



Luminescence Properties of Samarium

Doped YVO_4 Phosphor

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ABSTRACT

The trivalent Samarium ion (Sm^{+3}) activated YttriumVanadate (YVO_4) phosphor is synthesized via co-precipitation method. The prepared sample is characterized by X-ray diffraction (XRD), Fourier transform infrared red Spectroscopy (FTIR), scanning electron microscopy (SEM) and Photoluminescence (PL) spectroscopies techniques. The XRD pattern revealed the tetragonal crystalline phase. The morphological features studied by SEM revealed that nanocrystals are agglomerated. FTIR spectrum showed the presence of hydroxyl group in the prepared sample with two strong IR absorption bands at 771 and 1631 cm^{-1} . The optical absorption spectra Sm- YVO_4 nanocrystals obtained by co-precipitation method showed a strong absorption peak at 392nm. The PL emission spectrum of Sm-doped YVO_4 sample shows two prominent peaks at 486nm and 575nm with an excitation of 300nm respectively.

Keywords: Precipitation, YttriumVanadate, Dysprosium, X-ray diffraction, Photoluminescence.

I. INTRODUCTION

The development of nanophosphors is a research area with a great potential to make technologically advanced and useful materials. With nanotechnology it is possible to create materials from building blocks to the size of atomic clusters which exhibit enhanced electronic, magnetic, optical and chemical properties [1]. There are two major phenomena that are responsible for enhancing the physical properties. The first one is their high dispersity. As the size of a crystal is reduced, the number of atoms at the surface of the crystal compared to the number of atoms in the bulk material increases. The second phenomenon is size quantization. It arises due to the fact that their size is comparable to the de-Broglie wavelength. The spacing of the electronic levels and the band gap increases with decrease in particle size. This increase in band gap can be observed experimentally by the blue-shift in the absorption spectrum. The structural, electronic and optical properties can be tuned by controlling the sizes of the nanoparticles [2-4].

Phosphor materials in the nano range exhibit enhanced optical properties compared to the bulk counterpart. It is due to quantum confinement effect and increased surface to volume ratio. The resolution of a display device depends greatly on the size of the pixel of phosphors used in it. By using nanocrystallites phosphors the resolution of display devices can be greatly enhanced and the manufacturing cost can be significantly reduced.. The present tendency of development of such materials is oriented towards improvement of the optical properties of existing materials. Recently oxides have proved to be potential candidates for the light emitting device applications. Doped YVO_4 has been shown to have high potential as a blue thin film electroluminescent



(TFEL) phosphor material [5-6]. Hence it is planned to synthesize YVO_4 with suitable dopants as activators and study the increase in its efficiency for display devices.

Recent studies have revealed that, the luminescence of rare-earth-doped systems mainly reflects the properties of the dopants. A number of papers have reported the luminescence of nanocrystals YVO_4 doped with Tb, Sm, Eu, Nd, Ln. Among rare earth dopants samarium is widely used a activator for orange- red emission at 567,605 and 649nm. Which is most suitable for white LEDs.

Doping of YVO_4 nanoparticles with rear earth ions like Europium Dysprosium samarium, cerium have been reported using various methods as sol gel, hydrothermal, combustion, Co-precipitation method [7-8]. Among all the methods co-precipitation is one of the suitable method due to its mild reaction conditions, low cost and simple process. In the present work samarium doped YVO_4 phosphor is synthesized by co-precipitation method. The synthesized samples are characterized by the by X-ray diffraction (XRD), Fourier infra-red spectroscopy (FTIR) Scanning electron microscopy (SEM) and Photoluminescence (PL).

II. EXPERIMENTAL

Stoichiometric quantity of samarium oxide is taken in conical flask and small quantity of nitric acid ($1:1HNO_3$) is added in to it. The mixture is evaporated slowly on sand bath to convert samarium oxide to samarium nitrate. Stoichiometric amount of NH_4VO_3 is dissolved in hot water and Yttrium nitrate is dissolved in distilled water. Solution of Yttrium nitrate and samarium nitrate are mixed with constant stirring. Solution of ammonium Metavanadate is added to above solution. Subsequently, ammonia (NH_4OH) is slowly dropped into the solution under constant stirring to adjust the PH to the range 4-5. The obtained residue is centrifuged, washed with distilled water and acetone, and then dried at $50^{\circ}C$. Finally the obtained product is calcined at $800^{\circ}C$.

