



Synthesis and Characterizations of Dy³⁺ doped Y₂O₃:SiO₂nanopowder

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ABSTRACT

The sol-gel process combines the advantage of lower temperature and possibility of making of finely dispersed powders and coating with ease and low cost. In the present studies Y₂O₃:SiO₂ nanopowder doped with dysprosium ion was synthesized via sol-gel route. Then dried sample was annealed in a muffle furnace at 750°C. Structural and optical behavior of the annealed sample was investigated by different complementary characterization techniques such as X-Ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), UV-Vis spectroscopy, which are discussed at length. Particle size has been calculated by the well-known Debye-Scherrer formula. Band gap energy has also been calculated by Tauc's plot. There is increasing recognition that sol-gel synthesis offers growth control capabilities that can be conveniently exploited in preparing these desirable nanophosphor materials.

I. INTRODUCTION

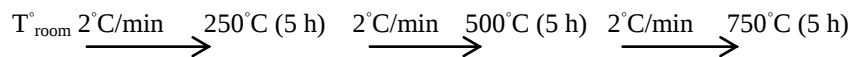
In recent years, rare earth nanophosphors activated by lanthanides are being witnessed with enhanced luminescence properties and hence find potential applications in field emission displays (FEDs), flat panel displays (FPDs), plasma display panels (PDPs), electro luminescent displays, colour tunable devices etc. due to their high performance, environment friendliness and energy saving capabilities. Nanophosphors activated with Lanthanide ions (Ln³⁺) have attracted great attention because of their wide range of colour emission and better luminescent properties. Yttrium oxide (Y₂O₃) is one of the best hosts for rare earth ions because of the similarities in the chemical properties and the ionic radii of rare earths. Moreover, Y₂O₃ possesses a higher melting point (2400 °C), higher thermal conductivity, wide transparency range (0.2 – 8 μm) with a band gap of 5.6 eV, high refractive index (~1.8) and low cut-off phonon energy (380 cm⁻¹). In the present work, we have used sol-gel technique to synthesize and investigated the structural properties of Dy³⁺ doped Y₂O₃:SiO₂ nanopowder. Dysprosium with its emission in greenish-yellow region has been chosen for its unique spectral properties and SiO₂ act as a stabilizing agent which protects the nanoparticles from aggregation [1, 4].

II. SYNTHESIS AND CHARACTERIZATION

Dy³⁺ doped Y₂O₃:SiO₂ sample was synthesized by sol-gel route [5, 6], which takes advantage of both bottom up and top down approaches, is a simple, low cost and environment friendly technique. The chemicals such as yttrium (III) nitrate tetrahydrate, dysprosium (III) nitrate hydrate used were purchased from Sigma Aldrich and were of high purity. An appropriate amount of ethanolic TEOS was titrated with dil. HCl acid for about 3hrs at a constant stirring rate of 750rpm at 40°C. Then solutions of yttrium nitrate and dysprosium nitrate in 1M dil.



HNO₃ (prepared separately) were added separately in one lot and stirred for about 2:30hrs. The prepared sol was converted into a dense gel after ageing for 3 weeks. The gel was then grinded into fine powder after drying in an oven at 120°C for 48hrs. The prepared nanopowder was further annealed as according to the scheme given below:



The structure of the prepared powders was investigated via X-ray diffraction (XRD) using a BrukerD8 Discover diffractometer with Cu K α radiation ($\lambda=0.154\text{nm}$) within a 2θ scan range of $20^{\circ} - 70^{\circ}$. FTIR spectrum of the nanocomposite was taken at room temperature using Perkin Elmer 400 spectrophotometer in the range 400-4000 cm⁻¹. The optical absorption spectra have been observed by using Lambda 750 (Perkin Elmer) UV-Vis spectrophotometer in 200-800 nm range.

III.RESULTS AND DISCUSSION:

3.1X-Ray Analysis:

The X-ray diffraction pattern taken within the 2θ scan range of $20^{\circ} - 70^{\circ}$ for the synthesized sample is shown in Fig.1. The result shows that the prepared sample is having a crystalline phase in which diffraction peaks can be assigned to monoclinic phase of Y₂O₃ when compared to JCPDS Files No. 44-0399 [7]. The average nano crystalline size has been calculated by well-known Debye Scherrer formula: $D = K\lambda / \beta \cos \theta$, where $K=0.94$, β is full width half maximum, $\lambda=0.154 \text{ nm}$. The detail studies of all peaks are given in Table-1.

