Raman and XPS studies of Combustion Route Synthesized Monoclinic Phase Gadolinium Oxide phosphors

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Abstract:- ***Gd_2O_3 nanoparticles have been synthesized by the low temperature solution combustion method using urea as fuels in a short time. The structural, morphology and luminescence properties have been carried out using powder X-ray diffraction (PXRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Raman and XPS. For synthesis gadolinium nitrate and Urea were mixed and kept stirring for 30 min, resultant was transferred to crucible and fired in a furnace for Few seconds at 600^0C soon the water got evaporated and a vigorous redox reaction occurred and Gd_2O_3 Nano crystals were achieved. The combustion synthesis method which is reported here is advantageous from the perspectives of small size of the nanoparticle.***

I. INTRODUCTION:-

In recent years, low dimensional structures having remarkable research interest owing to their novel electrical, optical and magnetic properties, elongated as compared to bulk and other It is reported that at nano scale, the differences in electrical and optical characteristics of very small particles are caused by quantum effects due to their high surface to volume ratio, which increases the band gap by reduction of the number of allowable quantum states in the small particles, and improves surface and interfacial effects[1-3]

Lanthanide hydroxides and oxides have actively been investigated because of their wide range of applications including dielectric materials for multilayered capacitors, luminescent lamps and displays, solid-laser devices, optoelectronic data storages, waveguides, and heterogeneous catalysts. Recently, lanthanide-doped oxide nanoparticles are of special interests as potential materials for an important new class of nanophosphors. When applied for a fluorescent labeling, they present several advantages such as sharp emission spectra, long life times, and resistance against photobleaching in comparison with conventional organic fluorophores and quantum dots [4-9].

Gadolinium oxide based nanophosphors are found to be promising candidates in the field of high performance luminescent devices, catalysis and other functional devices based on their excellent electronic, optical and physico-chemical responses arising from 4f electrons. Not surprisingly, all these properties could be largely influenced by their chemical composition, crystal structure, shape and dimensionality. Thus, high surface area nanomaterial which has a larger fraction of defect sites per unit area should be of interest as adsorbents in environmental remediation processes. Cost of synthesis, simplicity and morphological characteristics of prepared phosphor are important parameters for their use in the commercial applications, it is imperative that a self-propagating combustion route offers the best choice for the synthesis of Gd_2O_3 powder[10-13].

Nanoparticles prepared by this combustion route, have size of ~10 nm such approaches involve the use of fuel like urea, glycine, alanine, hydrazide etc. to initiate decomposition reaction of precursor metal salt at high temperature. The combustion synthesis and low temperature processing minimize the size of the materials, which is very important for the most applications in the electronic, optoelectronic, chemical industries etc. The higher reactivity of smaller size Gd_2O_3 particles is not only because of the large specific surface area but also due to the high concentration of low coordinated sites and structural defects on their surface. Due to these merits, these are in high demand for various technological applications including optoelectronic devices, high definition televisions, biological imaging and tagging, MRI, luminescent paints and inks for security codes etc. [14-17].

The Present paper deals with synthesis of Gd_2O_3 by combustion method. The particle size of the prepared phosphor was determined by using X-ray diffraction(XRD) analysis, the morphology of the prepared phosphor was determined by scanning electron microscopy(SEM) and transmission electron microscopy(TEM). The Raman and X-ray photoelectron spectroscopic studies of the prepared phosphor were also carried out.

II. MATERIALS AND METHODS

2.1. Chemicals

Chemicals used in this study are of analytical grade. Gadolinium nitrate and urea were purchased from Sigma-Aldrich Chemicals Limited. All reagents were used without further purification.

