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LUMINESCENCE STUDY ON $GDVO_4$: TM NANO-CRYSTAL MATERIALS

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Abstract: Nano-crystal $GdVO_4$:Tm materials of different doping concentrations were synthesized using chemical co-precipitation method in water medium. The materials were annealed at 500° C for 3 hours and then grained into powder form. The materials were characterized by recording XRD and TEM images. The materials showed tetragonal structures and their estimated crystallite sizes were in the range 40-50 nm. All luminescence spectra of as prepared nanocrystal materials were recorded at room temperature.

Keywords: XRD, TEM, Nanocrystal materials.

Introduction:

It is well-known that reduction of the particle in nano-sized in a crystalline system can result in remarkable modifications of properties which are different from those of the bulk because of high surface to volume ratio and the quantum confinement effect of nanomaterials [1]. The dependence of the behavior on the particle size can allow one to engineer their physical and chemical properties. Further, the band gap of nanomaterials is increased with the reduction in size of the particles [2]. On the basis of the above facts, the study on luminescent materials in nono-sized has been intensified in the last few years. Luminescent materials are the high-purity inorganic materials that can emit light when exposed to various excitation sources [3]. They are composed of a host lattice doped with a small amount of impurity (lanthanide) ions which activate the luminescent host.

Luminescent materials based on the lanthanide ion (Ln^{3+}) have wide applications in phosphor lamps, display devices, cathode ray tubes [4 & 5], and components of

telecommunication [6] as well as active laser materials [7]. These devices are very essential in the development of our society. Recently, there has been great interest in corporation of these luminescent materials in the polymer based materials because of easy processing of polymers and ease of integrating different components. With the recent development in the high resolution flat panel display and field emission displays, the demand for stable and highly bright luminescent materials has been sharply increased. Usually, efficient energy transfer from semiconductor host to lanthanide ions gives higher luminescence intensity [8]. Generally, oxide based luminescent materials such as YVO_4, $GdVO_4$, Y_2O_3, $LaPO_4$, Gd_2O_3 etc. doped with lanthanide ions play an important role in high-resolution optical devices such as cathode ray tubes, electroluminescent displays and field emission displays [9].They have advantages over the currently used sulfide phosphors in stability in vacuum and absence of corrosive gas emission under electron bombardment [10]. Among these materials, $GdVO_4$ is an interesting and excellent host material for lanthanide ion emission such as Eu^{3+}, Dy^{3+}, Tm^{3+}, Sm etc. due to the reasons (i) efficient energy transfer(ET) from the VO^{3-} (Vanadate) absorption to the excited states of the activators(Ln^{3+}) and (ii) Gd^{3+} ($4f^{7}$) has a strong absorption peak at ~280nm and thereby energy transfer (ET) is possible to the excited states of the activators(Ln^{3+}) [11]. Moreover, lanthanide ions doped $GdVO_4$ crystal is a promising laser material having strong and broad absorption band, its absorption coefficient and emission cross-section are much higher than those of lanthanide doped YVO_4 and YAG crystals [12]. As a result, lanthanide ions doped $GdVO_4$ crystals have been recognized as excellent materials in high-power LD solid-state lasers [13]. S. Lin et al reported that $GdVO_4$ has been used as a promising host material for laser, luminescent display, CRTs, and lamps when doped with different lanthanide ions [14]. On the basis of the above facts, the authors intended to study on the luminescence of $GdVO_4$: Tm nanocrystal materials which is expected to present new structural and enhanced photoluminescence properties, and is the main objective of the research project. $GdVO_4$ crystal belongs to tetragonal system with

zircon-type structure having space group of $I4_{1/amd}$. It composes of $[VO_4]^{3-}$ tetrahedron in which V ions are tetrahedrally co-ordinated and a distorted dodecahedral (eight) co-ordination in which Gd^{3+} ion is linked with eight neighbouring oxygen ions. Each V has four oxygen ion neighbours at a V-O distance of 1.710 Å . The distance between the Gd and O is 2.461 Å for four lengths along z-axis and 2.344 Å for four others on the x-y plane [2 &15].