III. CHARACTERIZATIONS

The XRD Measurements of synthesized samples was carried out using Philips X-pert PRO Powder diffractometer with $Cu-K\alpha$ radiation. In the scan range $10-80^{\circ}$. The morphology of synthesized sample was studied using scanning electron microscope by sputtering technique with gold as covering contrast material with attachment and elemental dispersive spectroscopy analysis. Fourier transform infrared (FTIR) spectra were recorded using Nicolet Magna 550 spectrometer Frontier with KBr pellets. PL emissions spectra of the samples were recorded using spectrofluorometer with 450W xenon lamp as the excitation source.

IV. RESULTS AND DISCUSSION

4.1 Powder X-ray diffraction (XRD)

Figure 1. Shows the XRD patterns of sm-doped YVO_4 Phosphor. The diffracted peaks are indexed to tetragonal crystal phase of YVO_4 (JCPDS74-1172). Some of the weak peaks are due to the impurities present in the material and this impurities did not play any role in luminescence characterization results. The substitute of samarium ions does not produce significant phase change. It reasonable because Y^{+3} and sm^{+3} ions, have same

valency and close ionic radius. The intense peaks such as (200), (112), (312) show that Yttrium vanadium nanoparticles are highly crystalline in nature. The crystallite size was calculated using the Scherer's formula $D = (k\lambda/\beta\cos\theta)$, Where K is a constant (0.99), λ is the incident wavelength of Cu-K α (0.154 nm) line, β is the diffracted full width half maximum (FWHM) and θ is the Bragg angle. The average crystallite size of the sample was found to be 4-5 nm. It confirms the formation of nanocrystallines in the YVO₄:Sm phosphor.

4.2 Scanning electron microscopy (SEM)

The morphology of the sample is studied from SEM images. Figure.2 shows a SEM photograph of as-prepared Sm-doped YVO₄ nanoparticles. The SEM micrograph shows that the particles are interlinked with each other in various nanometer ranges, and also confirms that particles are not uniformly distributed and agglomerated. It also reveals the characteristic features like voids and porosity.

4.3 Elemental Analysis (EDS)

Fig.3 shows the elemental dispersive spectroscopy of the samarium doped YVO₄ phosphor. The spectrum confirms the existence of elements Yttrium, Vanadium, Oxygen and samarium present in the compound. Further no impurities peaks are observed. Hence it proves the formation of YVO₄:sm⁺³.

4.4 Fourier Transform Infrared Spectrum (FTIR)

The purity and functional groups of all the samples are confirmed by the FTIR spectra. The FTIR spectrum of sm-doped YVO₄ Phosphor is shown in the Fig 4. The spectrum of YVO₄:Sm showed strong bands at 771,1631 and 3365cm⁻¹ respectively. Weak absorption band are observed at 1064cm⁻¹ and 2924cm⁻¹. The strong band at 771cm⁻¹ is due to the stretching frequency of V-O band in YVO₄ [9]. The peak observed at 1631cm⁻¹ is due to the presence of bending vibration of N-H bond. A broad band centered at 3365cm⁻¹ is assigned to symmetric stretching of H₂O molecules [9-10]. The weak band at 1064cm⁻¹ is due to C-N stretching vibration, The band at 2924cm⁻¹ is due to CH₂ asymmetric stretching of the in the sample.

4.5 UV-Visible Spectroscopy

Figure 5 shows the UV-Visible absorption spectra Sm-YVO₄ of the sample. The nanocrystals obtained by coprecipitation method showed a strong absorption peak at 392nm. This originates due to surface defects namely the oxygen vacancies (F-centers), The samples contains F-centers is excited with UV light, and energy absorbed by the VO₄³⁻ groups. This reveals the energy transfer of VO₄³⁻ groups. In the as prepared sample the charge transfer takes place from oxygen ligands to the central vanadium atom inside the VO₄³⁻ anion [10].

