

Photoluminescence properties of Gadolinium doped Yttrium Zirconate Phosphors for Optoelectronic Applications

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ABSTRACT: The Yttrium Zirconate $Y_2Zr_2O_7$ doped with various concentration (1.0, 1.5, 2.0 and 2.5 mol%) of Gd^{3+} were successfully synthesized by high temperature solid state reaction method. The confirmation of existence of expected phases, X-ray diffraction (XRD) pattern of the sample with optimum concentration of Photoluminescence (PL) emission spectra was observed. The diffraction peaks of observed XRD were significantly matched with COD card 96-152-8995 which confirmed the cubic crystal structure formation with the space group of $Fd\bar{3}m$ (227). The Fourier Transform Infrared Spectrum of the sample with optimum PL emission also supported the formation of discussed phases of $Y_2Zr_2O_7$. The morphological studies were carried out by scanning electron microscope (SEM) image recorded at various resolutions. Photoluminescence (PL) emission spectra were recorded at an excitation of 274 nm. PL spectra expressed the prominent peaks at 470, 587, 600, 615 and 627 nm. The peaks centered at 470 nm and 587 nm were attributed to the transition $^5D_4 \rightarrow ^7F_5$ occupied various sites of different energies due to host zirconium ions whereas, peaks centered at 600nm, 615nm and 627nm were attributed to transition $^4I_{9/2} \rightarrow ^4G_{5/2}$. The result obtained signifies the phosphor (s) discussed to be a promising material for LED's display devices.

KEYWORDS - FTIR, photoluminescence, phosphors, SEM, XRD.

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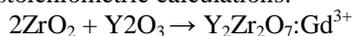
I. INTRODUCTION

Rare earth element are associated with 4f-4f inter-configuration and 4f-5d inter-configuration transition are used for characterizing optical transition of trivalent rare earth (RE) ions[1]. The photoluminescence (PL) is the phenomenon of light emission from a solid as a response to a electromagnetic stimulus gives to it the light emission induced by optical transition of RE ions. these phosphor are emit at distinct and different wave length in the electromagnetic spectrum which is useful for X-ray intensifying screen as well as various types of display devices likes LED's [2]. Oxide based phosphors attract many researcher attention due to the advantage of their good thermal stability, low thermal conductivity and ability to formation of defect[3]. Recently many new preparation method for $Y_2Zr_2O_7$ phosphors has been concentrated on the soft chemistry rules such as co-precipitation, sol-gel, inorganic sol-gel, hydrothermal method, combustion method which of the solid state reaction method is promising method to obtain Nano-crystalline materials with unique properties and better chemical uniformity because the materials are used homogeneously mixed in solid phases[4-5]. In this study $Y_2Zr_2O_7:Gd^{3+}$ phosphors were synthesized by solid state reaction method. Solid state reaction technique is chose as it is a high temperature synthesis technique and provides better morphology. Prepared phosphors were characterized by XRD technique; SEM images were taken for surface morphological studies and FTIR spectroscopy for the solid bond formation. PL properties were also investigated in order to study the optical properties of the phosphor.

II. EXPERIMENTAL

The Gd^{3+} doped $Y_2Zr_2O_7$ were synthesized by high temperature solid-state reaction method. The materials used for preparations of $Y_2Zr_2O_7:Gd$ were as follows: Y_2O_3 [Yttrium (III) Oxide purity > 99.99%], ZrO_2 (Zirconium Oxide purity >99%), Gd_2O_3 (Gadolinium Oxide purity >99.99% as an activator) and H_3BO_3 (as a flux) all of Hi-media (Analytic Grade) was used. All material are mixed with stoichiometric amount as available commercially weighed and grounded for approximately 30 minute into a fine powder by agate mortar and pestle an hour. The grounded phosphor was placed in an alumina crucible (150 ml) and heated at from room temperature to $1350^{\circ}C$ in a muffle furnace with a heating rate of $5^{\circ}C/min$. Material was kept for more than 3 hour after reaching the temperature of $1350^{\circ}C$. Then the furnace was off to cool at room temperature [6-10].

