A new self-activated vanadate phosphor of Na$_2$YMg$_2$(VO$_4$)$_3$ and luminescence properties in Eu$^{3+}$ doped Na$_2$YMg$_2$(VO$_4$)$_3$

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**Abstract**

A novel self-activated vanadate phosphor of Na$_2$YMg$_2$(VO$_4$)$_3$ was prepared using a sol–gel method. Phase formation was verified through X-ray diffraction studies. Luminescence characteristics such as photoluminescence excitation, emission spectra and decay curves were investigated. This host can be efficiently excited by ultraviolet (UV) light, and exhibits an intense green emission band in the regions from 400 nm to 750 nm with maximum at about 521 nm, originating from VO$_4^{3-}$ groups. The band gap energy of Na$_2$YMg$_2$(VO$_4$)$_3$ is estimated to be an approximate value of 2.95 eV by UV–visible absorption spectra. Intensities of host and Eu$^{3+}$ emissions and their decay curves depend on Eu$^{3+}$ doping concentration. Various luminescent colors, including warm white, can be easily tuned by adjusting concentrations. Spectrum analysis showed that energy transfer from host to Eu$^{3+}$ ions occurred with low efficiency. Luminescence properties of as-prepared materials indicate to be as a potential candidate for application in near-UV exciting white LEDs.

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**1. Introduction**

In past decades, much attention has been paid to synthesis and spectroscopic properties of self-activated phosphors such as nio-

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**2. Experimental**

**2.1. Samples preparation**

A white powder sample of Na$_2$YMg$_2$(VO$_4$)$_3$:Eu$^{3+}$ was synthesized via a sol–gel method. Original materials were NH$_4$VO$_3$ (A.R.), Mg(NO$_3$)$_2$ (A.R.), NaNO$_3$ (A.R.), Eu$_2$O$_3$ (99.99%) and Y$_2$O$_3$ (99.99%). Aqueous solutions of Eu(NO$_3$)$_3$ and Y(NO$_3$)$_3$ were respectively obtained through dissolving Eu$_2$O$_3$ and Y$_2$O$_3$ in diluted HNO$_3$ solution under heating with agitation. Respective nitrate solutions were mixed in the required ratio. Then a certain citric acid (the
The molar ratio of citric acid to total metal cation was 2:1 and NH₄VO₃ were added to the mixed nitrate solution. The resultant mixture continued to be stirred at 60 °C until homogeneous sol was formed. After being dried, the obtained gels were heated at 400 °C for 2 h in air, and then were fully grounded and sintered at 700 °C and 800 °C for 1 h, respectively. Until cooled down naturally to room temperature, white powder samples were obtained.

2.2. Measurements

Crystal phases of obtained samples were identified by an X-Ray Diffractometer (Max 18 XCE, Japan) using Cu Kα irradiation (λ=0.154056 nm). Morphology and sizes of samples were examined with scanning electron microscope (SEM). Diffuse reflection spectra were obtained by a scanning-type UV–visible spectrophotometer (Shimadzu UV-3600) with BaSO₄ as a reference. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured with a Jobin-Yvon Fluorolog 3 spectrophotometer. Fluorescence decay curves were measured under excitation of the third harmonics 355 nm of a pulsed YAG:Nd laser. The decay signal was analyzed with a Tektronix TDS2024 digital storage oscilloscope.

3. Results and discussion

3.1. Powder X-ray diffraction and crystal structure

Samples as prepared were identified by powder X-ray diffraction (XRD) measurements as shown in Fig. 1. Patterns of the sample prepared at 700 °C for 1 h are similar to those of the JCPDS standard card (No. 49-0412) according to Fig. 1(a). Diffraction peaks match well with those of the standard card, demonstrating that obtained samples are pure crystalline phases. When temperature of heat treatment rises up to 800 °C, it could be seen that intensities of diffraction peaks increase indicating increase of the Na₂YMg₂(VO₄)₃ crystallite size. Meanwhile, weak diffraction peaks (marked with asterisks *) from the second-phase YVO₄ (No. 76-1649) appear. As shown in Fig. 1(b), the XRD patterns of Na₂YMg₂(VO₄)₃:Eu³⁺ x mol% (x=0–15) samples can be indexed by Na₂YMg₂(VO₄)₃ phase, and no obvious trace of impurity phases is observed when Eu³⁺ doping concentration is up to 15 mol%. A schematic of the crystal structure of Na₂YMg₂(VO₄)₃ is shown in Fig. 1(c). In this vanadate garnet structure, Mg²⁺ ions are located in eightfold dodecahedral sites. The Y³⁺ and/or Na⁺ ions are in sixfold octahedral sites. The metal ion V³⁺ (in isolated [VO₄]³⁻) completely occupies the fourfold Td site [13]. The SEM image of Na₂YMg₂(VO₄)₃ phosphor prepared at 700 °C for 1 h is shown in Fig. 2. It could be seen that particles with size ranging from