Experimental details:

The starting materials were Gadolinium chloride ($GdCl_3.6H_2O$ 99.99% **Alfa Aesar**), Ammonium Metavanadate (NH_4VO_3 99.99% Aldrich), Thulium Nitrate hydrate ($Tm(NO_3)_3.5H_2O$ **Sigma** 99.99%) and double distilled water used as solution medium. In a typical synthesis of 2 % of $GdVO_4$:Tm materials, 500 mg $GdCl_3.6H_2O$, 12 mg of $Tm(NO_3)_3.5H_2O$ were dissolved in 50 ml of double distilled water and warmed at 40 °C for 5 minutes and then 160 mg of NH_4VO_3 was added to the solution. The solution was maintained pH value at 11 using sodium hydroxide (NaOH) pallet. With the introduction of NaOH, precipitation starts to form. The whole solution was stirred with a speed of 200 rpm at 40 °C for 30 minutes to complete the reaction using magnetic stirrer. The precipitation was collected by centrifugation. The collected precipitation was annealed at 500 °C for 3 hours and made in powder form. Similar procedures were done for synthesis of different doping concentrations.

The phase purity and crystal structure of as prepared materials were examined by powder X-ray diffraction (XRD) technique using **Philips Powder Diffractometer** with *CuKa* (1.5405 Å) radiation with Ni filter and Transmission electron microscopy (TEM) images recorded using JEM-2000 FX microscope at 160 KV. All the luminescence spectra were recorded in LS 55 Fluorometer (Perkin Elmer) at room temperature.

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Results and Discussion:

XRD patterns of $GdVO_4$:Tm materials for a particular dopant concentration (5%) annealed at 500˚C for 3 hours is shown in Fig.1. The diffraction peaks show the presence of tetragonal phase structure according to JCPDS 86-0996. By the application of Scherrer equation: $t = (0.9\lambda)/(\beta \cos\theta)$, where λ is the X-ray wavelength, β is line broadening at half at the maximum intensity in radians and θ is the Bragg angle, the crystallite sizes of as prepared materials were in the range of 40-50 nm. The sizes of as prepared materials were approximately confirmed by TEM images as shown in Fig. 2