Chemical reaction used for stoichiometric calculations:-



III. RESULT AND DISCUSION

3.1 XRD analysis

Fig. 1 exhibits the comparison of observed and calculated XRD pattern of $\text{Y}_2\text{Zr}_2\text{O}_7$ having 1.5 mol% of Gadolinium (III). The diffraction peaks were matched with COD card 96-152-8995 which seems to be in good agreement of the cubic structure formation with the space group of $Fd\bar{3}m$ (227) [11-13]. Although the Crystallographic Open Database with the data corresponding to $\text{Y}_2\text{Zr}_2\text{O}_7$ phase is still not available for comparison the COD card used was reported form $\text{La}_2\text{Zr}_2\text{O}_7$. The Crystallographic Open Database 96-152-8995 crystallographic information file (1528994.cif) was downloaded from the website <http://www.crystallography.net/>. In the process of lattice parameter refining, the information included in the crystallographic information file was used as a reference. Table 1 shows the initial and revised lattice parameters. While comparing the observed XRD pattern with the standard pattern drawn with the help of the crystallographic information file (cif) retrieved from Crystallographic Open Database (COD), some extra peaks could be observed. These peaks expressed the existence of defects in the crystal due to the presence dopant material (Gd^{3+}). These defects surely give rise to the various transitions results in the optical emission.

Table 01 Indexing and lattice parameters of $\text{Y}_2\text{Zr}_2\text{O}_7$; Gd^{3+} doped phosphor

Initial values :

Zero	Lambda	a	B	c	alpha	beta	gamma	Vol.
0	1.5418	10.8076	10.8076	10.8076	90	90	90	1262.4

Final values :

Zero	Lambda	a	B	c	alpha	beta	gamma	Vol.
0	1.5418	10.8001	10.8001	10.8001	90	90	90	1259.8

h	k	l	2T(Obs)	2T-Zero	2Th(Cal)	Dif
2	2	2	28.808	28.808	28.6313	0.1767
0	0	4	33.352	33.352	33.1793	0.1727
0	4	4	47.763	47.763	47.6294	0.1336
3	1	5	49.079	49.079	49.9576	-0.8786
6	2	2	56.641	56.641	56.5201	0.1209
4	4	4	59.39	59.39	59.2772	0.1128
2	6	6	77.034	77.034	76.9637	0.0703
0	4	8	79.411	79.411	79.35	0.061
4	4	8	88.788	88.788	88.7525	0.0355