4.6 Photo Luminescence (PL)

PL emission spectrum of Sm-doped YVO₄ nanoparticles is shown in the Fig 6. The photoluminescence spectrum shows series of emission bands with peaked at about 425,460,485,530 and 575nm when the samples are excited at 300nm. It is well known that the defects like oxygen vacancies, voids and dislocations are present on the surface of nano particles causes PL emissions at different wave lengths. Also in the co-precipitation method oxygen may enter in to the crystal lattice and causes distortion VO₄³⁻ tetrahedron, it leads PL emissions. The strongest emission peaks located around 575 nm is originated ⁴G_{5/2}→⁶H_{5/2} transition of Sm⁺³. Due to an energy transfer from the VO₄³⁻ groups.



The photoluminescence observed in our experiment is attributed to the following steps. In the emission mechanism of samarium ions, UV light is absorbed by a vanadate group and then it is transferred to the higher excited states of Sm ions. Finally the emission from Sm ions following the above mentioned transition occurs in the visible and NIR regions [11-13].

Figure Captions

Figure 1. X-ray diffraction spectrum of Sm-doped YVO₄ Nanocrystals.

Figure 2. Sem image of Sm-doped YVO₄ nanoparticles.

Figure 3. EDAX characterization of prepared Sm-doped YVO₄ Nanoparticles.

Figure 4. FTIR Spectrum of Sm-doped YVO₄ nanoparticles

Figure 5. UV-Visible spectrum of Sm-doped YVO₄ Nanoparticles.

Figure 6. Photoluminescence spectrum of Sm-YVO₄ Nano crystals.

Figure 1. X-ray diffraction spectrum of Sm-doped YVO₄ Nanocrystals.

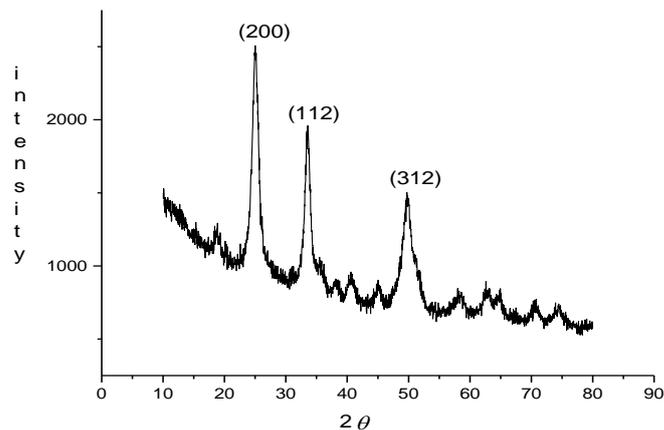


Figure 2. Sem image of Sm-doped YVO₄ nanoparticles.

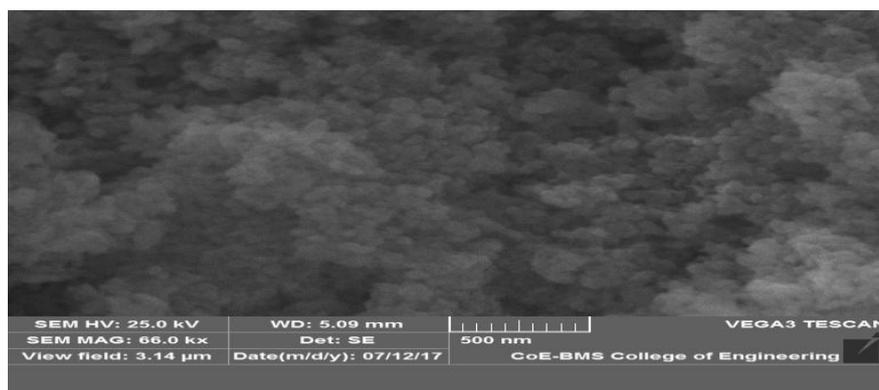


Figure 3. EDAX characterization of prepared Sm-doped YVO₄ Nanoparticles.

