of $SrVO_4$ phosphor was found to be 40.218 nm as estimated by Debye-Scherrer's formula [37]

$$D = \frac{K\lambda}{\beta \cos\theta},$$

where θ is the Bragg angle of diffraction lines, K is a shape factor taken as 0.90, λ is wavelength of incident X-rays ($\lambda = 0.154$ nm) and β is full-width at half-maximum (FWHM in radians).

3.2 *Photoluminescence properties and ET*

The excitation spectra illustrated in figure 2a was monitored at emission wavelength 506 nm. The maximum-intensity peak was observed in the absence of Nd^{3+} ion. Decrement in intensity as concentration of Nd^{3+} ion increased up to 4 mol% (0.04) was observed, indicating ET from VO_4^{3-} group to Nd^{3+} ion. Figure 2b demonstrates broad visible emission centered at 506 nm for the excitation of 349 nm
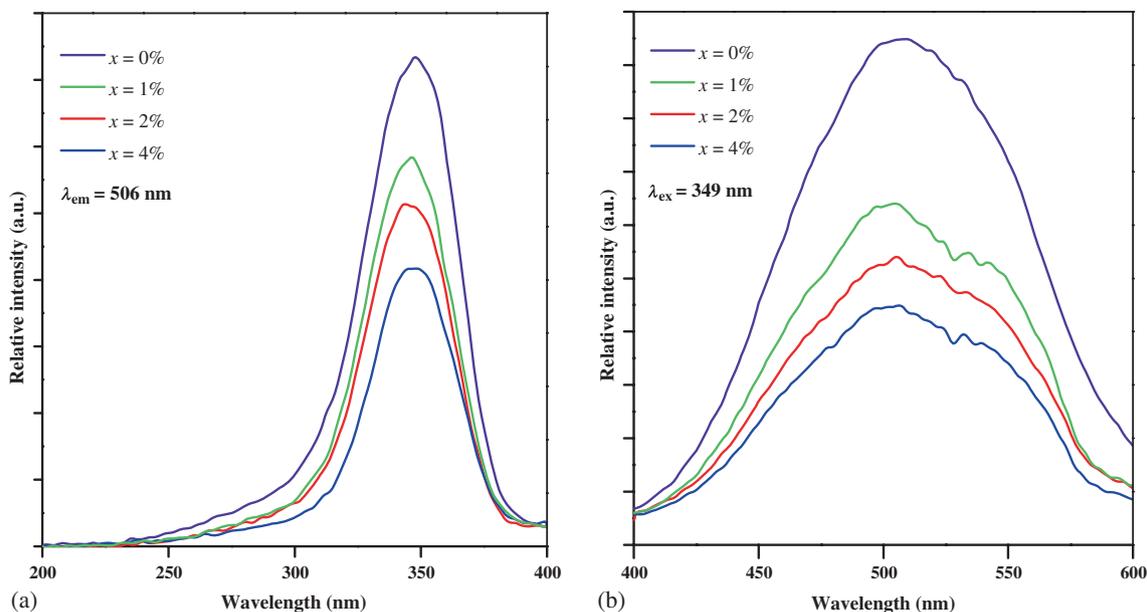
Figure 2. (**a**) PL excitation and (**b**) emission spectra of Sr$_{3-x}$(VO$_4$)$_2$:$_x$Nd^{3+} ($x = 0, 1, 2$ and 4%) measured on an F-7000 fluorescence spectrometer.