a, b, c are the lattice parameters, α , β and γ angel of lattice

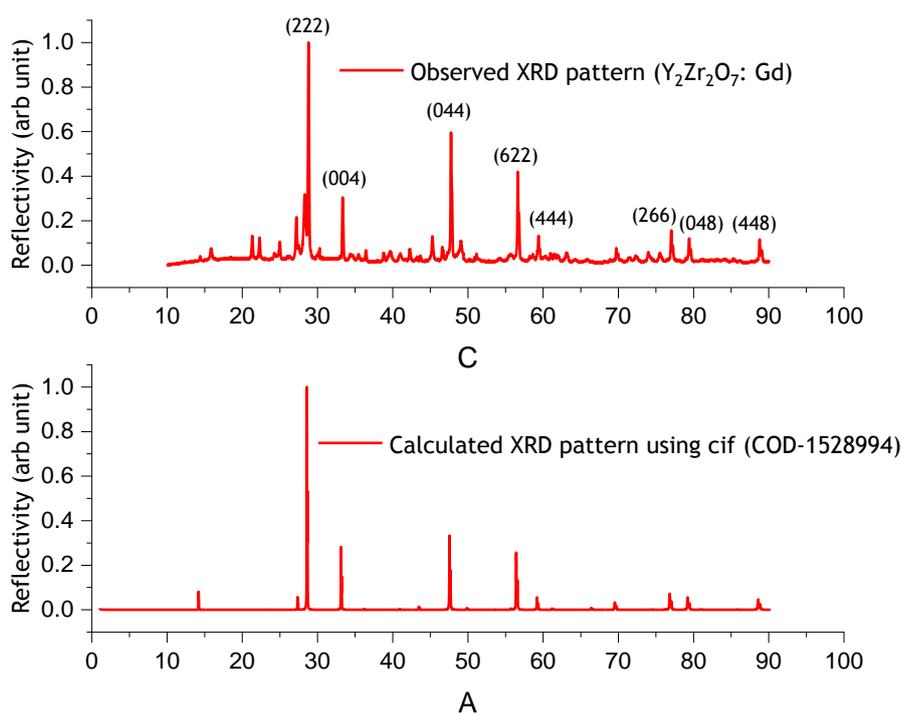


Fig. 1 exhibits the comparison of observed and calculated XRD pattern of $Y_2Zr_2O_7$

The average crystalline size calculated by Scherer Equation is about 44.37nm [14-15]. Table 1 indicated the comparison between standard and refined lattice parameters. The indexing and refinement of lattice parameter are calculated using software Celref V 3. The refinement values of the lattice parameters of $Y_2Zr_2O_7: Gd^{3+}$ doped phosphor were found as: $a = 10.8001 \text{ \AA}$, $b = 10.8001 \text{ \AA}$, $c = 10.8001 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$.

3.2 Scanning Electron Microscopy Images of prepared samples

Fig. 2 (a-c) provides the Scanning Electron Microscopic image of Gadolinium doped Yttrium Zirconate. The morphologies were taken at 10000x (Figure 2a), 50000x (Figure 2b), and 100000x (Figure 2c) magnification. From these photos, we can see that the phosphor $Y_2Zr_2O_7$ with a dopant concentration of 2.0mol% has irregularly shaped particles that range in size from a few microns to a few microns and are strongly agglomerated. The average particle size and shape are a few micrometres in diameter and spherical[16].