2.2 Synthesis: - In Combustion synthesis method aqueous solutions of $Gd(NO_3)_3.6H_2O$ is prepared by addition of a suitable amount to prepare the precursor solution and the mixture was stirred for 4 hour at 60˚C, the resultant solution converted in to a transparent gel form. Then the above sample was heated in a furnace at 600˚C for 2 min, the sample changed into its anhydrous form followed by a vigorous redox reaction to form Gd_2O_3 powder[10]. The resulting brownish powder was heated until a controlled explosion took place yielding a very fine, white powder. Since the reaction is so rapid, the crystal growth will be highly restrained.

$$2Gd(NO_3)_3 + CH_4N_2O \rightarrow Gd_2O_3 + CO_2 + 2H_2O + 4N_2$$

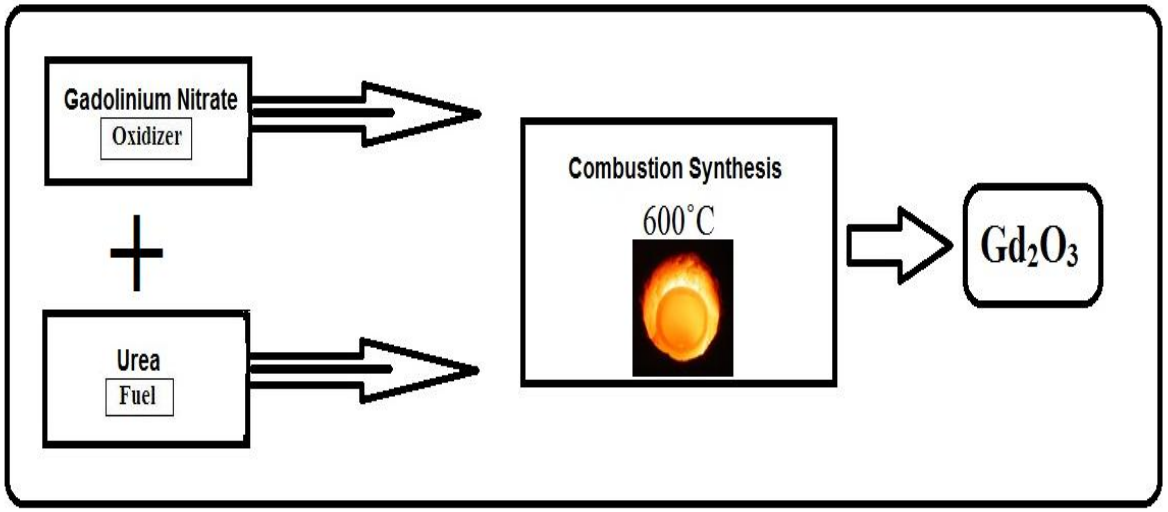


Figure 1. Show the flow chart of synthesis of Gd_2O_3

2.3. Material characterization: - The crystallinity as well as the particle size of the phosphor were monitored X-ray diffraction measurement. The X-ray powder diffraction data was collected by using Bruker D8 Advanced X-ray diffractometer using Cu Kα radiation. The X-rays were produced using a sealed tube and the wave length of X-ray was 0.154 nm. The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker Lynx Eye detector). The surface morphology of the prepared phosphor was determined by field emission scanning electron microscopy (FESEM) JSM-7600F. Energy dispersive X-ray analysis (EDX) was used for elemental analysis of the phosphor. Particle diameter and surface morphology of prepared phosphor were determined by Transmission Electron Microscopy (TEM) using Philips CM-200. Raman studies were carried out on Jobin-Yvon, France, Ramnor Hg-2s Spectrometer with Ar-Laser with 4 W power having resolution of 0.5 cm^{-1} and wave number accuracy 1 cm^{-1} over 5000 cm^{-1}. XPS analysis was performed in a VG instrument with a CLAM2 analyzer and a twin Mg/Al anode. The pressure in the analysis chamber was approximately $9x10^{-10}$ mbar. The measurements were carried out with unmonochromated Al Ka photons (1486.6 eV). The power of the X-ray source was kept constant at 300 W.