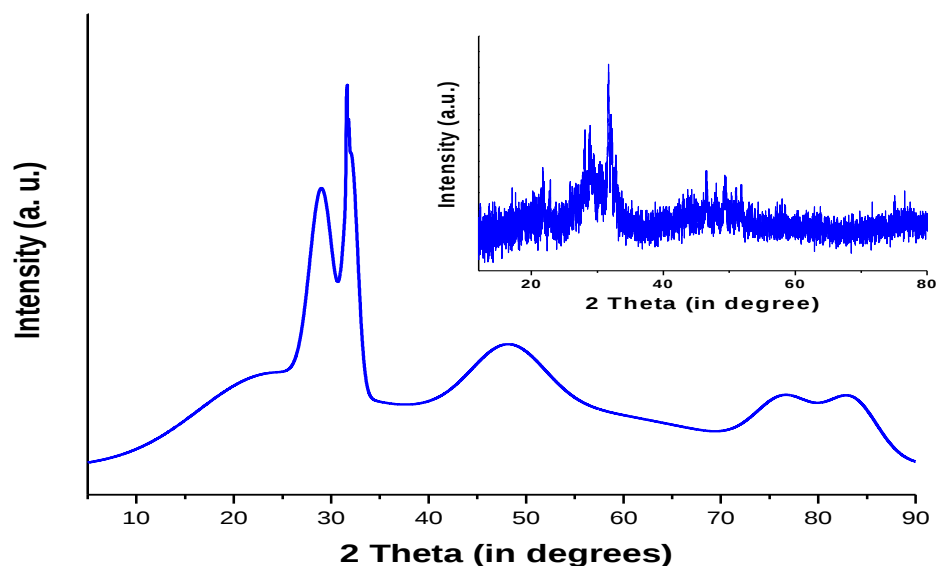


Figure1: XRD for Dy³⁺ doped Y₂O₃:SiO₂

Table 1: Details of XRD data.

Pos.[°2Th.]	Height [cts]	FWHM Left[°2Th.]	d-spacing [Å]	Rel. Int. [%]
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		21.74	20	0.23	4.08557	44.42
28.94	27	1.94	3.08298	58.80		
		31.64	46	0.34	2.82525	100.00
32.12	26	0.42	2.78423	57.38		
46.48	17	0.31	1.95219	36.10		
		49.35	10	1.2	1.84510	22.15

3.2 FTIR analysis:

FTIR analysis gives information about functional groups present in the sample at room temp. FTIR spectrum of the sample is shown in Fig.2. The absorption band at 3363 cm^{-1} and 1595 cm^{-1} corresponds to -OH, -NH groups. Small absorptions at 1469 cm^{-1} , 1392 cm^{-1} and 1300 cm^{-1} correspond to organic impurities. The FTIR peaks of SiO_2 molecule is obtained at 1085 , 798 and 464 cm^{-1} and corresponding to asymmetric, symmetric and bending vibrations, respectively. The band at 945 cm^{-1} can be attributed to Si-OH bond. The bands at 700 cm^{-1} and 553 cm^{-1} can be attributed to Y-O bond [8, 11].

