Photoluminescence characterization of some Vanadate based phosphors

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Abstract. Highly efficient new vanadate phosphor A₂NaMg₂V₃O₁₂ (A= Ba & Sr) doped with rare earth element Dysprosium (Dy) was synthesized at high temperature via solid-state method successfully and the formed compound was confirmed by X-ray diffraction method. Photoluminescence measurements revealed that Sr₂NaMg₂V₃O₁₂ phosphor doped with Dy is excited by near ultraviolet light ranging from 300 nm to 380 nm efficiently in order to realize the emission in visible spectrum (in the range 400 nm – 570 nm. Ba₂NaMg₂V₃O₁₂: Dy phosphor also showed emission at 569 nm on excitation at 325 nm. Hence this prepared phosphor can find application as a green emitting phosphor in solid state lighting area.

1. Introduction

The vanadate based phosphor doped with rare earth element are studied widely till date because of their ability to emit the variety of colors light owing to high luminescence quantum yield that are due to the f–f transition [1–8]. Out of these YVO₄:Eu³⁺ and GdVO₄:Eu³⁺ phosphors (red phosphor) have been center of attraction due to various properties such as good chemical stability, thermal properties and high photoluminescence quantum yield. This makes these phosphors applicable in the field of color TVs, field emission displays [9, 10], cathode ray tubes [11], light emitting diodes [12] and plasma display panels [13, 14]. White light generated by combination of UV -LED & appropriate phosphors is mostly desirable. The AlGaN-based LEDs which are developed in order to operate at the short wavelength region of UV light are possible to tune [15]. The nano particles of vanadate phosphor have been prepared by some researcher for converting UV pump light of III-N semiconductor light emitting diode into the bands of visible wavelength [16]. A vanadate compound LiZnVO₄ is used widely employed as a humidity sensor [17, 18]. The interesting properties of this phosphor are related to its luminescence which is due to its tetrahedrally coordinated V⁵⁺ ions [19]. The VO₃⁺-complex metal ion group wherein centrally located vanadium metal ion coordinated with four O²⁻ ions having tetrahedral symmetry has been recognize as a promising and efficient luminescent center as in other similar to that in other scheelite-type compounds [20].
In this communication, photoluminescence study on multicomponent vanadate phosphor LED by adjusting the yellow to blue intensity ratio suitably.\[39, 40\].\(\text{ions are capable of showing the strong luminescence in various lattices & also exhibit blue red emission due to }\)\(\text{transition of Dy}^{3+}\). As the outside surrounding strongly affects hypersensitive red emission transition of \(\text{Eu}^{2+}\) taken to prepared Vanadate based phosphors because of its outstanding luminescent properties\[35-38\]. The vanadate center gets excited on excitation and might display very efficient luminescent center. The vanadate center possesses tetrahedral symmetry where centrally located metal ions have coordination with four oxygen ions. This serves as an very efficient luminescent center. The vanadate center gets excited on excitation and might display broad luminescence in the UV region or it may result in the transfer of energy to another luminescent center which subsequently will reveal the characteristic emission\[34\]. Off let keen interest is being done intensively for application to various devices such as color TVs, CRT, high-pressure Hg-light, various displays, X-ray detectors and so on\[27, 28\]. Vanadates are important compounds owing to their superior characteristics such as long wavelength excitation & outstanding chemical stabilities\[29, 30\]. They have intense and broad charge transfer absorption bands in the near UV region and hence are able to capture the emission over a wide range of wavelength efficiently. Under photo excitation metal to oxygen CT band are very intense under photo-excitation. A non radiative mechanism is responsible for the transfer of energy to the luminescent center.\[31-33\]. High quality of phosphors for necessary brightness and stability over a long term is important requirement of lighting & display devices for better performance. Outstanding physical as well as chemical stability in the rare gas or mercury discharge environment along with high efficiency under the excitation with UV radiation are the most important qualities for good lamp phosphor. The \(\text{VO}_2^{3−}\) possesses tetrahedral symmetry where centrally located metal ions have coordination with four oxygen ions. This serves as an very efficient luminescent center. The vanadate center gets excited on excitation and might display broad luminescence in the UV region or it may result in the transfer of energy to another luminescent center which subsequently will reveal the characteristic emission\[34\]. Off let keen interest is being taken to prepared Vanadate based phosphors because of its outstanding luminescent properties\[35-38\]. As the outside surrounding strongly affects hypersensitive red emission transition of \(\text{Eu}^{3+}\)\(\text{transition generally used europium ion as a luminescence center. Dy}^{3+}\) ions are capable of showing the strong luminescence in various lattices & also exhibit blue\(\text{emission transition of Dy}^{3+}\) as well as yellow\(\text{emission transition of Dy}^{3+}\) emissions. They can be applied for fabrication of white LED by adjusting the yellow to blue intensity ratio suitably.\[39, 40\].

