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Synthesis, structural characterization and thermoluminescence glow curve study of gadolinium-doped Y_2O_3 nanophosphor

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Abstract

Gadolinium-doped Y_2O_3 nanophosphor was synthesized by a solid-state reaction method, which could be used for large-scale production of phosphors. The structure of the phosphor sample was characterized by powder X-ray diffraction, field emission gun scanning electron microscopy and high-resolution transmission electron microscopy. The particle size was calculated from Scherer's formula. X-ray diffraction showed a grain size of 35–55 nm, in good agreement with the scanning electron microscopy image. The synthesized sample showed good morphology and connectivity, with grains and formation of a nano-sized prepared sample. The diffraction pattern was measured by transmission electron microscopy with a selected area diffraction pattern. The prepared phosphor was also examined by thermoluminescence; to record the glow curve, 1 mg phosphor was irradiated with ultraviolet at 254 nm at a fixed heating rate of 7 °C s^{-1}. The sample showed a well-resolved peak at 99 °C for 1 mol% of Gd^{3+}. A lower temperature peak showed less stability and more fading of the prepared sample. A thermoluminescence glow curve gives information about trapping parameters such as activation energy and trap depth, order of kinetics and frequency. All the kinetics were calculated by the peak shape method.

Keywords: Y_2O_3:Gd^{3+}; X-ray diffraction; Scanning electron microscopy; Transmission electron microscopy; Thermoluminescence

1. Introduction

Thermoluminescence is simply thermally stimulated emission of photons (in the visible range) from an insulator or a semiconductor following previous absorption of energy from ionizing radiation or another source. The heating temperature should be lower than that required to produce incandescence. This method is widely used to measure ionizing radiation doses, with material known as thermoluminescent dosimetric material [1–3]. Thermoluminescence occurs when a semiconductor is exposed to ionizing radiation. A fraction of free electrons or holes are produced, which can be trapped by defects present within the crystal lattice of the phosphor materials. If the traps are deep, the energy requirement is too high, and the trapped charges may remain in the sites for a long time. When the material is heated by an external source, the trapped charges may escape from the traps and recombine with trapped charges with the opposite sign. The emission of light, the

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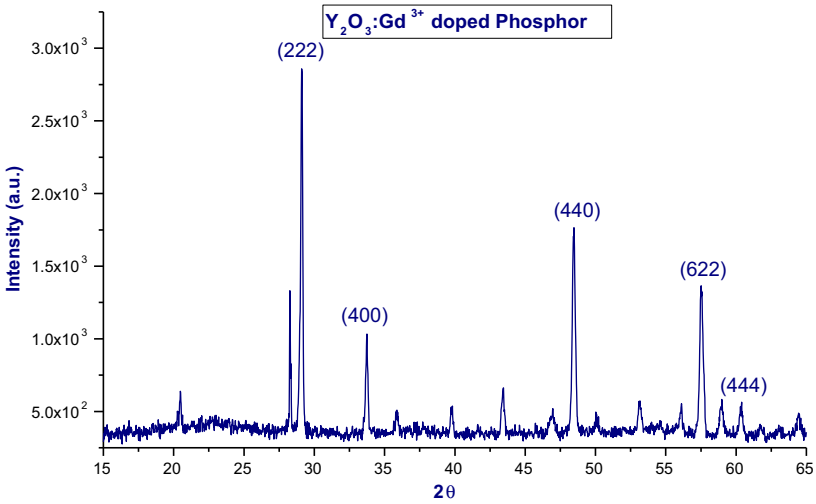

Fig. 1. Powder X-ray diffraction pattern of Y_2O_3:Gd^{3+} (1%)-doped phosphor.

thermoluminescent signal, occurs during recombination. Although many natural minerals are thermoluminescent, the most efficient materials are formulated synthetic materials, first because their thermoluminescent signal is proportional to the radiation dose delivered and, secondly, synthetic materials usually have reproducible responses. Moreover, for calibration, a linear relation between the thermoluminescent signal and the absorbed dose is desirable [2,4–6].

Yttrium sesquioxide (Y_2O_3) ceramics have been widely investigated for various technological uses. Yttrium oxide has been an important material in the ceramics industry for decades, from a constituent of ceramic superconductors to yttria-stabilized zirconia ceramics [7]. It is also used in the preparation of novel light-emitting materials. Y_2O_3 ceramics are useful because of their stable physical and chemical properties, and they have been widely used as host materials in various luminescent applications. They also present the advantage of highly saturated colour [8–13].