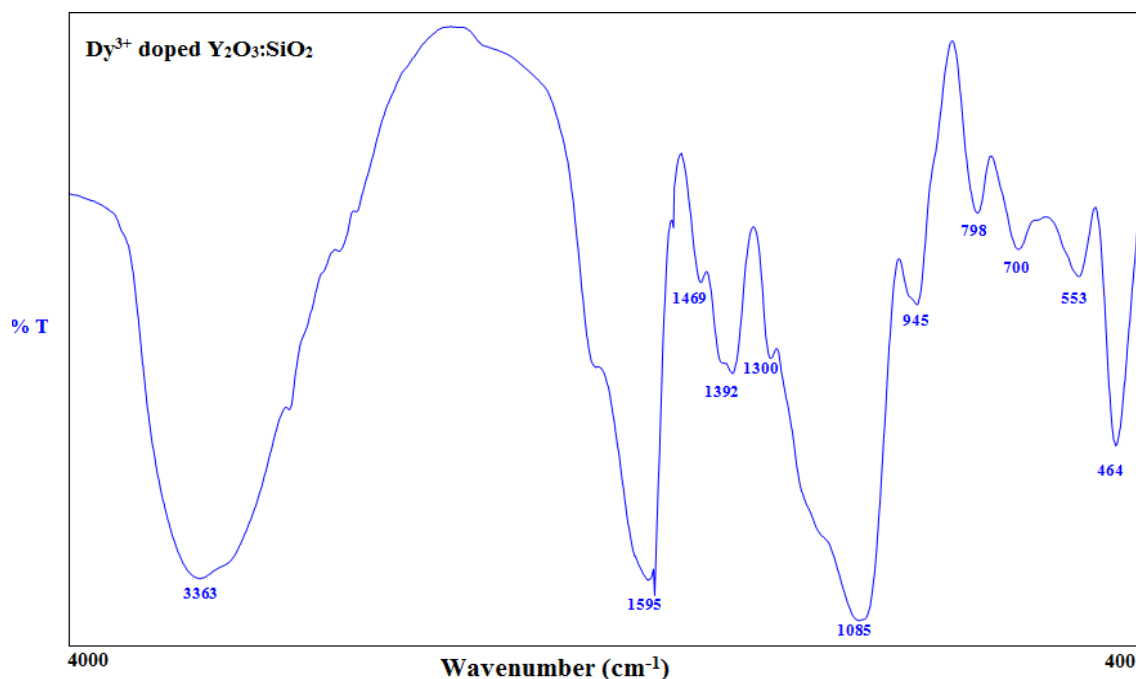


Figure 2: FTIR results for Dy^{3+} doped $\text{Y}_2\text{O}_3:\text{SiO}_2$ nanopowder.

3.3 Uv-Vis Spectroscopy:

The optical properties of the sample have been studied by UV-Vis spectroscopy in the wavelength range 200-800nm as shown in fig.3.

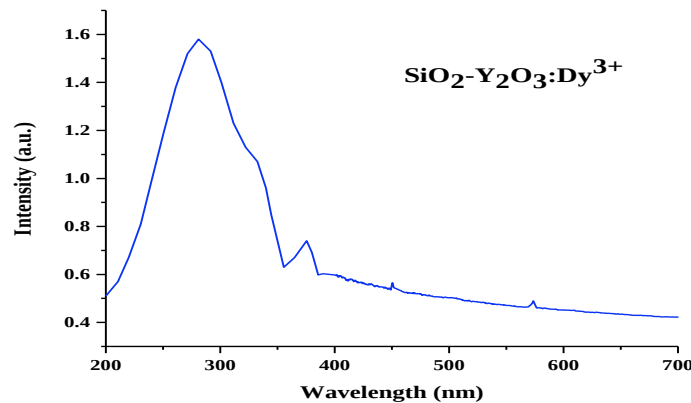


Figure 3: Absorption spectrum of Dy^{3+} doped $\text{Y}_2\text{O}_3:\text{SiO}_2$ nanopowder.

The absorption spectrum shows a broad peak at 280 nm due to the host matrix of Y_2O_3 lattice corresponding to charge transfer band $\text{O}^{2-} \rightarrow \text{Y}^{3+}$ [8]. The presence of electron and the p state of oxygen lying in close proximity with Y^{3+} site may result such bands. Other small absorption peaks at 377, 451 nm and 574 nm could be attributed to the transition lines ${}^6\text{H}_{15/2} \rightarrow {}^4\text{M}_{19/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{F}_{9/2}$ respectively [11, 12] of Dy^{3+} ion present within the host matrix of $\text{Y}_2\text{O}_3:\text{SiO}_2$.

3.4 Tauc's Plot

The relation between the incident photon energy ($h\nu$) and the absorption coefficient (α) is given by the following equation:

$$(\alpha h\nu)^{1/n} = A (h\nu - E_g)$$

Here A is a constant, α is absorption coefficient and E_g is the band gap energy of the material and the exponent n depends on the type of transition. For direct allowed transition $n = 1/2$, for indirect allowed transition $n = 2$, for direct forbidden $n = 3/2$ and for indirect forbidden $n = 3$. Direct band gap of the samples are calculated by plotting $(\alpha h\nu)^2$ versus $h\nu$ and then extrapolating the straight portion of the curve on $h\nu$ axis at $\alpha = 0$ as shown below in the Fig. 4. The band gap energy of the sample is found to be 3.508 eV.

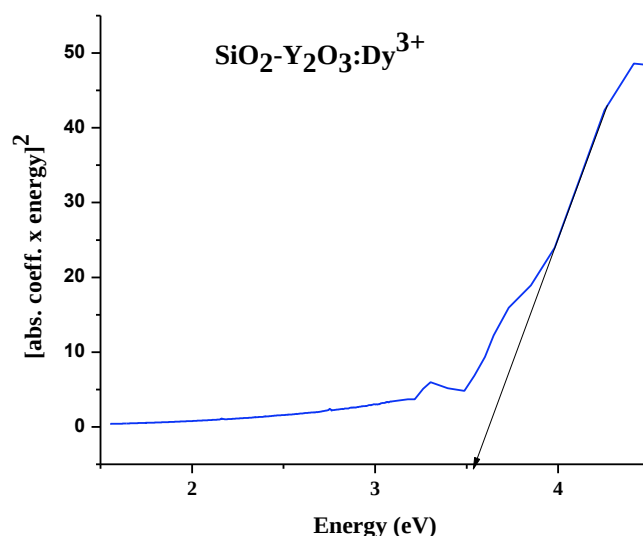


Figure 4: Tauc's plot of Dy^{3+} doped $\text{Y}_2\text{O}_3:\text{SiO}_2$ nanopowder.