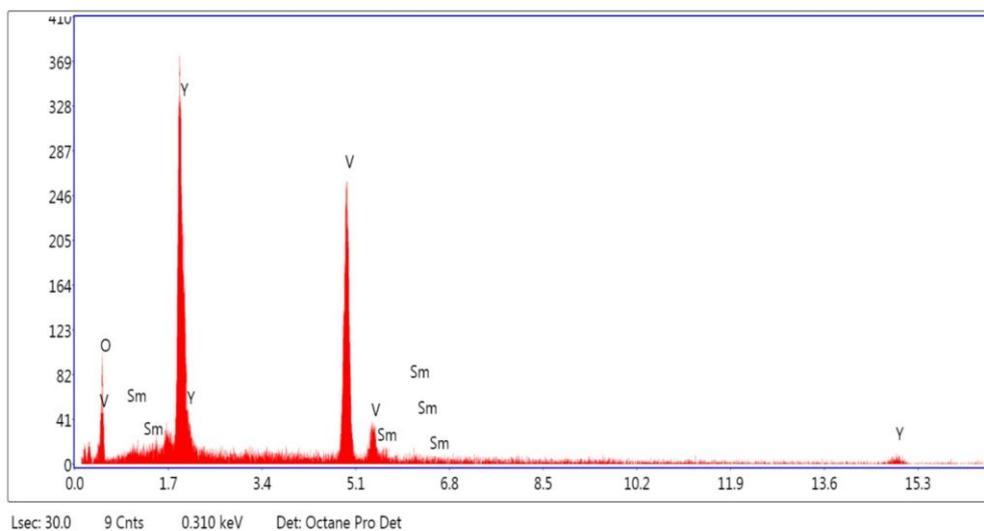


Figure4. FTIR Spectrum of Sm-dopedYVO₄ nanoparticles.

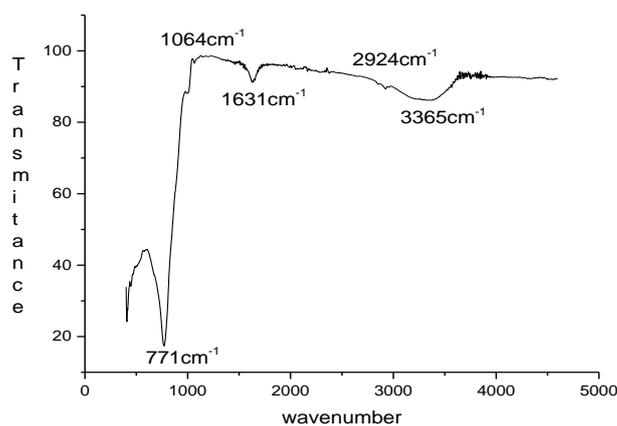


Figure 5. UV-Visible spectrum of Sm-doped YVO₄ Nanoparticles.