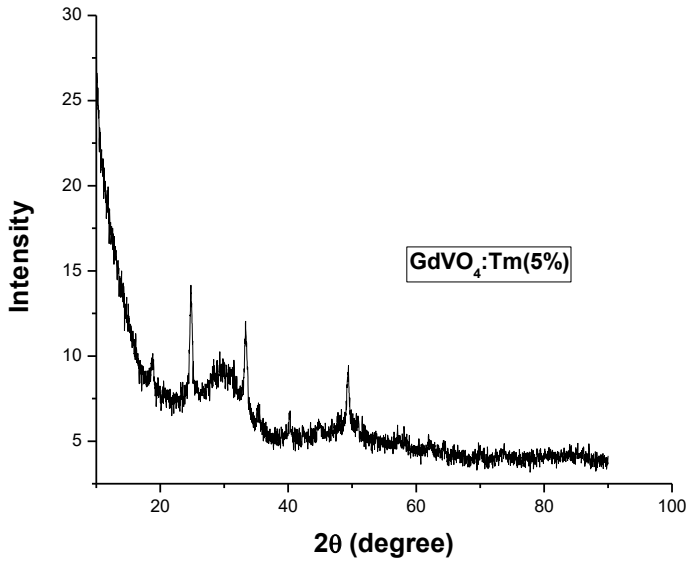

Fig. 1 XRD patterns of $GdVO_4$:Tm(5%) nano crystal materials

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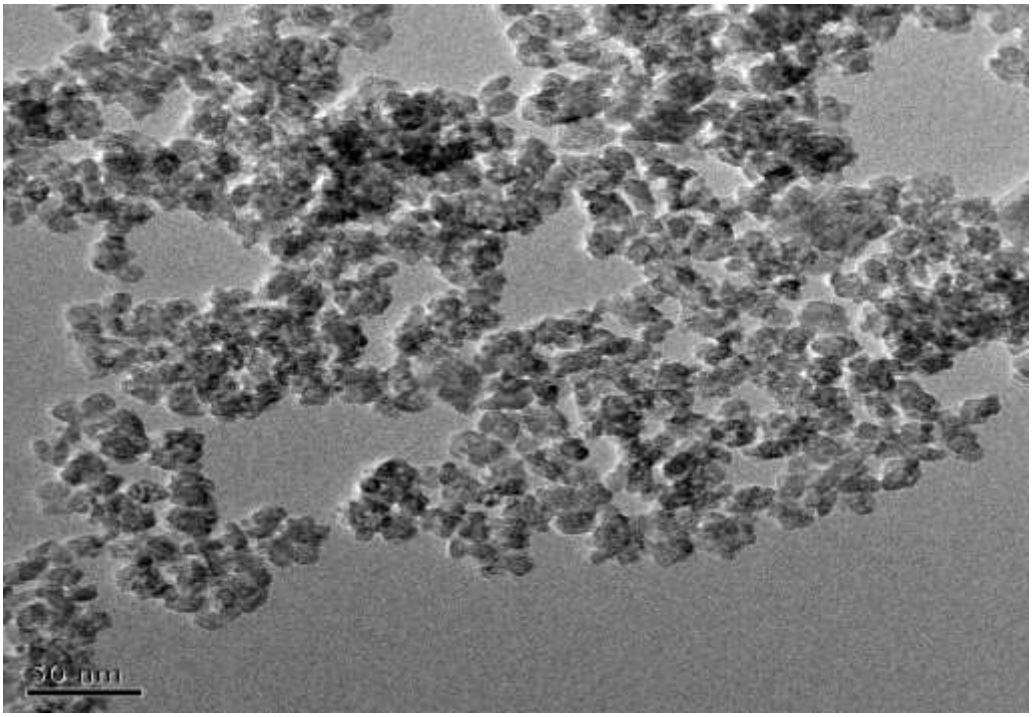

Fig. 2 TEM images of $GdVO_4$:Tm(5%) nano crystal materials

Fig. 3(a) shows excitation spectra of as-prepared $GdVO_4$:Tm(2%) nanocrystal materials annealed at 500° C for 3 hours by monitoring the emission wavelength at 477 nm recorded at room temperature. The spectra show a charge-transfer band covered the UV region from 235 to 345 nm with a maximum at approximately 272 nm. The strong wide band centered at 272 nm is attributed mainly due to charge transfer from the oxygen ligands to the central vanadium atom inside VO_4^{3-} ions. Similar excitation spectra of $GdVO_4$:Tm(5%) nanocrystal materials annealed at 500° C for 3 hours by monitoring the same emission wavelength 477 nm are observed as shown in Fig 3 (b).

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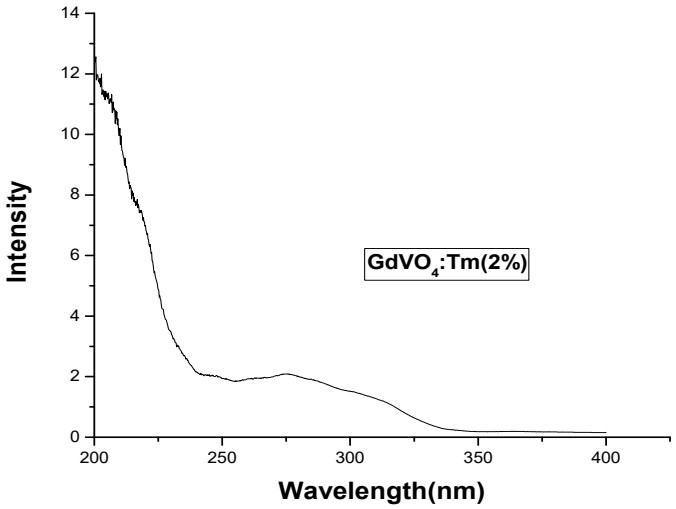