Commercially available blue light emitting diodes are used in solid-state lighting sources in recent time. In order to convert the blue emission into yellow light \(\text{Y}_3\text{Al}_2\text{O}_{12}:\text{Ce}^{3+}\) (YAG: \(\text{Ce}^{3+}\)) phosphor is applied on top of these LEDs\[21\]. The white light source having a color rendering index in middle 70s and color temperature in the range 5000 K to 8000 K can be made by complementary blue and yellow emission bands. The red phosphors \((\text{Ba},\text{Sr},\text{Ca})_2\text{Si}_2\text{N}_8:\text{Eu}^{2+}\) or \((\text{Sr},\text{Ca})_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}\) can be used to achieve lower CCTs and higher CRIs\[22\]. Though the invention and subsequent development of such phosphor for application in LED-based illumination helps lamps for general illumination markets, still many more questions needs to be addressed in this area. For instant, the thickness of phosphor coating strongly affects the blue component of the lamp spectra coming from LED light which bleeds through the phosphor coating. As a consequence of this it becomes difficult for LEDs to match the specifications in uniformity of lamp color in fluorescent lighting due to variations in lamp manufacturing.

A series of pure phase garnets of \((\text{Ca},\text{Na})_2\text{M}_2\text{V}_5\text{O}_{12}\) where \(\text{M}\) may be \(\text{Ni}^{2+}\) or \(\text{Mg}^{2+}\) or \(\text{Cu}^{2+}\) or \(\text{Co}^{2+}\) and \(\text{Zn}^{2+}\) has been reported by Bayer et.\[23\]. In this garnet \(\text{Ca}^{2+}\) or \(\text{Na}^+\) occupies an eightfold decahedral sit) and \(\text{M}^{2+}\) is in a six-fold octahedral site where as the four fold tetrahedral site is completely occupied by \(\text{V}^{5+}\). The luminescence of \(\text{Eu}^{3+}\) in such vanadates having \(\text{M} = M g^{2+}\) was described by Blasse and Brill. They demonstrated transfer of energy between \((\text{VO}_3)^{3−}\) and \(\text{Eu}^{3+}\)[24]. In the present communication effort is made to show that this single phosphor can convert UV-LED radiation into white light with high luminosity\[25\] which is described as the matching of the spectral output with the eye sensitivity curves and good CRI. A single white LED phosphor has a significant benefit that it can remove the variation in the coating process and eventually insures uniformity in lamp color despite variations in manufacturing process.