![Fig. 1.](image1.png) (a) XRD patterns of Na₂YMg₂(VO₄)₃ powders (a) prepared at 800 °C for 1 h, (b) prepared at 700 °C for 1 h, which are compared with those of the standard pattern cards no. 490412 of Na₂YMg₂(VO₄)₃ and no. 761649 of YVO₄. (b) XRD patterns of Na₂YMg₂(VO₄)₃:Eu³⁺ x mol% (x=0–15) samples. (c) The schematic view of Na₂YMg₂(VO₄)₃ structure along b-direction.

![Fig. 2.](image2.png) SEM image of Na₂YMg₂(VO₄)₃ powders prepared at 700 °C.
3.2. Luminescence of Na₂YMg₂(VO₄)₃

Fig. 3 exhibits PL and PLE spectra of Na₂YMg₂(VO₄)₃ host. Excitation spectrum by monitoring at 521 nm consists of a broad band ranging from 230 nm to 410 nm with the maximum excitation peak at around 350 nm. Under 350 nm excitation Na₂YMg₂(VO₄)₃ phosphor presents green and bright luminescence. A broad band ranging from about 400 to 700 nm can be observed, a broad band at 340 nm similar to the origin of the broad emission band in vanadate based systems has been well documented [14]. It could be assigned to the initial intensity, and effective decay time could be estimated to be 9378 cm⁻¹. For comparison, Ca₂NaZn₂(VO₄)₃ phosphor was used as a reference phosphors, and was also prepared which have been reported recently to be the desirable vanadate phosphors potentially applicable in LEDs [10].

The origin of the broad emission band in vanadate based systems has been well documented [14]. It could be assigned to the ligand–metal charge transfer of 2p of O²⁻ to 3d of V⁵⁺ within tetrahedrally coordinated VO₄²⁻ groups [15]. It could be noted that the emission band presents an asymmetric shape, which could be decomposed into two Gaussian emission bands. These two bands are attributed to transitions of VO₄²⁻ groups, namely 3T₁₂₋₁A₁ and 3T₁₋₁A₁ transitions

Luminescence decay curves of the Na₂YMg₂(VO₄)₃ powder under excitation of the third harmonic 355 nm of the pulsed YAG: Nd laser are shown in the inset of Fig. 3. Luminescence decay curves consist of fast and slow decay components and exhibit biexponential feature. It can be well fitted with the second order exponential equation as following:

\[ I = I_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \]  

(1)

Here, \( I \) is the luminescent intensity at time \( t \), and \( I_0 \) is the initial luminescent intensity. \( A_1 \) and \( A_2 \) are two constants which are related to the initial intensity, and \( \tau_1 \) and \( \tau_2 \) are decay times for exponential components, respectively. Values of \( \tau_1 \) and \( \tau_2 \) extracted from the decay curve are 175 ns and 1417 ns. Furthermore, the effective decay time \( \tau \) could be calculated by the following equation [17]:

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

(2)

3.3. Luminescence of Na₂YMg₂(VO₄)₃:Eu³⁺

Luminescence properties of Na₂YMg₂(VO₄)₃:Eu³⁺ 1 mol% are investigated as shown in Fig. 5. Excitation spectrum was obtained that of a typical charge transfer emission of VO₄²⁻ groups at 521 nm. It is an intense broad band at 340 nm similar to the 3.2. Luminescence of Na₂YMg₂(VO₄)₃. Under the same experimental condition, the relative PL intensity of Na₂YMg₂(VO₄)₃ is 1.2 times higher than that of the Ca₂NaZn₂(VO₄)₃.

According to Eq. (2) and parameters fitted from the decay curve, effective decay time was determined to be 1.25 µs.

In order to assess absorption edge of the host, UV–visible absorption spectra of Na₂YMg₂(VO₄)₃ powders annealed at 700 °C for 1 h are measured, as shown in Fig. 4. Broad bands peaking at 260 nm and 340 nm are attributed to the charge transfer from oxygen ligands to the central vanadate atom inside VO₄ groups. For a direct band gap semiconductor, absorbance in the vicinity of the onset due to the electronic transition is given by the following equation [18]:

\[ \alpha = \frac{C (\hbar \nu - E_g)^{1/2}}{\hbar \nu} \]

(3)

where \( \alpha \) is absorption coefficient, \( C \) is a constant, \( \hbar \) is photon energy and \( E_g \) is the band gap.