(I) XRD RESULT:-The XRD patterns of the Gd_2O_3 sample is shown in Figure 2. The diffraction patterns are well matched with standard JCPDS card no. 43-1015 [18]. The particle size were calculated by the Scherer formula[19]

$$\text{Scherer formula } D_v = \frac{k\lambda}{\beta_{hkl}\cos\theta}$$

where Dv=volume weighted crystallite size, k=shape factor (0.9),λ=wavelength of Cu Kα1 radiation, β_{hkl}=instrumental corrected integral breadth of the reflection (in radians) located at 2θ, and θ=angle of reflection (in degrees) was utilized to relate the crystallite size to the line broadening. The average crystallite size of Gd_2O_3 nanoparticles was found to be in the range of ~10nm.

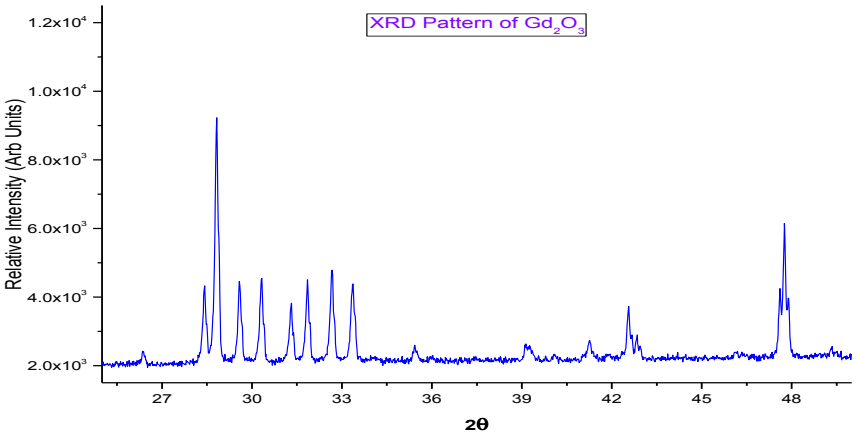
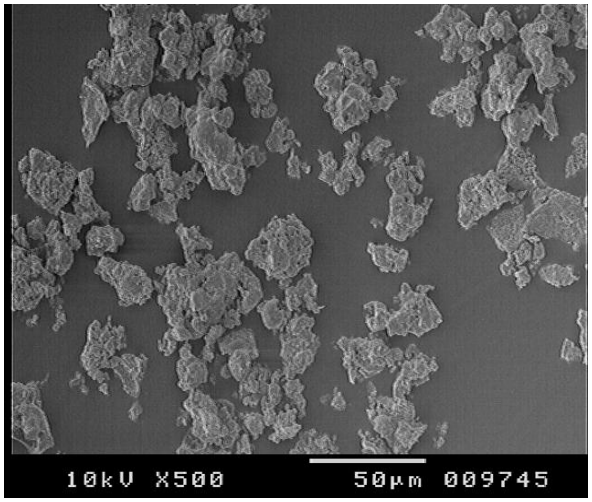
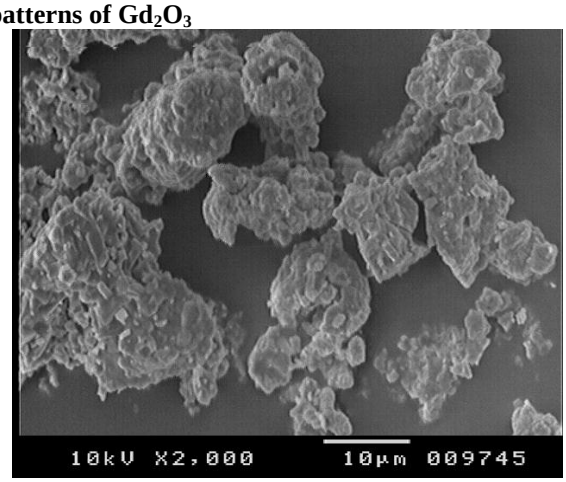


Figure 2. Show the XRD patterns of Gd_2O_3

No impurity peaks or other possible phases of Gd_2O_3 were observed. Further, the strong and sharp diffraction peaks confirm the high crystallinity of the products.