The luminescent phosphor having high efficiency are produced for applications such as compact light source, display screens and photonics devices\[26\]. The study of phosphors that are vanadate-based is being done intensively for application to various devices such as color TVs, CRT, high-pressure Hg-light, various displays, X-ray detectors and so on\[27, 28\]. Vanadates are important compounds owing to their superior characteristics such as long wavelength excitation & outstanding chemical stabilities\[29, 30\]. They have intense and broad charge transfer absorption bands in the near UV region and hence are able to capture the emission over a wide range of wavelength efficiently. Under photo excitation metal to oxygen CT band are very intense under photo-excitation. A non radiative mechanism is responsible for the transfer of energy to the luminescent center.\[31-33\]. High quality of phosphors for necessary brightness and stability over a long term is important requirement of lighting & display devices for better performance. Outstanding physical as well as chemical stability in the rare gas or mercury discharge environment along with high efficiency under the excitation with UV radiation are the most important qualities for good lamp phosphor. The \(\text{VO}_2^{3−}\) possesses tetrahedral symmetry where centrally located metal ions have coordination with four oxygen ions. This serves as an very efficient luminescent center. The vanadate center gets excited on excitation and might display broad luminescence in the UV region or it may result in the transfer of energy to another luminescent center which subsequently will reveal the characteristic emission\[34\]. Off let keen interest is being taken to prepared Vanadate based phosphors because of its outstanding luminescent properties\[35-38\]. As the outside surrounding strongly affects hypersensitive red emission transition of \(\text{Eu}^{3+}\)\(\text{D}_0\rightarrow\text{F}_2\) & yellow emission transition of \(\text{Dy}^{3+}\)\(\text{D}_0\rightarrow\text{H}_{13/2}\)\). The various phosphors that show characteristics red emission due to \(\text{D}_0\rightarrow\text{F}_2\) transition generally used europium ion as a luminescence center. \(\text{Dy}^{3+}\) ions are capable of showing the strong luminescence in various lattices & also exhibit blue\(\text{emission transition of Dy}^{3+}\) as well as yellow\(\text{emission transition of Dy}^{3+}\) emissions. They can be applied for fabrication of white LED by adjusting the yellow to blue intensity ratio suitably.\[39, 40\].

In this communication, photoluminescence study on multicomponent vanadate phosphor \(\text{A}_2\text{NaMg}_2\text{V}_5\text{O}_{12}\); \(\text{Dy} (\text{A} = \text{Ba} & \text{Sr}))\) is reported. This type of vanadate group is critical to prepare due to
the combination of multi-elements. An attempt therefore has been made to introduce this combination of vanadate group to the research field.

2. Experimental

$A_2NaMg_2V_3O_{12}$: Dy ($A =$ Ba & Sr) phosphor was synthesized by using the modified solid state methodology. The highly purity SrCO$_3$, BaCO$_3$, Na$_2$CO$_3$, MgO, NH$_4$VO$_3$ and Dy$_2$O$_3$ were used as starting materials. All the reagent were mixed thoroughly in appropriate proportion & were ground. It was then taken in silica crucible. It was then gradually heated in a muffle furnace at 600°C for 6 hour & 800°C for duration of 24 hours. It was then cooled progressively to ambient temperature.

The phase composition and phase structure were characterized by X-ray diffraction (XRD) pattern using a PAN–analytical diffractometer. Shimadzu RF-5301 PC spectrofluorophotometer was used to evaluate the photoluminescence properties of prepared phosphor and same were carried out at room temperature.

3. Result & Discussion

3.1. XRD spectra of $A_2NaMg_2V_3O_{12}$ ($A =$ Ba & Sr)

![XRD patterns of (a) Ba$_2$NaMg$_2$V$_3$O$_{12}$ & (b) Sr$_2$NaMg$_2$V$_3$O$_{12}$](image)

The XRD patterns of Ba$_2$NaMg$_2$V$_3$O$_{12}$ & Sr$_2$NaMg$_2$V$_3$O$_{12}$ powder which were annealed at the temperature at 800°C for 24 hours are shown in Figure 1. The single phase was exhibited by all samples & the complete formations of both the prepared compounds were represented by all the peaks. Standard file is not available for the comparison so the XRD patterns were not compared with any data.

3.2. Photoluminescence properties of $A_2NaMg_2V_3O_{12}$: Dy ($A =$ Ba & Sr)

Photoluminescence study of Ba$_2$NaMg$_2$V$_3$O$_{12}$ phosphor activated with Dy$^{3+}$ with different concentration is elaborated in this section. Figure 2 (a) shows excitation spectrum of
Ba$_2$NaMg$_2$V$_3$O$_{12}$:Dy$^{3+}$ phosphor. When monitored at 569 nm, two excitation peaks were observed at 326 nm & 349 nm respectively. These correspond to the transitions towards the charge transfer state owing to Dy$^{3+}$-O$^{2-}$ interactions [41-42].