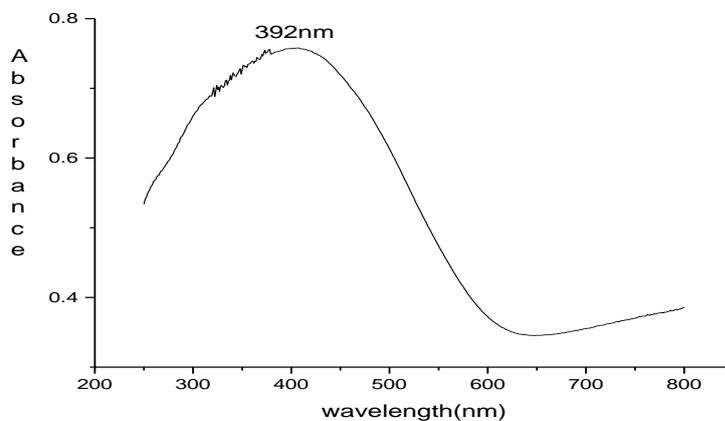
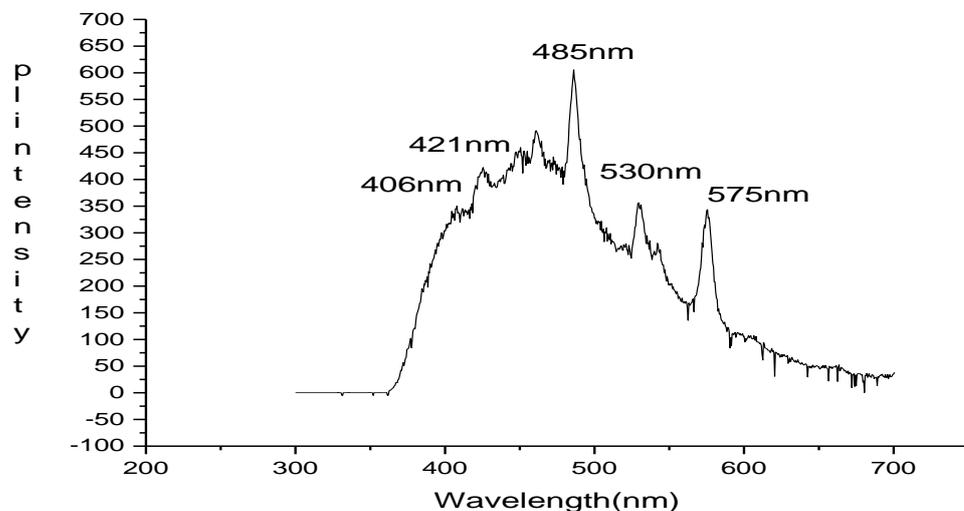


Figure 6. Photo luminescence spectrum of Sm-YVO₄Nano crystals.



V. CONCLUSIONS

YVO₄:Sm³⁺ doped phosphor is successfully synthesized by co-precipitation method. XRD patterns confirm that the synthesized sample shows tetragonal structure. SEM micrograph and EDAX confirmed formation of YVO₄:Sm. The optical absorption spectra revealed the presence of surface defects. The PL emissions bands indicate the presence of intrinsic defects in the prepared sample.

REFERENCES

- [1.] The Royal Society, Royal Academy of Engineering report (2004)
- [2.] R.W.Cahn.Nature 348 (1990) 389
- [3.] R.Dagani,Chem.Eng.News.72 (1992) 18
- [4.] H.Gleiter,Nanostruct.Mater.6 (1995) 3
- [5.] Yee-Shin chang, Feng-Ming Huang, Yeou-Yih Tsai, Lay-Gaik Teoch, Journal of Luminescence 129(2009) 1181-1185.
- [6.] Lasheng Jiang, ZhengyangZhang, YuchanXiao, QianmingWangn-Journal of Luminescence 132 (2012) 2822-2825.
- [7.] Lianhua Tian, Sun-il Mho-journal of Luminescence 122-123(2007)99-103.
- [8.] Xiuzhen Xiao et al-Material science and Engineering B 176(2011)72-78.
- [9.] Yi-Chin Chen, Yun-Chen Wu, De-Yin Wang and Teng-Ming Chen-J. Mater.Chem. 2012, 22, 7961.
- [10.] HaiYan Xu Hao Wang,, YongQiang Meng, Hui Yan Solid State Communications 130 (2004) 465-468.
- [11.] Guang Jia, Kai Liu, Yuhua Zheng, Yanhua Song, and Hongpeng You crystal growth and design 2009 Vol 9 No.8 3702-3706.
- [12.] Juhong Miao , Jing Su, Yan Wen, Weifeng Rao Journal of Alloys and Compounds 636 (2015) 8-11.
- [13.] L. Krishna Bharat, Yong Il Jeon, Jae Su Yu Journal of Alloys and Compounds 685 (2016) 559-565.
- [14.] 685 (2016) 559-565.