IV. CONCLUSIONS

The present study demonstrates the versatility of the sol gel method to yield highly dense nanopowder of the dysprosium doped in the composite of $\text{Y}_2\text{O}_3\text{-SiO}_2$ binary oxide at a low annealing temperature (750°C) when compared to the temperature ($>1400\text{--}1600^\circ\text{C}$) required for the usual solid-state synthesis. The XRD analysis indicates that Dy^{3+} ion is perfectly integrated in to the crystal lattice of monoclinic yttrium oxide. The average sizes of the nanocrystallites were calculated from the diffraction line width based on the D-S formula, is found to be 25 nm for annealed sample. The band gap energy of the sample is found to be 3.54 eV on the basis of which, the prepared nanomaterial offers possibility for applications in security printing, boillable technology, lamps for illumination purposes etc.

REFERENCES

- [1] G. K. Das and T. T. Y. Tan, *Rare-earth-doped and codoped Y_2O_3 nanomaterials as potential bioimaging probes*, *J. Phys. Chem. C*, 112, 2008, 11211, DOI: 10.1021/jp802076n
- [2] T. S. Atabaev, Y. H. Hwang, H. K. Kim, *Color-tunable properties of Eu^{3+} and Dy^{3+} codoped Y_2O_3 phosphor particles*, *Nanoscale Research Letters*, 7, 2012 556, <https://doi.org/10.1186/1556-276X-7-556>
- [3] M. Jayasimhadri, B. V. Ratnam, K. Jang and Ho Sueb Lee, *Greenish-yellow emission from Dy^{3+} doped Y_2O_3 nano phosphors*, *J. Am. Ceram. Soc.*, 93 (2), 2010 494–499 DOI: 10.1111/j.1551-2916.2009.03426.x
- [4] A. Dupont, C. Parent, B. Le Garrec, and J.M. Heintza, *Size and morphology control of Y_2O_3 nanopowders via a sol-gel route*, *Journal of Solid State Chemistry*, 171, 2003 152–160, DOI: org/10.1016/S0022-4596(02)00202-5
- [5] A. E. Danks, S. R. Hall, Z. Schnepf, *The evolution of 'sol-gel' chemistry as a technique for materials synthesis*, *Mater. Horiz.*, 3, 2016 91-112, DOI: 10.1039/C5MH00260E



- [6] E. Zelazowska, E. R. Pasek, M. B. Laczka, K. C. Kowalska, *Sol-gel-derived hybrid materials multi-doped with rare-earth metal ions*, *Materials Science-Poland*, 30(2),2012, 105-120, DOI: 10.2478/s13536-012-0014-3
- [7] C. Hua, C. Li, J. Guo, X. Yan, J. Liu, L. Chen, J. Wei, L. Hei, *Optical properties of cubic and monoclinic Y₂O₃ films prepared through radio frequency magnetron sputtering*, *Surface and Coatings Technology*,320(25),2017, 279-283, <https://doi.org/10.1016/j.surfcoat.2017.01.004>
- [8] K. Mishra, S.K. Singh, A.K. Singh, S.B. Rai, *Optical characteristics and charge transfer band excitation of Dy³⁺ doped Y₂O₃ phosphor*, *Materials Research Bulletin*, 47, 2012, 1339–1344, DOI:10.1016/j.materresbull.2012.03.017
- [9] B.N. Lakshminarasappa, J.R. Jayaramaiah, B.M. Nagabhushana, *Thermoluminescence of combustion synthesized yttrium oxide*, *Powder Technol.*, 217, 2012, 7, <https://doi.org/10.1016/j.powtec.2011.09.042>
- [10] P.A. R. Pereira, D.A. Ceccato, A.G.B. Junior, M.F.S. Teixeira, S.A.M. Lima, A.M. Pires, *Study on the structural and electrocatalytic properties of Ba²⁺-and Eu³⁺-doped silica xerogels as sensory platforms*. *RSC Adv.*, 6, 2016, 104529–104536, <https://doi.org/10.1039/C6RA22508J>
- [11] T. Verma, et al., *Photoluminescent and Thermoluminescent Studies of Dy³⁺ and Eu³⁺ Doped Y₂O₃ Phosphors*, *J.Fluoresc.*, 28,2018, 453-464,<http://doi.org/10.1007/s10895-018-2208-5>.
- [12] K. V. Krishnaiah, K. U. Kumar and C. K. Jayasankar, *Spectroscopic properties of Dy³⁺-doped oxyfluoride glasses for white light emitting diodes*, *Materials Express*, 3, 061, 010, 2013, 2158-5849, doi:10.1166/mex.2013.1094