(II) **SEM RESULT:** - The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions. Figure 3. Shows the SEM micrographs of the Gd_2O_3 prepared by combustion synthesis using urea as a fuel.





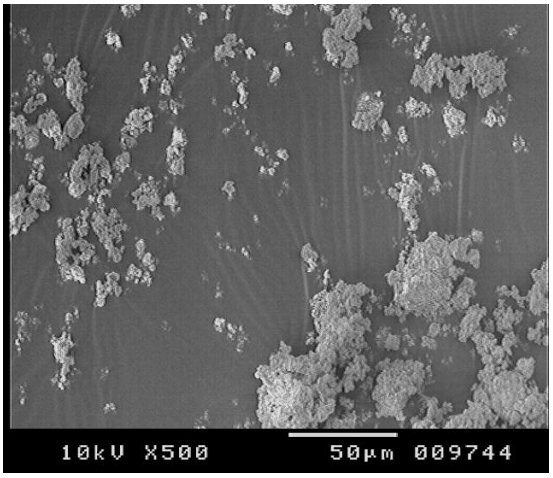


Figure 3. SEM image result of Gd_2O_3

(III)**TEM RESULT**:-. Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is focused onto a specimen causing an enlarged version to appear on a fluorescent screen or layer of photographic film or to be detected by a CCD camera. The first practical transmission electron microscope was built by Albert Prebus and lames Hillier at the university of Torondo in 1938 using concepts developed earlier by Max Knoll and Emsl Ruska. In the most powerful diffraction contrast TEM instruments, crystal structure can also be investigated by High Resolution Transmission Electron Microscopy

(HRTEM), also known as phase contrast imaging as the images are fonned due to differences in phase of electron waves scattered through a thin specimen. In Figure 4 HRTEM micrograph shows a Gd_2O_3 nanocrystal with a diameter of ~8 nm are seen throughout the particle[20].

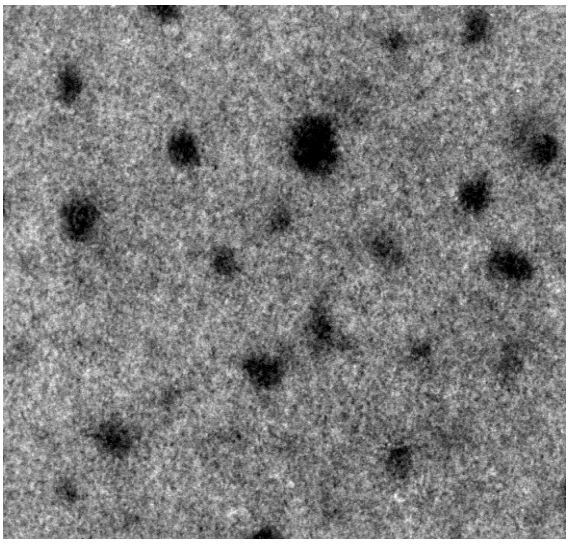


Figure 4. HRTEM images of Gd2O3 prepared by the combustion method

(IV) X-ray photoelectron spectroscopy (XPS):- XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its as-received state, or after some treatment, for example: fracturing, cutting or scraping in air or UHV to expose the bulk chemistry, ion beam etching to clean off some or all of the surface contamination (with mild ion etching) or to intentionally expose deeper layers of the sample (with more extensive ion etching) in depth-profiling XPS, exposure to heat to study the changes due to heating, exposure to reactive gases or solutions, exposure to ion beam implant, exposure to ultraviolet light.The chemical composition of Gd_2O_3 nanoparticles was studied with X-ray Photoelectron Spectroscopy (XPS) and the experimental data was analyzed using curve fitting. The Gd(3d) level consists of a spin orbit split, with the $Gd(3d)_{5/2}$ peak is found at 1186.74 eV (Fig. 5). The line shape and peak positions are in good agreement with earlier published data on Gd_2O_3 powder pressed into an in sheet[13,21-25].