The main objective of the study was to determine the thermoluminescent glow curve and its kinetics on the basis of trapping parameters to evaluate the suitability of a prepared sample of thermoluminescent dosimetric material.

2. Experimental

Gd^{3+} doped Y_2O_3 phosphor was prepared by a high-temperature solid-state reaction. The starting materials were yttrium oxide, gadolinium oxide and ultra-pure boric acid (as a flux), and stoichiometric amounts in a molar ratio were used to prepare Y_2O_3:Gd^{3+} (1%) phosphor. The mixture was taken up in an alumina crucible and fired in air at 1300 °C for 4 h in a muffle furnace [11,13].

The structure was characterized by X-ray diffraction, field emission gun scanning electron microscopy and high-resolution transmission electron microscopy. Luminescence was characterized with a thermoluminescent dosimetric material reader, and X-ray diffraction was performed with a Bruker D8 Advance X-ray diffractometer. X-rays were produced in a sealed tube at a wavelength of 0.154 nm (Cu K-alpha). X-rays were detected in a fast counting detector based on silicon strip technology (Bruker Lynx Eye detector). Particle morphology was investigated by field emission gun scanning electron microscopy (JEOL JSM-6360). Thermally stimulated luminescence glow curves were recorded at room temperature on a thermoluminescent dosimetric material reader I1009 supplied by Nucleonix Systems Pvt. Ltd Hyderabad. The phosphor obtained under thermoluminescent examination was given ultraviolet (UV) radiation from a 254-nm source [12,13].

3. Results and discussion

The prepared phosphor material was analyzed by powder X-ray diffraction to reveal phase compositions and crystal size (Fig. 1) [13]. The crystallite size was calculated by the diffraction pattern from the Scherer equation [14,23,24]:

$$d = \frac{k\lambda}{\beta \cos \theta},$$

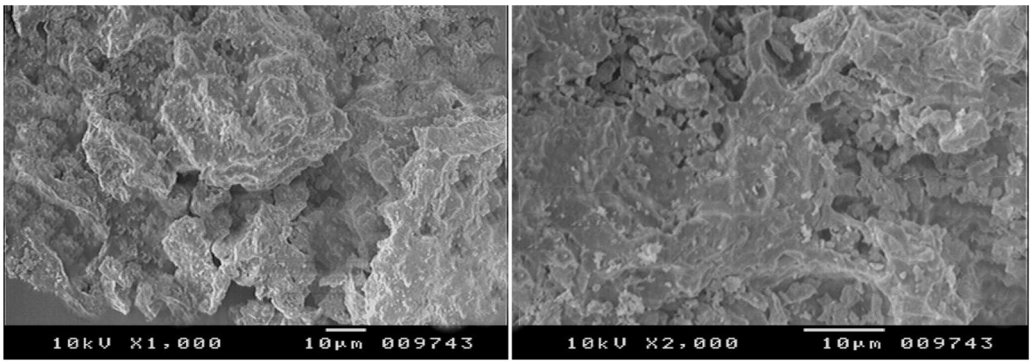

Fig. 2. Scanning electron microscopy images of Y_2O_3:Gd^{3+} (1%)-doped phosphor.

where $k = 0.89$ is a constant, d is the crystallite size for the $(h\,k\,\ell)$ plane, λ is the wavelength of the incident X-radiation (CuKα = 0.154 nm), β is the full width at half-maximum in radians, and θ is the diffraction angle for the $(h\,k\,\ell)$ indices. The powder X-ray diffraction pattern showed that the main phase formed is pure Y_2O_3. The diffraction peaks were indexed as International Centre for Diffraction Data No. 89-5591, which shows that the structure of Y_2O_3 is cubic. The calculated crystal size of the prepared phosphor is 35–55 nm.

3.1. Scanning electron microscopy

Fig. 2 shows the morphology of Y_2O_3:Gd^{3+} (1%)-doped phosphor. The sample showed good morphology and connectivity, with grains and the formation of a nano-sized sample [13].

3.2. High resolution transmission electron microscopy

The high resolution transmission electron microscopy images are shown in Fig. 3. The prepared sample showed compact distribution over the surface and good connectivity between grains, with a cluster-like structure. The images show a selected area electron diffraction pattern, which forms a ring. X-ray diffraction showed that the $(h\,k\,\ell)$ planes are similar, with five intense rings found from the selected area electron diffraction pattern and also from the X-ray diffraction pattern. The $(h\,k\,\ell)$ planes were 222, 400, 440, 622 and 444 [13].