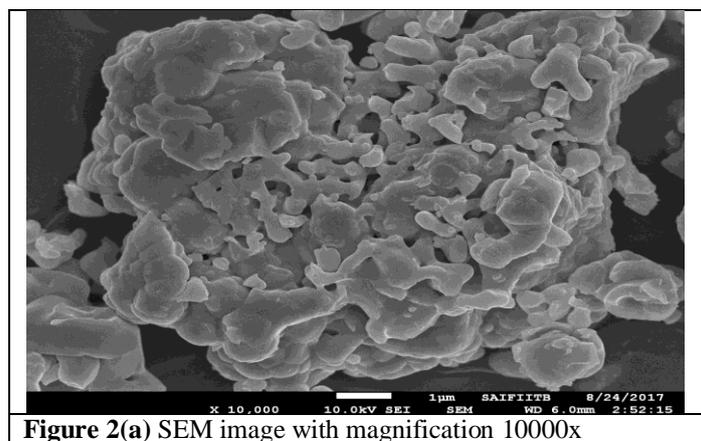


Figure 2(a) SEM image with magnification 10000x

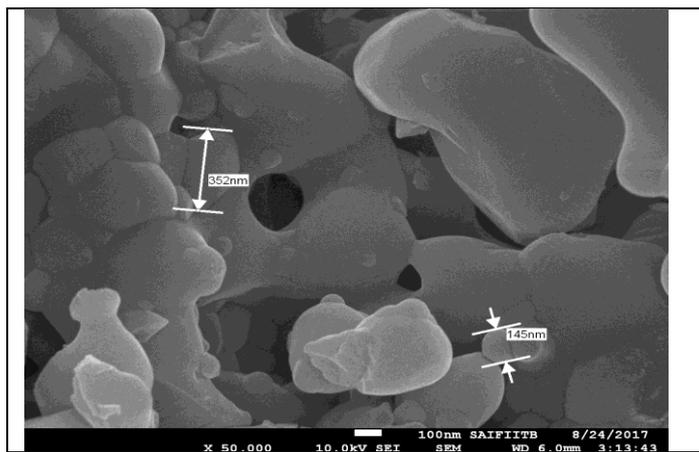


Figure 2(b) SEM image with magnification 50000x

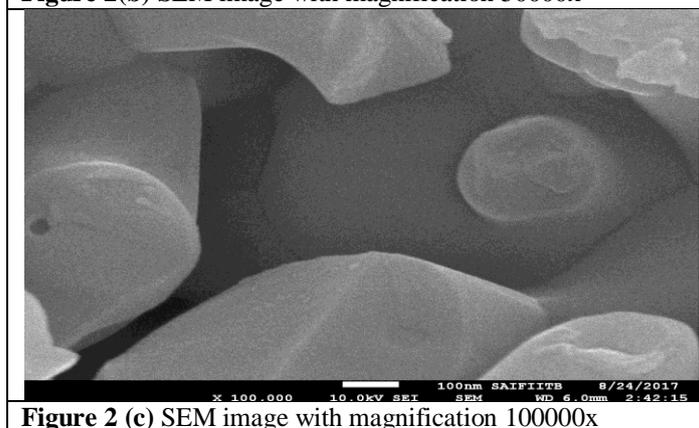


Figure 2 (c) SEM image with magnification 100000x

3.3 Fourier Transform Infrared Spectroscopy of the sample

The FTIR analysis was carried out to determine the atomic bonds in a molecule of prepared in compound. In FTIR spectrum is used to identify the reaction between solids by monitoring the rotational and vibrational motion of the molecules during reaction. Fig. 3 showed the FTIR spectrum of $Y_2Zr_2O_7:Gd^{3+}$ (2.0 mol%)doped phosphor. The peak originated at 460 and 590 cm^{-1} is expected to be there because of the Zr-O bending and stretching vibrations respectively. The bands available at 924 and 997 cm^{-1} are because of stretching vibrations of Y-O [17-18].

Fig. 3 exhibited the bonding analysis of prepared phosphors for conformation of materials bonding.

