Effect of fuel on the Photoluminescence properties of Gd$_2$O$_3$ nanoparticles

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Abstract: - Recent research on Ln$_2$O$_3$-type oxide nanomaterials provide challenges to both fundamental and breakthrough development of technologies in various areas such as electronics, photonics, display, lasing, detection, optical amplification, fluorescent sensing in biomedical engineering and environmental control. Gadolinium oxide (Gd$_2$O$_3$) is a Ln$_2$O$_3$-type oxide. Gd$_2$O$_3$ nanocrystalline phosphor was synthesized by solution combustion method by using citric acid and urea fuels. The final product was examined by well characterized techniques such as powder X-ray diffraction pattern (PXRD), UV-Visible, photoluminescence (PL) measurements etc. A broad PL emission band at ~375 nm was observed in all samples excavated at 270 nm. This emission band may be attributed to recombination of a delocalized electron close to the conduction band with a single charged state of surface oxygen vacancy, according to Wang’s proposal.

Key-Words: - Gadolinium; Oxides; Combustion; Nanoparticles; Photoluminescence;Phosphor

1 Introduction

Rare earth oxides have been extensively investigated due to their fascinating properties such as enhanced luminescence efficiency; lower lasing threshold, high-performance luminescent devices, drug-carrying vehicle, contrast agent in Magnetic Resonance Imaging (MRI), up-conversion materials, catalysts, and time-resolved fluorescence (TRF) labels for biological detection etc. It is reported that these 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. Among rare earth oxides Gadolinium oxide (Gd$_2$O$_3$) is a Ln$_2$O$_3$-type oxide have been extensively studied due to its optoelectronic, data storage, sensor and display applications. It has polymorphic forms, (A, B and C) such as hexagonal, monoclinic and cubic, respectively. The C-form structure cubic bixbyite type is known as the low-temperature form at ordinary pressures. The rare earth oxides prepared by various methods it includes chemical vapor deposition, hydrothermal, laser ablation, sol gel etc. Among them, combustion synthesis is a highly promising method, for producing the desired phase-pure nanosized powders in a very short time, at low cost and using simple equipment. Through the combustion method it is also possible to achieve a better control of stoichiometry and particulate properties of the final product. Typically, the combustion process involves a self-propagating, gas producing, exothermic redox reaction between the corresponding metal nitrate and a suitable organic fuel that results in the desired products. Different organic compounds, such as citric acid, urea (CH$_4$N$_2$O), glycine, carbohydrazide (CH$_6$N$_4$O), ODH etc., have been used as fuels. To achieve the desired combustion reaction, the redox mixtures need to be carefully formulated for example F/O, initial furnace temperature, nature of fuels and quantity of the initial precursor. Glycine consisting of the –NH$_2$ group is a more reactive fuel than citric acid containing –OH and –COOH groups. The combustion reactions with citric acid are less violent and more controllable due to its weak exothermic nature. On the other hand, glycine with higher heat of combustion results in combustion reactions that are more violent and different to control.

The objective of this work is to study the effect of citric acid and urea fuels on Gd$_2$O$_3$ nanophosphor structural and luminescent properties.

2. Experimental

2.1. Chemicals used

The starting materials used for preparation of Gd$_2$O$_3$ nanoparticles were of analar grade. Gadolinium nitrite (Gd(NO$_3$)$_3$) used as oxidizer and
urea and citric acid were used as fuels for solution combustion synthesis.

2.2. Synthesis of Gd$_2$O$_3$

An aqueous solution containing stoichiometric amounts of gadolinium nitrite Gd(NO$_3$)$_3$ and fuel were taken in a crystalline Petri dish of approximately 300 ml capacity. The excess water is allowed to evaporate by heating over a hot plate until a wet powder is left out. Then the crystalline Petri dish is introduced into a pre heated muffle furnace maintained at ~300 ± 10 °C. The reaction mixture undergoes thermal dehydration and ignites at one spot with liberation of gaseous products such as oxides of nitrogen and carbon. The combustion propagates throughout the reaction mixture without further need of any external heating, as the heat of the reaction is sufficient for the decomposition of the redox mixture. The flame temperature was found to be ~1000 °C and it was measured by an optical pyrometer placed inside the crystalline petri dish without touching the solution.

2.3. Instruments Used

The phase of the as formed and heat treated Gd$_2$O$_3$ nanophosphor has been characterized by powder X-ray diffractometer (PANalytical X’Pert Pro) using CuKα(1.541Å) radiation with a nickel filter. The FT-IR studies have been performed on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellets. The UV-VIS absorption of the samples was recorded on SL 159 ELICO UV – VIS Spectrophotometer. The photoluminescence (PL) measurements was performed on a Shimadzu Spectroflourimeter (Model RF 510) equipped with 150W Xenon lamp as an excitation source.

3. Characterization

3.1. Powder X-ray diffraction (PXRD)

![Fig. 1. PXRD of Gd$_2$O$_3$ calcined at 800 °C (a) Citric acid (b) urea](image)

The PXRD patterns of the citric acid and urea fuels are shown in Fig. 1. To get pure phase these samples were further calcined at 800 °C for 3 hrs. Now all the diffraction peaks were readily indexed to a pure phase. The citric acid and urea readily gives pure cubic phase of Gd$_2$O$_3$ [Ia3 (206)]. The diffracted patterns are well matching with the literature [1]. No impurity peaks and other possible phases of Gd$_2$O$_3$ is not observed. Further, the strong and sharp diffraction peaks confirm the high crystallinity of the products.