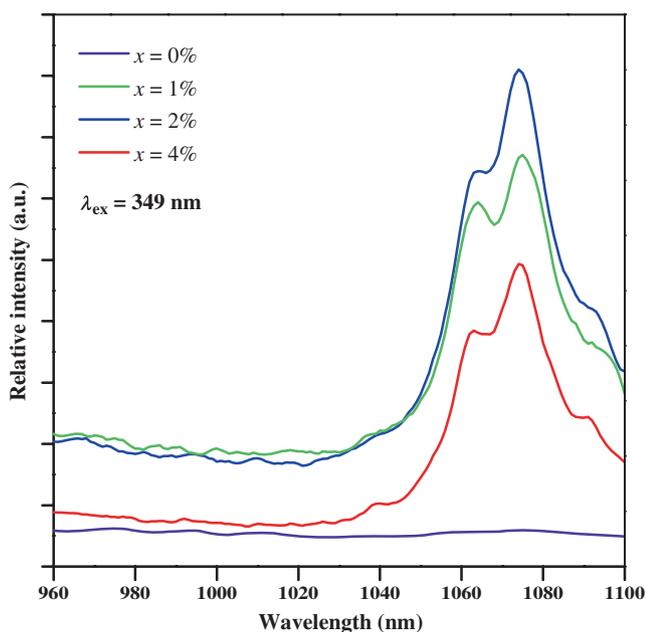**Figure 3.** NIR PL emission spectra of Sr$_{3-x}$(VO$_4$)$_2$:$_x$Nd^{3+} ($x = 0, 1, 2$ and 4%) measured on an FLS980 fluorescence spectrometer.
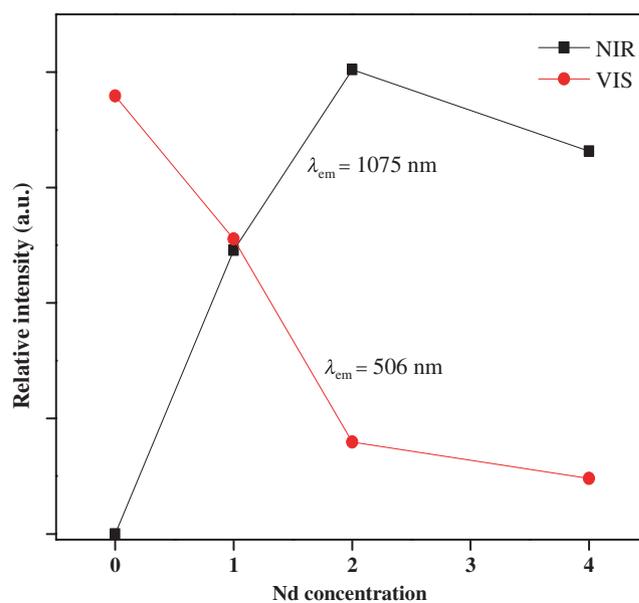
Figure 4. Dependence of VO$_4^{3-}$ emission (506 nm) and Nd^{3+} (1075 nm) emission on the doping concentration (in mol%) of Nd^{3+} in Sr$_3$(VO$_4$)$_2$:Nd^{3+} phosphor.

which is due to energy transition of molecular orbital of VO$_4^{3-}$ group inside Sr$_3$(VO$_4$)$_2$. Figure 3 shows the NIR emission centered at 1075 nm with a shoulder peak at 1064 nm monitored at 349 nm. The highest intensity was observed at 2 mol% concentration of Nd^{3+} ion. At 4 mol% concentration of Nd^{3+} ion the NIR emissions were suppressed, indicating that concentration quenching took place.

The dependence of VO$_4^{3-}$ and Nd^{3+} emission intensities on Nd^{3+} doping concentration in Sr$_3$(VO$_4$)$_2$:Nd^{3+} is shown in figure 4. Emission intensities were recorded under identical conditions for excitation at 349 nm at room temperature. The Nd^{3+} ion concentration of 2 mol% (0.02) is determined to be the best value for the strongest NIR emission at excitation of 349 nm in Sr$_3$(VO$_4$)$_2$. As the concentration of Nd^{3+} ion increases up to 2 mol%, the NIR emission intensity increases, while above that value intensity decreased. The decrease in the emission intensity at 4 mol% (0.04) Nd^{3+} is due to the concentration quenching of Nd^{3+} ions.

Figure 5 pictures the energy level diagram of VO$_4^{3-}$ and Nd^{3+} and ET process from vanadate ion to Nd^{3+} ion in Nd^{3+} doped

$Sr_3(VO_4)_2$ phosphor. In this system, VO_4^{3-} absorbs a UV photon (349 nm) and is excited from the filled oxygen 2p levels in the valence band to the empty V 3d levels of the conduction band. The excited state will relax to the ground state by emitting photon of 506 nm or transferring its energy to nearby Nd^{3+} ions followed by NIR photons emissions at 1075 ($^4F_{3/2} \rightarrow {^4I_{11/2}}$) nm and 1064 ($^4F_{3/2} \rightarrow {^4I_{9/2}}$) nm.

Figure 6 shows the luminescence decay curves of VO_4^{3-} emission intensity for $Sr_3(VO_4)_2$:Nd^{3+} samples with various Nd^{3+} ion concentrations. These curves can be well fitted using a non-exponential equation, $I_t = I_0 \exp(-t/\tau) + A$,
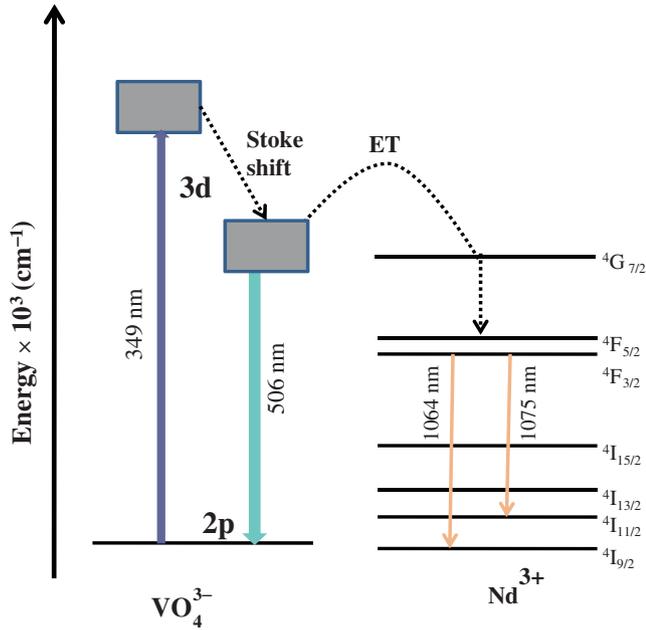