A curve of \( \alpha \) vs \( h\nu \) is constructed, as shown in the inset of Fig. 4. Extrapolation of the linear region gives a band gap of 2.95 eV. Although this typical method for the direct band gap semiconductor may not be so exact for Na₂YMg₂(VO₄)₃, it does give an approximate value. For vanadate, absorption in this spectral region corresponds to typical charge transfer emission of VO₄²⁻ groups.

Fig. 3. Excitation (λ_em=521 nm) and emission (λ_ex=350 nm) spectra of Na₂YMg₂(VO₄)₃ powders at room temperature, inset shows decay curves of host emission.

300 nm to 1000 nm show irregular shapes, and also there is a big amount of agglomeration in the particles.
to those of undoped samples. Meanwhile, characteristic emission peaks of \( \text{Eu}^{3+} \) appear between 580 nm and 710 nm, which correspond to intra-4f transitions of \( \text{Eu}^{3+} \) ion. It is well known that variation in the crystal field environment of \( \text{Eu}^{3+} \) ions can produce modifications in the number of \( ^5\text{D}_0\rightarrow^7\text{F}_j \) transitions and their relative intensities. If \( \text{Eu}^{3+} \) ion holds a site without inversion symmetry, the \( ^5\text{D}_0\rightarrow^7\text{F}_j \) electronic transition predominates. However, when \( \text{Eu}^{3+} \) ion has a site with inversion symmetry, the \( ^5\text{D}_0\rightarrow^7\text{F}_j \) magnetic transition becomes the strongest [19]. In the case of our sample, it is found that emission intensities from the magnetic dipole \( ^5\text{D}_0\rightarrow^7\text{F}_j \) at 587 nm are weaker, and the electric dipole \( ^5\text{D}_0\rightarrow^7\text{F}_j \) transition at 609 nm dominates emission spectra. The result indicates \( \text{Eu}^{3+} \) ions locate at a position with a non-centrosymmetric point group.

The excitation spectrum is obtained by monitoring the \( ^5\text{D}_0\rightarrow^7\text{F}_2 \) transition of the \( \text{Eu}^{3+} \) emission at 609 nm. It could be observed, the spectrum consists of an intense broad band with a maximum at 350 nm and a group of sharp absorption lines in the 380–430 nm wavelength regions, which is overlapped with the broad band. The former dominant broad band is similar to but not exactly the same as undoped sample. It is not composed of only one Gaussian component. We conclude that the broad band is assigned to the overlap of \( ^5\text{D}_0\rightarrow^7\text{F}_2 \) and \( ^5\text{D}_0\rightarrow^7\text{F}_2 \) charge transfers, which can be explained by the following discussion. The latter sharp lines between 380 nm and 430 nm correspond to the f-f transitions of the \( \text{Eu}^{3+} \) ion, such as the transitions from the ground state to the excited levels, \( ^7\text{F}_1 \) (390 nm) and \( ^7\text{D}_1 \) (412 nm) of \( \text{Eu}^{3+} \).

In order to identify the component of excitation spectra in the \( \text{Na}_2\text{YMg}_2(\text{VO}_4)_3: \text{Eu}^{3+} \) sample, Fig. 6(a) displays emission spectra of \( \text{Na}_2\text{YMg}_2(\text{VO}_4)_3 \) phosphors with various concentrations of \( \text{Eu}^{3+} \) excited at 350 nm. Emission spectra are normalized at the strongest peak of 609 nm, as shown in Fig. 6(b). With the increase of \( \text{Eu}^{3+} \) concentrations, intensity of \( ^5\text{D}_0 \) emission grows drastically and becomes dominant while characteristic charge transfer emissions of \( \text{VO}_4^3— \) groups decrease slowly in a small range. Meanwhile, \( \text{Eu}^{3+} \) concentration has a critical influence on spectral distribution of phosphor. Host emission of \( \text{VO}_4^3— \) groups has a comparable intensity of sharp emission lines in the 1% \( \text{Eu}^{3+} \) doped sample. While in the 15% \( \text{Eu}^{3+} \) doped sample, intensity of host emission is too weak, and \( \text{Eu}^{3+} \) emission dominates emission spectrum. Fig. 7 shows dependence of intensities of the emission from host and \( \text{Eu}^{3+} \). In the range of current doping, intensity of \( \text{Eu}^{3+} \) emission is enhanced greatly. Charge transfer emission changes slowly. For example, intensity of \( \text{Eu}^{3+} \) emission in the 15% \( \text{Eu}^{3+} \) doped sample is twelve times than that in the 1% \( \text{Eu}^{3+} \) doped sample, while for the host emission this value becomes 73%. This indicates that energy transfer from \( \text{VO}_4^3— \) groups occurs, but inefficiently. When the sample is excited by a 355 nm light, \( \text{VO}_4^3— \) groups are first excited to a \( ^1\text{O}_2^– \rightarrow^5\text{F}_5 \) charge transfer band, and then inefficient energy transfer from \( \text{VO}_4^3— \) groups to the \( ^5\text{D}_0 \) energy level of \( \text{Eu}^{3+} \) occurs. If only above-mentioned process exists, \( \text{Eu}^{3+} \) emission should not increase so drastically. Another process should exist. Taking location of \( ^5\text{D}_0 \rightarrow^7\text{F}_2 \) charge transfer band into account, this process is supposed to involve \( ^1\text{O}_2^– \rightarrow^5\text{F}_5 \) charge transfer. Now the strong broad band of excitation spectra monitored by \( \text{Eu}^{3+} \) emission at 609 nm can be deduced to being overlap of \( ^5\text{D}_0 \rightarrow^7\text{F}_2 \) and \( ^5\text{D}_0 \rightarrow^7\text{F}_2 \) charge transfers.