Fig. 3 (a) Excitation spectra of $GdVO_4$:Tm(2%) nanocrystal materials

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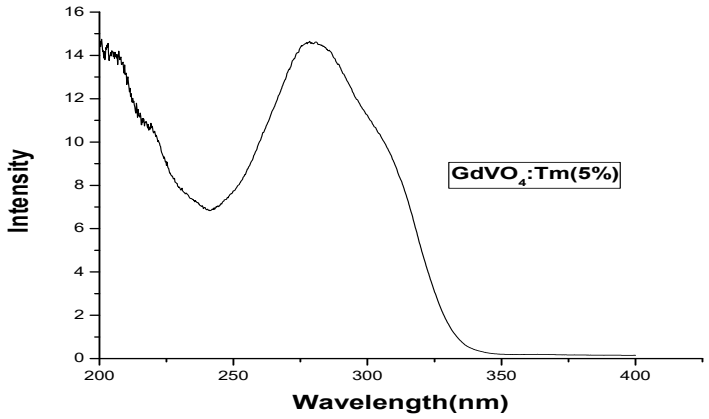

Fig. 3 (b) Excitation spectra of $GdVO_4$:Tm(5%) nanocrystal materials

Fig. 4 (a) shows the emission spectra of as-prepared $GdVO_4$:Tm(2%) nanocrystal materials annealed at 500˚C for 3 hours by monitoring the excitation wavelength at 272 nm recorded at room temperature. The emission spectra exhibit the main characteristic emission lines of Tm^{3+} in the strong blue region at 477 nm corresponding to $^1G_4 - {}^3H_6$ transition. These materials emit a relatively a high pure and strong blue light, which is relative to high efficient of the host-to-guest energy transfer [16]. Similar emission spectra of $GdVO_4$:Tm(5%) nanocrystal materials annealed at the same temperature 500˚C for 3 hours by monitoring the same excitation wavelength 272 nm are observed as shown in Fig 4 (b).