3.3. Thermoluminescence

The thermoluminescent glow curves of the prepared phosphors were obtained by heating the samples from room temperature up to 400 °C at a rate of 7 °C s^{-1}.

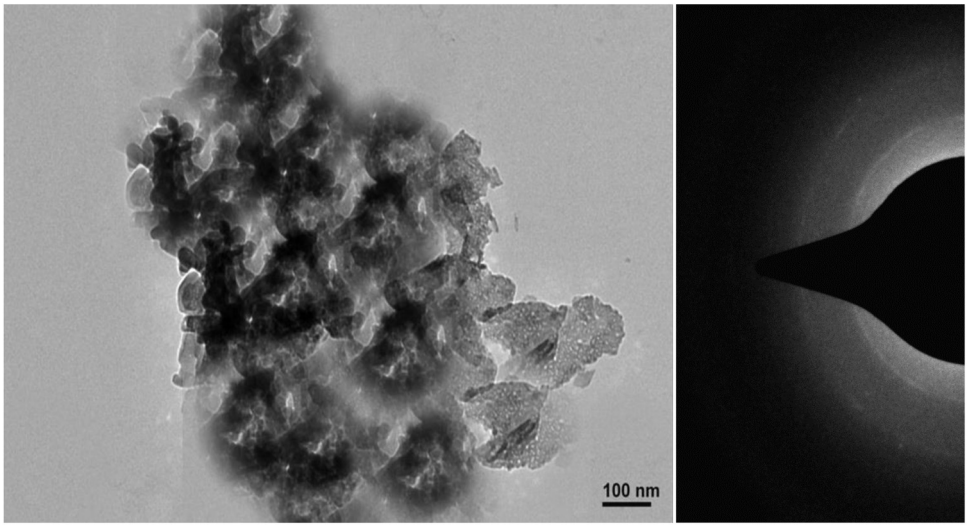

Fig. 3. Transmission electron microscopy images of Y_2O_3:Gd^{3+}.

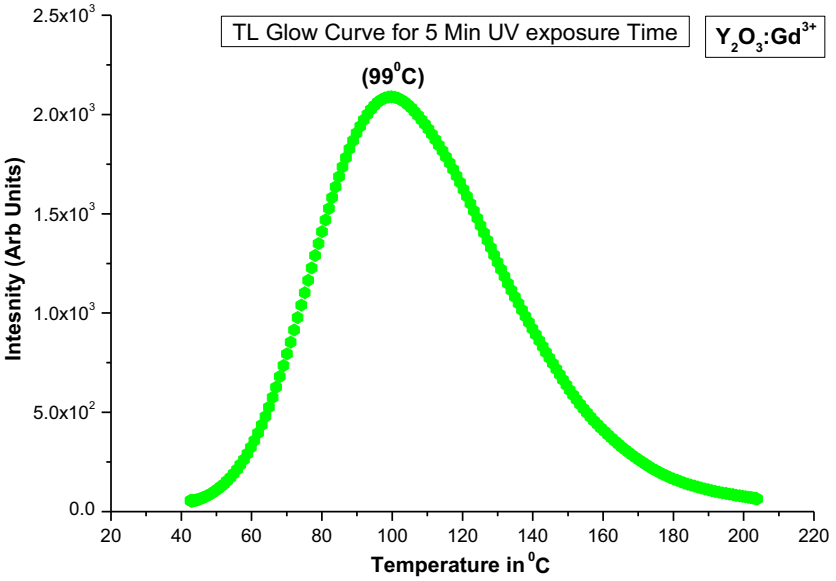

Fig. 4. Thermoluminescent glow curve of Y_2O_3:Gd^{3+} phosphor after 5 min exposure to UV.

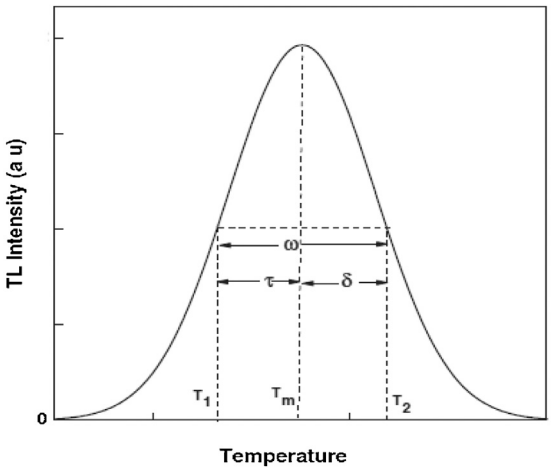

Fig. 5. Representative diagram of parameters used in the glow curve shape method [2,6].

