Synthesis, Structural and Spectroscopic investigation of Gd$_2$(WO$_4$)$_3$ phosphor

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Abstract. In the present work we synthesis Gd$_2$(WO$_4$)$_3$ phosphor by hydrothermal method. X-ray diffraction results show that the samples are crystallized in monoclinic crystal structure without any impurity phases. Rietveld refinement data confirms the phosphors belong to space group C2/c. FTIR spectra showed the stretching and bending vibration modes. UV-Visible absorption spectroscopy illustrate the optical band gap ($E_g$) value of prepared sample. SEM micrographs indicate the agglomerated spherical particles. Gd$_2$(WO$_4$)$_3$ phosphor exhibits high optical and structural stability.

1. Introduction

The Tungstates of rare earth metals RE$_2$(WO$_4$)$_3$ [RE$_2$(WO$_4$)$_3$ ;Ln=Sm ,Ce , Gd ,Tm] have been attracted and extensively studied in photoluminescence, super capacitor, solar cells , scintillators [1-3] Numerous report are available in literature regarding the tungstate due to its 4f shell of their ions because it possess novel magnetic and optoelectronic properties. Rare earth tungstate are excellent host for photoactive lanthanide ions which have potential application in phosphors, lasers, photo catalysis and negative thermal expansion [4-5] RE$_2$(WO$_4$)$_3$ are exist in two structure and called as the dimorphic which shows monoclinic structure at low temperature and orthorhombic structure at high temperature. The electronegativity of the rare earth ion is the main cause for these phase transitions. The tungstates shows high monochromaticity, high energy efficiency, high resistance and long-life compared to quantum dots, organic dyes [6]. Gd$_2$(WO$_4$)$_3$ is important class of inorganic material, which can be used in various applications in optical fiber, sensors,scintillators, light emitting diodes, photo catalyst, solid state lasers. It has much attracted due to its structure, low toxicity and excellent ferroelectricity [7] The substitution of Gd in WO$_4$ tetrahedral geometry have been widely studied due to its low photon energy, high quantum yield and shows good photochemical stability. These tungstates have a pure monoclinic structure with a space group of C2/c. In the monoclinic structure the tungstate ion arecoordinated with the overall six fold coordination. These tungstate exhibit self -luminescence in visible spectrum which be decomposed into red blue and green components. The position of the emission peak depends on the excitation wavelength and the function of the synthesis method. The excitation of longer wavelength gives red and green emission and the excitation of the shorter wavelength gives blue emission. The emission in the blue region was due to the charge transfer of WO$_4$$^{2-}$ group [8].
Several methods were reported for the synthesis of RE$_2$(WO$_4$)$_3$ solid state method, Pechinisolgel method, solvothermal method, molten salt method, low temperature solution method, vapor deposition method [9-10]. The structure of the tungstates and molybdates with rare earth and along with the rare earth series are reported by Nassau et al.[11]. Europium tungstates have been extensively reported in literature. Some reports show the preparation of ZnWO$_4$, FeWO$_4$, CdWO$_4$ by hydrothermal method [12] and Recently, La$_2$(MoO$_4$)$_3$, Y$_2$(WO$_4$)$_3$ and Gd$_2$(WO$_4$)$_3$ microcrystals with complex 3D hierarchical architectures were synthesized by hydrothermal methods by You Zhou, Bing Yan [13] reported the Morphology controllable synthesis of RE$_2$(MO$_4$)$_3$:Ln$^{3+}$ (RE = Y, La, Gd, Lu; M = W, Mo; Ln = Eu, Sm, Dy) through hydrothermal process. Zalkin [14] reported the crystal structure of europium tungstate.

In the present study, we report the synthesis of Gd$_2$(WO$_4$)$_3$ phosphors using hydrothermal method at shorter duration and analyzed structural, optical characterization in detail. The structural parameters were analyzed by the powder X-ray diffraction (XRD). Rietveld refinement structural parameter analysis were carried using the JANA 2006 software. The functional group were analyzed by Fourier transform infrared spectroscopy (FTIR). Optical properties were investigated by UV-Vis spectroscopy. The surface morphology and elemental mapping were analyzed by scanning electron microscope with EDS.

### 2. Experimental
The gadolinium oxide (Gd$_2$O$_3$), Sodium tungstate dehydrate (Na$_2$WO$_4$.H$_2$O) and nitric acid (HNO$_3$) were used as starting materials required for synthesis of Gd$_2$(WO$_4$)$_3$ procured from sigma Aldrich with 99.9% purity compounds. All the chemical reagents are used without further purification.

#### 2.1 Synthesis of Gd$_2$(WO$_4$)$_3$
The samples Gd$_2$(WO$_4$)$_3$ were prepared by the hydrothermal method. We dissolve Gd$_2$O$_3$ in hot nitric acid to get the Gd(NO$_3$)$_3$. After the preparation of above process the stoichiometrically amount of Sodium tungstate dehydrate (Na$_2$WO$_4$.H$_2$O) white particles are dissolved in 20ml of distilled water and kept for magnetic stirrer for 10 minutes. The Gd(NO$_3$)$_3$ is mixed to the above solution and again stirrer until it dissolve completely. The resultant solution was transferred to the 50ml capacity of Teflon-lined stainless-steel autoclave and set at a temperature of 100 °C for 12 hour. After the autoclave was cooled naturally to room temperature. The precipitate thus formed removed by centrifugation and washed with ethanol two times, then dried at 80 °C for 3h to get the required final product.