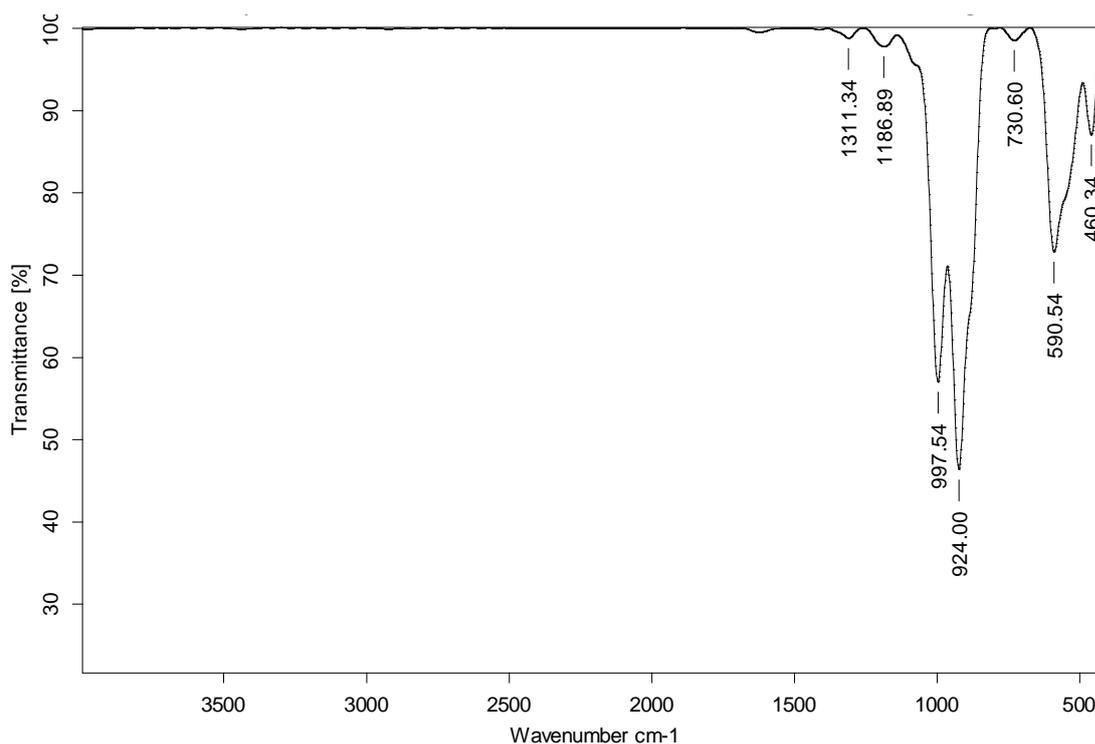


Fig. 3 FT-IR spectrum of Gd (2.0 mol%) doped $Y_2Zr_2O_7$ phosphor

3.4 Photoluminescence Studies of the samples

The excitation spectra of $Y_2Zr_2O_7$ doped with 2 mol% Gd^{3+} are shown in Fig 4. At a wavelength of 575 nm, the excitation spectrum was seen. At 244 nm and 274 nm, respectively, there were three strong emission peaks in the excitation spectrum. At a wavelength of 274 nm, we recorded the emission spectrum of $Y_2Zr_2O_7$ doped with various concentrations of Gd^{3+} (Figure 5). The emission spectrum exhibited two prominent peaks centered at 470nm, 587nm, 600nm, 615nm and 627 nm respectively. The emission peak centered at 470 nm may be attributed to ${}^6G_{11/2}/{}^6G_{9/2}/{}^6G_{5/2} \rightarrow {}^6P_{7/2}$, peak centered at 592 nm is assigned to ${}^6G_{7/2} \rightarrow {}^6P_{7/2}$ whereas the peak centered at 616 nm may corresponds ${}^6G_{11/2}$, ${}^6G_{9/2}$, ${}^6G_{5/2} \rightarrow {}^6P_{3/2}$ transitions of Gd^{3+} ions. [19]. The existence of peaks centered at 587nm, 600nm, 615nm and 627 nm resulting emission spectrum may be present due to ${}^5D_{0,1,2} \rightarrow {}^7F_J$ ($J=0, 1, 2, 3, 4$) transition lines of Eu^{3+} , with the ${}^5D_0 \rightarrow {}^7F_2$ hypersensitive transition (592 & 616 nm) being the most prominent. There are also the possibilities of overlapping of the Eu^{3+} and Gd^{3+} transition peaking at 592 and 616 nm [20-22]. For varying Gd^{3+} doping concentrations, Fig. 4 showed the variations in peak emission intensity. Fig. 5 shows that the emission intensity increases with increasing Gd^{3+} ion concentration until it reaches 2.0 mol %, after which it falls for 2.5 mol % Gd^{3+} doping. Concentration quenching is responsible for this. It was noticed that when the concentration of Gd^{3+} ions increased, the distance between the Gd^{3+} ions decreased. This results in the non-radiative transitions in Gd^{3+} ions. It emphasizes the fact that the distance between the Gd^{3+} ions has a significant impact on the transfer of excitation energy. Finally all emission of the synthesized phosphor lay in orange region, which was further confirmed using the CIE coordinates.