The glow curve of the Y_2O_3:Gd^{3+} phosphor obtained with a fixed UV exposure time of 5 min is shown in Fig. 4. A prominent peak was found at 99 °C, and the sample showed second-order kinetics determined by a shape factor (Fig. 5). The kinetics of Y_2O_3:Gd^{3+} (1%) phosphor are listed in Table 1. The peak shape factor ($\mu = \delta/\omega$ in Table 1, where $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$ (Fig. 5)) of the thermoluminescent glow curve of the phosphor was ~0.57.

3.4. Kinetics

The glow curve is characteristic of the trapping levels in the band gap of the material. Kinetics such as trap depth (E), order (b) and frequency factor (s) are reliable dosimetric study parameters for thermoluminescent materials. When the sample was irradiated at 254 nm, shallower traps were found in the material and therefore with a lower temperature peak (99 °C). Although there are various methods for obtaining the number of glow peaks in complex glow curves, kinetics best describe the peaks [1,2]. The loss of dosimetry information stored in materials after irradiation depends strongly on the position of trapping levels in the forbidden gap, which is known as trap depth or activation energy (E). The mechanism of recombination of detrapped charge carriers with their counterparts is known as the order of kinetics (b). The frequency factor (s) represents the product of the number of times an electron hits the wall and the wall reflection coefficient, with the trap considered a potential well. Thus, reliable dosimetric study

Table 1
Shape factor (μ), activation energy (E) and frequency factor (s) of Y_2O_3:Gd^{3+} (1 mol%) irradiated with UV for 5 min.

T_1	T_m	T_2	τ	δ	ω	$\mu = \delta/\omega$	Activation energy (E), eV	Frequency factor (s), s^{-1}
72	99	136	27	37	64	0.578	0.68	2.6×10^{10}

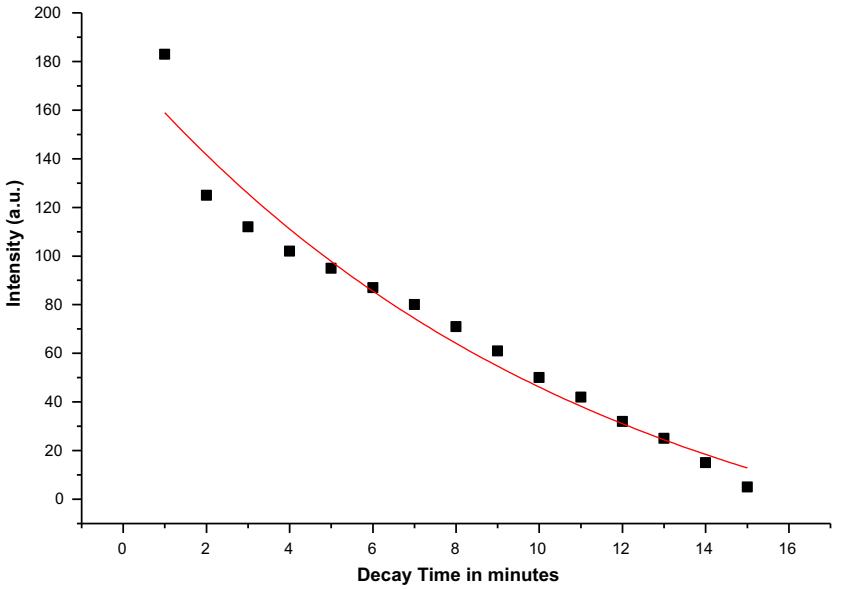

Fig. 6. Decay curve of Y_2O_3:Gd^{3+}.

of thermoluminescent material is based on its trapping parameters [15–19,25].

The glow curves obtained after 5 min of UV exposure were analyzed from their shapes [5,17] (Fig. 4). The order of kinetics was calculated from factor $\mu_g \sim 0.5$ (Fig. 5). The values of τ, δ and ω were calculated, where τ is the low-temperature half-width of the glow curve (i.e. $\tau = T_m - T_1$), δ is the high-temperature half-width of the glow curve (i.e. $\delta = T_2 - T_m$), and ω is the full width of the glow peak at its half-height (i.e. $\omega = T_2 - T_1$) (Fig. 5). The value of μ_g (shape factor = δ/ω) indicates that the glow peaks obey second-order kinetics.