#### 2.2 Characterization of the samples
Powder X-ray diffraction (PANalyticalX’Pert Pro Powder diffractometer) using CuKα radiation (λ = 1.5418 Å) with a nickel filter was used to look into the crystallinity and phase purity of the synthesized phosphor. FTIR spectra in the range 400-4000 cm$^{-1}$ were recorded on Burker Alpha spectrometer. The spectord-210 plus analytic jee spectro meter is used to measure the UV-Visible measurement in the wavelength range of 200-1000 nm. The morphology of the sample was investigated using a scanning electron microscope (FEI Sirion XL 30) at accelerating voltage of 10 kV and transmission electron microscope (JEOL 2100F microscope operated at 200 kV with resolution point:0.23nm and lattice:0.14nm). All the above measurements were performed at room temperature.

### 3 Results and Discussion
#### 3.1 Structural analysis of Gd$_2$(WO$_4$)$_3$ phosphors
Figure 1 shows the XRD pattern for Gd$_2$(WO$_4$)$_3$ phosphors which are synthesized at 100 °C for 12 hour by hydrothermal method. All the observed diffraction peaks are well match with the JCPDS card
number 00-023-1076. There is no impurity peaks are observed in fig 1 which confirms the formation of pure Gd$_2$(WO$_4$)$_3$ phase.

![PowderXRD patterns of Gd$_2$(WO$_4$)$_3$ phosphors.](image)

**Figure 1.** PowderXRD patterns of Gd$_2$(WO$_4$)$_3$ phosphors.

The average crystalline size of synthesized Gd$_2$(WO$_4$)$_3$ phosphors were calculated using the Scherrer’s equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where, $\lambda$ is the wavelength of the X-rays equal to 1.5418 Å, $k$ is the shape factor equal to 0.9, $D$ is the average crystalline size, $\theta$ is the glancing angle and $\beta$ is full width at half maximum (FWHM) of peaks in XRD. Based on the above equation the average crystalline size of Gd$_2$(WO$_4$)$_3$ powders was found to be 29 nm.

Williamson-Hall (W-H plot) Figure 2 is used to estimate the effect of the lattice strain and the crystalline size on the FWHM using the relation:

$$\beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta$$  \hspace{1cm} (2)

Where, $k$ is the shape factor equal to 0.9, $\beta$ is the full width at half maximum (FWHM) of the diffraction peak (in radians), $\lambda$ is the wavelength of the X-rays equal to 1.5418 Å and $\varepsilon$ is the total strain associated with the lattice. For estimation of crystalline size and lattice strain we plot the graph of $4\sin \theta$ along X-axis and $\beta \cos \theta$ along Y-axis. The average strain component are obtained from slope ($\varepsilon$) is 4.5x10$^{-3}$ respectively and the intercept $\frac{k\lambda}{D}$. The crystalline size obtained from W-H method for Gd$_2$(WO$_4$)$_3$ was 30 nm good agreement those obtained form Scherrer’s formula. Both the size and strain components are considered for observed peak broadenings.
The XRD data is further employed to perform Rietveld refinement and Structural analysis of Gd$_2$(WO$_4$)$_3$ sample. All the peaks are indexed with pseudo-cubic indices and refined structural parameters extracted from JANA 2006 program. The XRD data are refined with pseudo-Voigt peak profile function and also carried out on other parameters, scale factor, zero correction, background, profile half-width parameter, lattice parameter, asymmetry parameter, positional coordinates, and isotropic thermal factors are tabulated in Table 1. The lattice parameters of the Gd$_2$(WO$_4$)$_3$ were obtained from the La Bail fit using the JANA 2006 software for C2/c monoclinic phase shown is Figure 3.

![Figure 2. W-H plot of Gd$_2$(WO$_4$)$_3$ phosphor.](image1)

**Figure 2.** W-H plot of Gd$_2$(WO$_4$)$_3$ phosphor.

![Figure 3. Observed, calculated and the difference XRD patterns for Gd$_2$(WO$_4$)$_3$ compounds.](image2)

**Figure 3.** Observed, calculated and the difference XRD patterns for Gd$_2$(WO$_4$)$_3$ compounds.
The structure of Gd$_2$(WO$_4$)$_3$ is scheelite and considered as an ordered defect with a threefold scheelite supercell and one Gd$_2$ site unoccupied. The Gd$^{3+}$ cations are coordinated by eight O atoms forming a distorted trigonal prism. The two unique W cations are tetrahedrally surrounded by O atoms. One of the WO$_4$ tetrahedrons is relatively undistorted whereas the other tetrahedron differs considerably from an ideal geometry. The resulting WO$_4$+1 polyhedral form W2O8 dimers through edge sharing along with the WO4 and GdO8 units, forms the three-dimensional structure as shown in Figure 4.