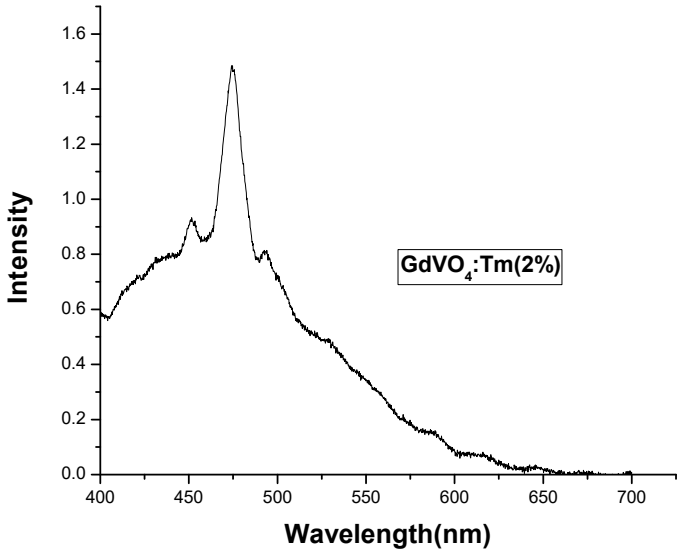

Fig. 4 (a) Emission spectra of $GdVO_4$:Tm(2%) nanocrystal materials

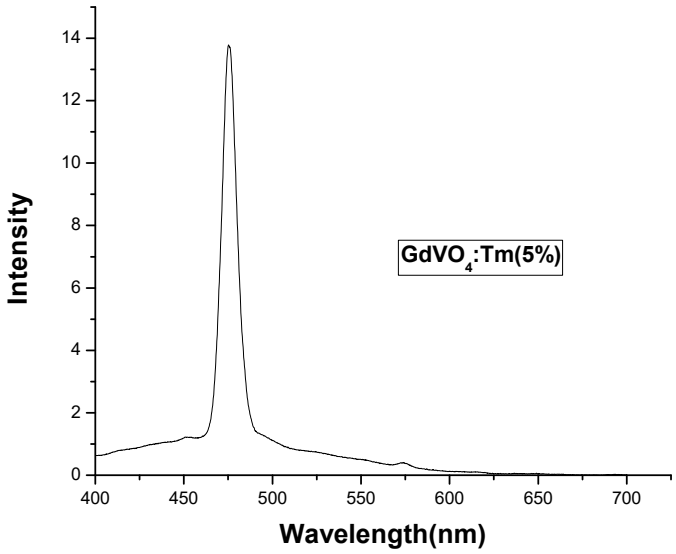

Fig. 4 (b) Emission spectra $GdVO_4$:Tm(5%) nanocrystal materials

Conclusions: $GdVO_4$:Tm(2%) and $GdVO_4$:Tm(5%) nanocrystal materials were synthesized by chemical method in water medium. The crystallite sizes of as prepared materials estimated from XRD data are in the range 40-50 nm which were critically confirmed by TEM images. Luminescence study of both as prepared naoncrystal materials was observed to emit strong blue light.

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References:

1. A.P.Alivisatos, ***Science,* 271(1996) 937.**
2. B.C.Chakoumakos,M.M.Abraham, and L.A.Boatner, ***J.Solid State Chem***., **109(1994) 197**.
3. W.J.Park, M.K. Jung,D.H.Yoon, ***Sensors and Actuators B,* 126(2007)324-327**.
4. G. Blasse and B.C. Grabmaier, Luminescent materials, ***Springer, Berlin*,1994**.
5. G. Blasse, ***J. Chem.Phys.,* 45(1966)2356** Cross Ref CAS Search Pub Med.
6. J.W. Stouwdam and F.C.J.M.van Veggel, ***Nano Lett.,* 2(2002)733** Cross Ref CAS Search Pub Med.
7. E.A. Manders and L.G.Deshazer, ***J. Opt. Soc. Am.,* 61 (1971) 684** Search Pub Med.
8. R.S.Ningthoujam, R.Shukla, R.K Vatsa, V.Duppel, L.Kienle, and A.K.Tyagi, ***Journal of Applied Physics,* 105 (2009) 084304.**
9. M. Yu, J. Lin, Z. Wang, J. Fu, S. Wang, H.J. Zhang, Y.C. Han, ***Chem. Matter***., 14 (2002) 2224.
10. K. S. Shim, H .K. Yang, Y. R. Jeong, B. K .Moon, B. C. Choi, J. H. Jeong, J. S. Bae, S. S. Yi, and J. H. Kim, ***Appl. Suf. Sci***., **253 (2007) 8146**.
11. N. Shanta Singh,R.S. Ningthoujam, Ganngam Phaomei, S. Dorendrajit Singh,A. Vinu and R.K. Vasta, ***Dalton Trans***, **41 (2012) 4404-4412**.
12. H. L. Ma, J. C. Zang, Y. L. Liu, J. H. Zhu, X. M. Song, ***J. Rare Earths***, **21 (2003) 415**.
13. J. Su, Q. L. Zhang, S. T. Yin, C. X. Guo, ***Physica B,* 403 (2008) 3002-3008**.
14. S.Lin,W.XIONG,L.Li, and Y.Xie. ***J.Cryt. Growth***, **270 (2004) 133**.

15. D.F.Mullica,E.L.Sappenfield,M.M.Abraham,B.C.Chakoumakos,and L.A.Boatner, **Inorg.Chim. Acta, 248 (1996)85**.

16. J. Wang, Y. Xu, M. Hojamberdiev, Y. Cui, H. Liu, J. Zhu, ***Journal of Alloys and Compounds,* 479 (2009)772-776.**