![Figure 2 (a). Excitation spectrum of Ba$_2$NaMg$_2$V$_3$O$_{12}$: Dy](image)

On excitation at 325 nm, the phosphor gave the highly intense emission peaks in comparison to that observed at 349 nm. Owing to this 325 nm wavelength was chosen as the excitation wavelength for phosphors excitation. The excitation spectrum for all phosphors is same that is why it was not mentioned individually. Generally Dy$^{3+}$ shows two dominant bands in emission spectra in many host. In our case one located in yellow region is due to hypersensitive transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ ($D_l=2$, $D_J=2$). The other band is located in blue region and is contributed to transition $^4F_{9/2} \rightarrow ^6H_{15/2}$. Near white emission with Dy$^{3+}$ activated phosphor is possible by appropriate adjustment of yellow to blue intensity. Thus Dy$^{3+}$ activated phosphors can be seen as promising source for white light phosphors &

![Figure 2 (b). Emission Spectra of Ba$_2$NaMg$_2$V$_3$O$_{12}$:Dy (a=0.1, b=0.3, c=0.5 & d=1mol %)](image)
can find application in lamps that are free of mercury. VUV is the main excitation energy for mercury free lamp. Since VUV energy is absorbed by the host crystal most of the times the energy can be transferred from host to rare earth ions, then rare earth ions can emits the visible light. Hence the host absorption wavelength is of prime importance for VUV excited phosphor that are used in mercury free lamp [43-44].

![Excitation Spectrum of Sr₂NaMg₂V₃O₁₂:Dy](image)

**Figure 3 (a):** Excitation Spectrum of Sr₂NaMg₂V₃O₁₂:Dy

![Emission Spectra of Sr₂NaMg₂V₃O₁₂: Dy (a=0.1, b=0.3, c=0.5 & d=1mol %)](image)

**Figure 3 (b):** Emission Spectra of Sr₂NaMg₂V₃O₁₂: Dy (a=0.1, b=0.3, c=0.5 & d=1mol %)

Figure 3(a) & Figure 3(b) depicts the excitation and emission spectra of Sr₂NaMg₂V₃O₁₂:Dy. An excitation spectrum is placed in between the region of 300-380 nm & it gives the excitation spectrum peak point as 345 nm. A broad band with some lower intense peaks which were not resolved was observed again on excitation of phosphor at at 345 nm. Emission spectrum starts from region 425 nm to 550 nm. It can be seen that, three peaks are observed at 488 nm, 502 nm & 580 nm on the broad band. This is established fact that Vanadate gives self-emission spectra in green region covering a broad band from 400 nm to 570 nm. Figure 3 (b) shows the two weak emission bands one at 488 nm (blue) (\( ^{4}F_{9/2} \rightarrow ^{6}H_{15/2} \)) and other at 580 nm (yellow \( ^{4}F_{9/2} \rightarrow ^{6}H_{13/2} \)). The bright yellow emission as a result of transition at 580 nm \( ^{4}F_{9/2} \rightarrow ^{6}H_{13/2} \) is observed when Dy³⁺ occupies low symmetry local site.
& often emission is prominent. The transition at 488 nm ($^4F_{9/2} \rightarrow ^6H_{15/2}$) which is generally magnetically allowed & does not get affected with the crystal field strength around Dy$^{3+}$ ion. It’s probable to obtain near white emission by appropriate adjustment of yellow to blue intensity ratio with Dy$^{3+}$ doped phosphors.

4. Conclusion

In the present study, new multicomponent vanadate based phosphors was prepared using solid state synthesis at high temperature. Two characteristics emission peaks were shown in photoluminescence spectra. One peak was observed in blue region & other in yellow region. This can be used for the lamp phosphors for solid state lighting in environment friendly manner. Also $A_2NaMg_2V_3O_{12}$: Dy ($A$= Ba & Sr) phosphors maybe applicable for solid state lighting. In this paper, photoluminescence study on vanadate phosphor $A_2NaMg_2V_3O_{12}$: Dy ($A$= Ba & Sr) is included and at the same time an attempt has been made for the Thermoluminescence (TL) study. But due to the over dominancy property of VO$_4^{3-}$ group and self-emission in green region, the suitable environment for trapping centers which are responsible for Thermoluminescence (TL) emission were not created in the prepared powder and we failed to get TL in these compounds. So, in present communication we are only reporting PL characteristics of these phosphors.

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