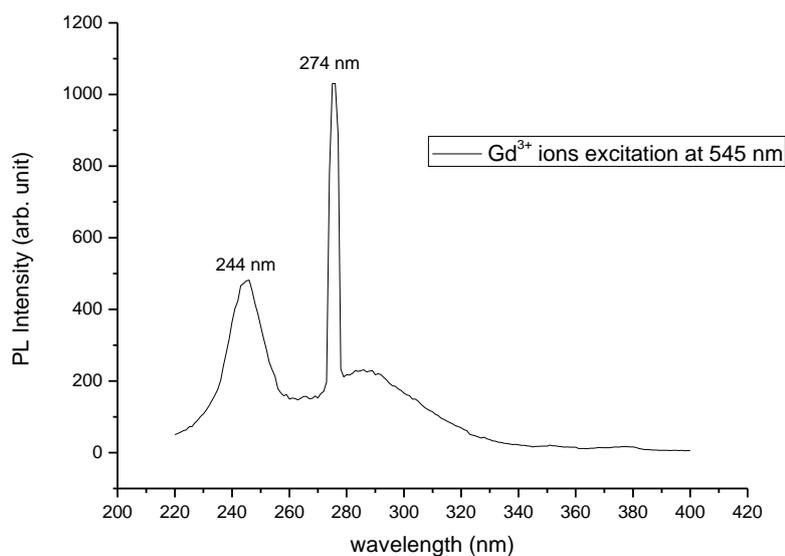


Fig. 4 is the excitation spectra of $Y_2Zr_2O_7$ doped with 2 mol% of Gd^{3+}

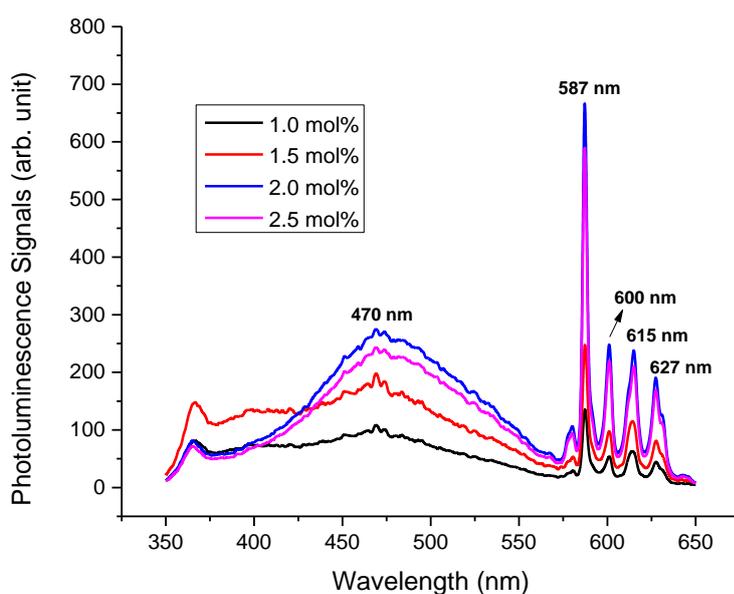


Fig.5 emission spectra of $Y_2Zr_2O_7 : Gd^{3+}$ ion doped excitation at 274 nm

Fig. 6 shown The CIE 1931 chromaticity used to calculate CIE coordinate the orange intense light emitted at different coordinate of $X=0.55$ and $Y=0.32$, $X=0.56$ & $Y=0.35$ and $X=0.54$ & $Y=0.31$ [11].

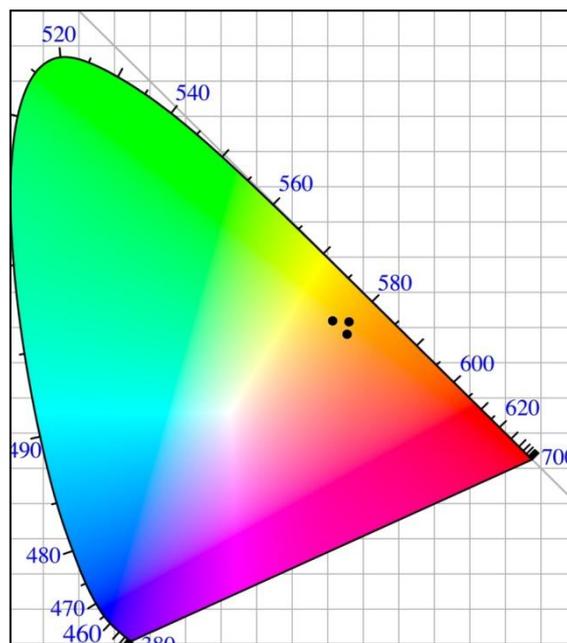


Fig. 6 CIE Coordinate of $Y_2Zr_2O_7 : Gd^{3+}$ ion doped.

IV. CONCLUSION

$Y_2Zr_2O_7:Gd^{3+}$ doped phosphor synthesized by solid state reaction method at $1350^{\circ}C$ and characterized by XRD, SEM and FTIR analysis of the phosphor. PL study was observed at the 470nm, 587nm, 600nm, 615nm and 627 nm emissions in the visible region and increasing the doping concentration the intensity of emission spectra increasing. The CIE diagram confirmed intense orange emission co-ordinate with increasing doping concentration. Therefore, the synthesized phosphors would find tremendous application in optoelectronic display devices and dosimeters.

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