Low efficiency of energy transfer between host and \( \text{Eu}^{3+} \) can be further confirmed by measuring decay time. Luminescence decay curves of \( \text{Na}_2\text{YMg}_2(\text{VO}_4)_3 \) doped with different concentration of \( \text{Eu}^{3+} \) were conducted to further verify occurrence of energy transfer from host to the \( \text{Eu}^{3+} \) ion. As shown in Fig. 8, Decay curves of host emission in \( \text{Na}_2\text{YMg}_2(\text{VO}_4)_3 \) with different \( \text{Eu}^{3+} \) concentrations.
Increasing concentration of $\text{Eu}^{3+}$ mol% monotonously decrease from 1.20 to 1.18, 1.05, 1.03 and 0.97 in $\text{Na}_2\text{YMg}_2(\text{VO}_4)_3$:\text{Eu}^{3+}$. This result certifies that energy transfer from host to $\text{Eu}^{3+}$ ions occurs with a tiny change of their decay curves depend on doping concentration. Effective energy transfer time of host emission decreases from a value of about 1.25 μs to 0.96 μs with increasing the doping content, while decay time of $\text{Eu}^{3+}$ emission shows no obvious change. The result indicates that energy transfer from host to $\text{Eu}^{3+}$ ions occurs with a low efficiency. The CIE coordinates can be adjusted by controlling the rare earth ions concentration. These results reveal the potential applicability of this phosphor in the near VU chip excited white LEDs.

### 4. Conclusions

In summary, self-activated $\text{Na}_2\text{YMg}_2(\text{VO}_4)_3$ phosphors have been prepared by a sol–gel method. Structural and optical properties of samples were carried out. $\text{Na}_2\text{YMg}_2(\text{VO}_4)_3$ powders only show intense intrinsic luminescence in the region from 400 nm to 750 nm. This self-activated green emission with a peak located at 521 nm corresponds to typical charge transfer emission of $\text{VO}_4^{3-}$ groups. The band gap energy of $\text{Na}_2\text{YMg}_2(\text{VO}_4)_3$ was estimated to be an approximate value of 2.95 eV. In $\text{Eu}^{3+}$ doped samples, tunable luminescence can be observed by adjusting the concentrations. The intensity of host emission and $\text{Eu}^{3+}$ emission and their decay curves depend on doping concentration. Effective decay time of host emission decreases from a value of about 1.25 μs to 0.96 μs with increasing the doping content, while decay time of $\text{Eu}^{3+}$ emission shows no obvious change. The result indicates that energy transfer from host to $\text{Eu}^{3+}$ ions occurs with a low efficiency. The CIE coordinates can be adjusted by controlling the rare earth ions concentration. These results reveal the potential applicability of this phosphor in the near VU chip excited white LEDs.

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\[ I = I_0 \exp \left(-t/\tau \right) \]

where $I$ is intensity at time $t$, $I_0$ is intensity at $t=0$, and $\tau$ is decay lifetime. The fitted lifetime values of $\text{Na}_2\text{YMg}_2(\text{VO}_4)_3$ doped with x mol% $\text{Eu}^{3+}$ are 0.70, 0.78, 0.75, 0.73, 0.78 and 0.76 ms corresponding to the $\text{Eu}^{3+}$ concentration of 1, 3, 6, 9, 12 and 15 mol%, respectively. It can be seen that the decay curves of emission at 609 nm with various $\text{Eu}^{3+}$ concentration are very similar to each other, and lifetime of $\text{Eu}^{3+}$ shows no obvious changes. The result implies that high quenching concentration can be achieved in this kind of host.

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Fig. 10. CIE (X, Y) coordinate diagram showing chromaticity points of luminescence in $\text{Na}_2\text{YMg}_2(\text{VO}_4)_3$:\text{Eu}^{3+}$ samples. Data points 1–7 are assigned to samples with $\text{Eu}^{3+}$ contents of $x=0$, 1, 3, 6, 9, 12, and 15, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### References