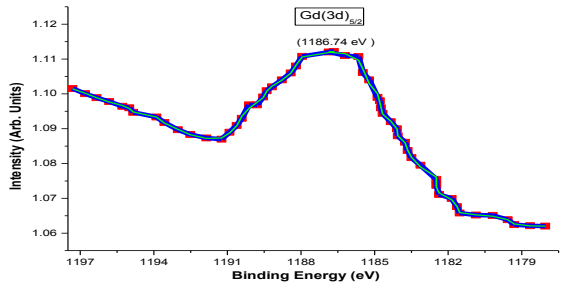


Figure 5. The Gd (3d) XPS spectrum of Gd_2O_3 nanocrystals

(V) Raman spectroscopy: - The Raman Effect has been an important technique for the elucidation of molecular structure. Similar information is obtained from the infrared spectra. Since the infrared and Raman spectra are governed by different selection rules, the information obtained from Raman Spectroscopy supplements the information obtained from infrared spectra. Samples which cannot be handled in the infrared (e.g. Aqueous solutions, biological samples etc.) can easily be studied through Raman Spectroscopy. Raman spectroscopy is highly informative to elucidate the structure of the synthesized sample. It is a nondestructive tool to explore vibrational, rotational and other low frequency modes in the systems under study[26]. Figure 6 shows the Raman spectra of Gd_2O_3 prepared by combustion syntheis using urea as a fuel, recorded at room temperature with an excitation wavelength of 633 nm He–Cd laser. A broad and intense Raman peak at 340 cm^{-1} along with less intense peaks were observed at 375, 395, 424 and 451 cm^{-1}. The results are good agreement with the previously published Raman spectroscopic studies on Gd_2O_3 nanoparticles[,14,17,25,27].

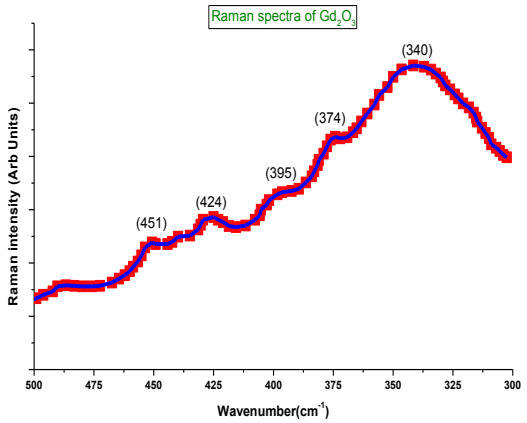


Figure 6. Raman spectra of Gd_2O_3 nanoparticles

III. CONCLUSION:

Formation of stable gel is an important criterion for a successful solution combustion synthesis process. Urea form stable gel with mixed nitrate solution of gadolinium and the combustion of the gel produces phase pure nano-crystalline powder without any residual reactant. In this study, Lattice parameter (a) for cubic Gd_2O_3 was found to be 10.7602. The particle sizes are confined by powder X-ray diffraction studies. The particle size estimated from Debye–Scherrer's was well comparable to TEM results. The advantages of the phosphors prepared by this combustion process are the easy availability of homogeneous spherical morphology in different size, and its wide practicality for other phosphor materials. X-ray Photoelectron Spectroscopy (XPS) show the Gd(3d) level consists of a spin orbit split doublet, with the $Gd(3d)_{5/2}$ peak is found at 1186.74 eV. Raman spectra with excitation of 633 nm

wavelength, we found a broad and intense Raman peak at 340 cm^{-1} along with less intense peaks were observed at 375, 395, 424 and 451 cm^{-1}.

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