The average particle size (D) of the as-formed and heat treated Gd$_2$O$_3$ nanophosphor used for different fuels was estimated from the full width at half maximum (FWHM) of the diffraction peak of the powders, using Scherrer’s formula [2].

\[
D = \frac{K\lambda}{(FWHM) \cos \theta} \quad \text{......}(2)
\]

where \(\lambda\) is the wavelength of X-ray used, \(\theta\) the Bragg angle, \(K\) is the constant, which depends on the grain shape (0.9Å for circular grains). It is observed that the average particle size of the Gd$_2$O$_3$ with different fuels varies from 40 to 70 nm.

Further, strain present in Gd$_2$O$_3$ nanophosphors prepared for all the fuels was estimated using the W–H equation [3].

\[
\beta \cos \theta = \frac{0.9 \lambda}{D} + 4 \varepsilon \sin \theta \quad \text{......} \quad \text{(3)}
\]

where \(\varepsilon\) is the strain associated with the nanorods. Equation (3) represents a straight line...
between 4 \sin \theta (X\text{-}axis) and \beta \cos \theta (Y\text{-}axis). The slope of line gives the strain (\varepsilon) and intercept (0.9\lambda/D) of this line on Y\text{-}axis gives grain size (D). Fig. 2 shows the W\text{-}H plots of the fuels.

![Fig. 2 Williamson-Hall plots of Gd_2O_3 prepared by different fuels (a) Citric acid and (b) Urea](image)

Absorption spectrum of different fuels of Gd_2O_3 nanophosphor is shown in Fig. 4. The absorption peaks seen at 243 and 305 nm. Absorption in the UV region by Gd_2O_3 nanophosphor can be explained using the following considerations: Gadolinium has the free ion (Gd^{3+}) configuration of \[1s^22s^22p^63s^23p^64s^24p^65s^25p^7\] which means that both +2 and +4 oxidation states are unavailable. Unavailability of the oxidation states +2 and +4 means that both Ligand to Metal Charge Transfer (LMCT) and Metal to Ligand Charge Transfer (MLCT) are prohibited in Gd complexes. Consequently, the possible mechanisms for energy absorption in Gd is via transition of a 4f electron to 5d level or reorganization of the seven 4f electrons into various multiplets. Transition of an electron from 4f to 5d involves high energy and absorption peaks appear below 220 nm which we do not consider here. The seven electrons in Gd 4f orbitals have a total of 3432 multiplets and the ground state is \(^8S_{7/2}\). The absorption peak at 274 nm is characteristic for all Gd_2O_3 particles and may be attributed to \(^{8}S_{7/2}\) to \(^{1}I_{7/2}\) transition. The weak peak at 253 nm is probably one of the transitions from \(^{3}S_{7/2}\) to \(^{4}I_{5/2}\) multiplets, where \(J = 9, 11, 13, 15, 17\) [4].

For a direct bandgap the absorption coefficient near the band edge is given by the relation

\[
\alpha = \frac{A}{h\nu} (h\nu - E_g)^{1/2} \\
\]

where \(\alpha\) is the absorption coefficient, \(h\nu\) the photon energy, \(E_g\) the energy gap and \(A\) is constant depending on the type of transition. Equation 4 for
any energy can be rearranged and written in the form

\[
(ah\nu)^2 = A^2(h\nu - E_g) \quad \text{..................(5)}
\]

From equation, it is clear when \( h\nu = 0, E_g = h\nu \), the energy gap is determined by plotting \( (ah\nu)^2 \) against \( h\nu \) and finding the intercept on the \( h\nu \) axis by extrapolating the plot to \( (ah\nu)^2 = 0 \) as shown in Fig. 5. A band gap energy of 5.3 and 5.5 eV was observed which is slightly higher than the reported bandgap of bulk Gd\(_2\)O\(_3\) suggesting a blue shift which can be attributed to the quantum confinement due to small size of Gd\(_2\)O\(_3\) nanophosphor.

![Fig. 5. Energy band gap of Gd\(_2\)O\(_3\) calcined at 800 °C (a) citric acid (b) urea](image)

![Fig. 6. PL spectra of Gd\(_2\)O\(_3\) calcined at 800 °C (a) Citric acid (b) Urea](image)

It is known that lanthanide oxides are ideal hosts for photoluminescence and pure lanthanide oxides seldom radiate luminescence according to luminescence theory of rare-earth atoms. However, during our photoluminescence experiments at room temperature, a green emission band at ~375 nm was observed in all products at excitation wavelength of 270 nm, as shown in Fig. 6. The green emission band may attribute to recombination of a delocalized electron close to the conduction band with a single charged state of surface oxygen vacancy, according to Wang’s proposal [4]. For different fuels different density of oxygen vacancies might arouse differences of PL intensities.

### 4 Conclusion

Gd\(_2\)O\(_3\) nanophosphors with cubic phase were successfully synthesized by a solution combustion method. The particle size from Scherer’s and W-H method was estimated to be in the range 40 – 70 nm. At room temperature, a green emission band at ~375 nm was observed at excitation wavelength of 270 nm. These studies reveal that Gd\(_2\)O\(_3\) is a versatile material with high application potential in several technological fields (photonics).

**References:**