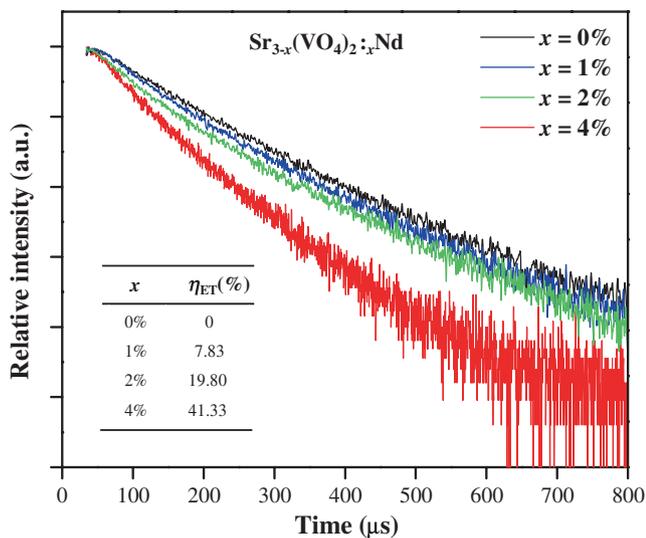**Figure 5.** Energy transfer (ET) mechanism from VO_4^{3-} to Nd^{3+} ions.

Figure 6. The decay curves of the vanadate emission at 506 nm for $Sr_3(VO_4)_2$:Nd^{3+} samples with various Nd^{3+} concentrations. The inset shows the ET efficiency η_{ETE} as a function of Nd^{3+} concentration.

where I_t and I_0 are the luminescence intensities at time t and at time $t = 0$, respectively, A is constant and τ is the decay time. We obtained decay time $\tau = 149.116, 130.605, 115.198$ and 86.049 μs for Nd^{3+} ion concentration of 0, 1, 2 and 4%, respectively. With increasing Nd^{3+} doping concentration, the decay time of VO_4^{3-} emission reduces slowly. This is due to the ETs from VO_4^{3-} to Nd^{3+}, which reduces the VO_4^{3-} decay time. This result gives further evidence of the efficient ET from VO_4^{3-} to Nd^{3+} ions.

From the luminescence decay curves, the ET efficiency (ETE) is [5,38]

$$\eta_{ETE} = 1 - \frac{\int I_{x\%Nd} dt}{\int I_{0\%Nd} dt},$$

where I denotes the decay intensity and $x\%$ Nd represents the Nd^{3+} content. The upper-limit values of the theoretical ETE (%) were calculated to be 7.83, 19.80 and 41.33% for the samples with Nd^{3+} ion doping concentration of 1, 2 and 4 mol%, respectively. The concentration quenching of Nd^{3+} emission is a serious problem for the application of this downconversion material. Higher the doping concentration of Nd^{3+}, the more the number of the defects caused by the dopants and there will be more ET from VO_4^{3-} to quenching centers directly. This process will reduce the optimal doping concentration of Nd^{3+} ion [39,40].

4. Conclusions

The pure phase of $Sr_{3-x}(VO_4)_2$:$_xNd^{3+}$ was synthesized by solid-state reaction method, which is a time-saving and cost-effective method as compared with the reported ones. The ET process was studied by PL spectra and confirmed by luminescence time-decay curves technique. The $Sr_{3-x}(VO_4)_2$:$_xNd^{3+}$ is a downconversion phosphor, which can convert each UV (349 nm) photon into two NIR photons (1075 nm) by ET from the excited VO_4^{3-} to two neighboring Nd^{3+} ions. The NIR emission of 1075 nm due to $^4F_{3/2} \rightarrow {^4I_{11/2}}$ transition dominates in this host matrix. The theoretically calculated ETE can reach as high as 41.33% for the sample doped with 4 mol% Nd^{3+}. However, this value can be overestimated for two reasons: (1) the concentration quenching effect of Nd^{3+} and (2) the quenching effect caused by the direct energy transfer from VO_4^{3-} to quenching centres. Our results demonstrated that Nd^{3+}-doped $Sr_3(VO_4)_2$ phosphors are promising NIR DC phosphors. However, concentration quenching effect was observed at 2 mol% of Nd^{3+}-doped $Sr_3(VO_4)_2$ phosphor. In future this material may be used as a luminescent solar spectrum convertor to enhance the solar cells performance.

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