The trap depth or activation energy (E_α) of the luminescence centres was calculated from Chen's equation [2,5,17,26]:

$$E_\alpha = C_\alpha \left(\frac{k_B T_m^2}{\alpha}\right) - b_\alpha(2T_m) \quad (1)$$

where k_B is Boltzmann's constant, T_m is peak temperature, and C_α and b_α are constants. The mean activation energy was ~0.68 eV, and the frequency factor was $2.6 \times 10^{10}\ s^{-1}$ for 5 min of UV exposure [17–22].

Fig. 6 presents the thermoluminescence decay plot for Y_2O_3:Gd^{3+} after UV exposure for 1–15 min. The intensity decreased exponentially with time, which shown high fading and less stability than $CaSO_4$:Dy and Al_2O_3:C [19], both of which showed second order kinetics. The Y_2O_3:Gd^{3+} phosphor showed similar kinetics.

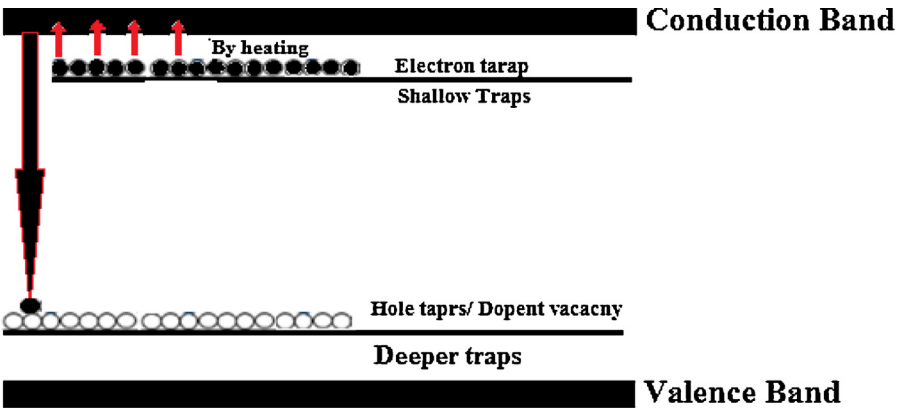

Fig. 7. Schematic representation of thermoluminescent process for UV-irradiated Y_2O_3:Gd^{3+} phosphor.

3.5. Localized transition model

We present a model to explain the thermoluminescence response of Y_2O_3:Gd^{3+} phosphor to UV radiation. In existing models, irradiation of a sample with an electron beam creates two types of trap, one shallower and the other deeper, in the forbidden band gap of the material. When a sample is irradiated with UV, it forms shallower traps, as confirmed by the lower temperature peak of the glow curve (Fig. 4). Upon heating of the UV-irradiated material, the charge carriers trapped during irradiation are released and transition to the conduction band (Fig. 7). The electrons that transition from the conduction band are either be re-trapped at the trap level or defect centre or at the hole trap or luminescence centre, where they recombine with holes, giving rise to luminescence or the glow peak. Trapped charge carriers are found inside the forbidden band gap, as confirmed by the calculated trap parameters [17,21,22].

4. Conclusion

A sample of Y_2O_3:Gd^{3+} doped phosphor was synthesized by the solid-state reaction method. The X-ray diffraction pattern showed that the sample has a cubic structure. The crystallites were 35–55 nm in diameter, and X-ray diffraction confirmed that the phosphors are nano-crystallites in single phase. The synthesized sample showed good morphology and connectivity, with grains and formation of a nano-sized sample. The diffraction pattern was determined by transmission electron microscopy with a selected area diffraction pattern. The phosphor was also examined by thermoluminescence, and the thermoluminescent glow curve was recorded for 1 mg of phosphor were irradiated with UV at 254 nm and a fixed heating rate at 7 °C s^{-1}. The sample showed a well-resolved peak at 99 °C for 1 mol% of Gd^{3+}. At lower temperature peaks, the sample was less stable and high fading. The thermoluminescent glow curve gives information on trapping parameters, such as activation energy, trap depth, order of kinetics and frequency factor. All the kinetics were calculated by the peak shape method. An activation energy of 0.68 eV was found, and the sample showed second-order kinetics. The rate of escaped electrons per second, calculated from the frequency factor, was 2.6×10^{10} s^{-1}.

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