3.2 FT-IR studies
To determine the chemical structure and the functional group composition of Gd$_2$(WO$_4$)$_3$ samples the FT-IR infrared spectroscopy are obtained which shows in Figure 5. The FTIR spectra of synthesized sample are measured in the wavelength range 400-4000 cm$^{-1}$. The presence of the absorption band at 499-419 cm$^{-1}$ is generally due to the antisymmetric bending vibration of W-O. The absorption peak around 770 cm$^{-1}$ - 857 cm$^{-1}$ related to O-W-O antisymmetric stretch vibrations of [WO$_4$] clusters. The strong peak absorption at 916 cm$^{-1}$ due to the symmetric stretching vibration of the WO$_4$. The adsorbed water molecule on the surface of the sample above 1500 cm$^{-1}$ is reduced which shows the crystallinity of the samples. The typical absorption band of the WO$_4$ group shows the presence of the tungstate group.

| Compound         | Crystal System | Space group | Lattice Parameters(Å) | R-Factors |
|------------------|----------------|-------------|-----------------------|-----------|
|                  |                |             | a         | b        | c         | β(⁰)   | Cell volume (Å$^3$) | Rp     | Rwp | GOF(χ$^2$) |
| Gd$_2$(WO$_4$)$_3$ | Monoclinic     | C2/c        | 7.8112     | 11.6292  | 11.5371   | 109.72 | 986.55          | 4.43   | 5.97 | 1.58       |

Table 1. Rietveld refinement structural parameters of Gd$_2$(WO$_4$)$_3$ phosphor.
3.3 UV–Visible absorption spectroscopy

The diffuse reflectance spectrum of Gd$_2$(WO$_4$)$_3$ phosphors is present in Figure 6(a). It shows the absorption band in the range of 200 nm -550 nm. The Gd$_2$(WO$_4$)$_3$ shows the deep fall in the reflectance below 350 nm due to the band transition from the occupied O 2p orbital to the empty W 5d orbital of synthesized sample.

By employing Kubela-Munk function [17] the Absorption spectrum F(R) is obtained and calculate the energy bandgap of the prepared phosphor[equation (3)].

\[ F(R_\infty)h\nu = C(h\nu - E_g)^n \]

Where, \( F(R_\infty) \) is the Kubelka-Munk function [equation (4)] which as follows

\[ F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{k}{s} \]

Where \( E_g \) is the band gap energy, \( s \) is the scattering co-efficient, \( h\nu \) is the energy of the photon, \( k \) is the molar absorption coefficient, \( C \) is the constant and \( n \) is the constant associated with different kinds of electronic transition, \( n = \frac{1}{2}, 2, 3/2 \). which corresponds to direct allowed transition, indirect allowed transition, direct forbidden transition and indirect forbidden transition. \( R \) is reflectance \( R_\infty = R_{\text{sample}}/R_{\text{standard}} \). Form the extrapolating line for \([F(R_\infty)h\nu]^{1/n} = 0\) energy bandgap Figure 6(b) can be calculated which is approximately equal to the 3.8 eV which is highly consistent with the reported results.

Figure 5. FTIR spectra of Gd$_2$(WO$_4$)$_3$ compound.
Figure 6. (a) DRS spectra of Gd$_2$(WO$_4$)$_3$ phosphor. (b) Optical band gap of Gd$_2$(WO$_4$)$_3$ phosphor.

3.4 SEM and EDS analysis
The surface morphology and elemental mapping of the phosphors were characterized by the Scanning electron microscope and energy dispersive X-ray (EDS). The surface morphology depends on the synthesis method and conditions used in the process of synthesis. Figure 7 shows the morphology of Gd$_2$(WO$_4$)$_3$ phosphors and it revealed that the particles were form spherical like morphology. The particle size was found in the range within 70-100 nm. Figure 8 shows the EDX spectrum and elemental composition of Gd$_2$(WO$_4$)$_3$ phosphors. The EDX spectrum reveals the strong peaks from Gd, W and O. All the elements were homogeneously distributed over the entire area.

Figure 7. SEM images of Gd$_2$(WO$_4$)$_3$ phosphor

Figure 8. EDX spectrum and elemental mapping of Gd$_2$(WO$_4$)$_3$ phosphor.

4. Conclusions
In Summary Gd$_2$(WO$_4$)$_3$ phosphor was prepared by hydrothermal technique. The phase purity is confirmed by PXRD data. Structural parameters are refined by the Rietveld analysis using powder X-ray data. Gd$_2$(WO$_4$)$_3$ was crystallized in the monoclinic structure with space group C2/c. The Crystallize size and lattice strain are consider for the observed peak broadening. The XRD and SEM analysis reveal a strong structural dependence of the crystal structure on Gd$_2$(WO$_4$)$_3$ phosphor. FTIR spectra showed the bending and stretching bonds of O-W-O and W-O. UV-Visible absorption spectroscopy illustrated the optical band gap energy ($E_g$) calculated indicates a Semiconductor character. All the results show that Gd$_2$(WO$_4$)$_3$ phosphor exhibits high optical and structural stability.

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