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UV LIGHT INDUCED THERMOLUMINESCENCE OF RARE EARTH DOPED NANOMATERIALS Y_2O_3:Eu^{3+}, Gd_2O_3 :Eu^{3+} AND Gd_2O_3:Er^{3+}

NGUYEN THI QUY HAI[1], TRAN KIM ANH[1], VU THI THAI HA[2],
PHAM THI MINH CHAU[1], HO VAN TUYEN[1], NGUYEN TRONG THANH[2]
AND LE QUOC MINH[1,2]

[1]*Institute for Research and Development of High Technology, Duy Tan University, Da Nang, Vietnam*

[2]*Institute of Materials Science, Vietnam Academy of Science and Technology, Hanoi, Vietnam, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam*

[†]*E-mail:* nguyenquyhaivie@yahoo.com

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Abstract. *Thermoluminescence properties of ultraviolet irradiated Y_2O_3:Eu^{3+}, Gd_2O_3:Eu^{3+} and Gd_2O_3:Er^{3+} nanophosphors have been reported. The materials were synthesized by gel-combustion method with Disodium Ethylenediamine Tetraacetic acid (EDTA-Na_2) as organic agent. This method allows production of fine white powder at low temperature with high efficiency. XRD has been used to determine the structure of the prepared nanopowders. The obtained materials exhibit sufficient sensibility to UV radiation and may be useful in UV light measurements.*

Keywords: combustion, EDTA-Na_2, nanomaterials, Y_2O_3:Eu^{3+}, Gd_2O_3:$Eu^{3+}$and Gd_2O_3:Er $^{3+}$, UV light, thermoluminescence.

Classification numbers: 78.60.Kn, 78.67.Bf, 81.20.-n .

I. INTRODUCTION

Ultraviolet (UV) is an electromagnetic radiation within the wavelength range from 200 nm to 400 nm. UV radiation has various applications in medicine, biology and industry. However, it can damage living tissue, cause painful burns, destroy the membrane of eyes, and even cause skin cancer, when too much UV exposure exist. There were different methods for detection and measurement of UV radiation, most of them usually require a series of annealing operations and the thermoluminescence (TL) output depends on the prior treatments. Therefore, some simple and practical methods for detection and measurement of UV radiation are necessary. Currently, the

synthesis and development of new generation phosphors that exhibit TL response, higher stability, especially phosphors in nano-size, has attracted several researchers [1–5]. TL phosphors of high sensitivity to UV radiation have been considered as suing materials for UV radiation dosimetry. S. M. Yeh [1] investigated TL properties of Gd_2O_3:Tb^{3+}, Gd_2O_3:Dy^{3+} and Gd_2O_3:Eu^{3+} synthesized by pressing oxides into pellets, then sintering at 1200˚C for 4 h. They found that Gd_2O_3:Eu^{3+} may be used for UV measurement. R. K. Tamrakar and co-authors [2] reported the TL behavior of Gd_2O_3 and Gd_2O_3:Er^{3+} prepared by solid state reaction at 1400˚C/4h. They showed that the prepared phosphors are nano-crystalline in nature, cubic phase structure and the glow curves presented well resolved single peak for UV and gamma radiation.

Y_2O_3:Eu^{3+} were fabricated by means of solid state reaction method using high temperature sintering at 1500˚C for 4 h. After exposure to UV light one stable glow peak at 380˚C with acceptable sensitivity to UV was found, however its position changes with radiation dose [1]. J. R. Jayaramaiah [3] studied the TL phenomena of Y_2O_3:Eu^{3+} obtained by solution combustion, irradiated by gamma rays. Thermoluminescence and mechanoluminescence of Eu^{3+} doped Y_2O_3 nanophosphors prepared by combustion method using urea as fuel at 600˚C have been demonstrated by N. Brahme [5]. The glow curve of their sample shows 2 maximum peaks at 381.6 K and 555.2 K after UV exposure. The activation energies of those peaks were calculated to be 0.47 eV and 0.74 eV for the first and the second peak, respectively. In Vietnam, up to now there were some studies related to these materials, however, their interests concerned only on photoluminescence, excitation luminescence, up – conversion luminescence properties [6, 7].

In this work, the preparation of some nanophosphors such as rare earth doped oxides (Y_2O_3:Eu^{3+}, Gd_2O_3:$Eu^{3+}$and Gd_2O_3:Er^{3+}) and the investigation of their thermoluminescence (TL) induced by UV radiation have been presented and discussed.

II. EXPERIMENT

II.1. Materials Preparation

Y_2O_3:Eu^{3+}(3 and 5 mol%), Gd_2O_3:Eu^{3+}(5 and 7 mol%) and Gd_2O_3:Er^{3+} (0.5 and 1 mol%) nanophosphors were prepared by gel – combustion synthesis using Y_2O_3, Gd_2O_3, Er_2O_3 and $Eu(NO_3)_3.5H_2O$ as starting compounds, Disodium Ethylenediamine Tetraacetic acid (EDTA-Na_2) as fuel, following the same process reported in our previous paper [4]. The success of this synthesis depends on choosing suitable fuel or complexing agent (UREA or EDTA etc) in an aqueous solution with a right oxydizer / fuel ratio. At the point of spontaneous combustion, the solution begins burning, vaporizes immediately, releases lot of heat and liberates carbon- and nitrogen oxides. Normally the combustion completed in a few minutes [4, 8]. This method allows production of homogeneous phosphors with fine particle size at relatively low temperature, especialy in the case of EDTA as fuel (350˚C). At good conditions the reaction efficiency is very high (95%). Futhermore, the method is simple and needs only simple equipments. These advantages make the combustion method more effective for large production of nanomaterials.

The freshly prepared nanopowders underwent thermal treatments at different temperatures (350˚C, 700˚C and 900˚C) to study the influence of heat treatment on structure of the samples.

II.2. Characterization

The X-ray diffraction patterns of the samples have been obtained by x-ray diffractometer model Siemens D5000 using CuKα($\lambda = 0.15406$ nm), 40 kV, 20 mA at Institute for Materials

Science, Vietnam Academy of Science and Technology (VAST). The particle size was determined by the Scherrer's formula. A D2 lamp was used for irradiation the samples, and then TL glow curves and TL response glow curves were obtained by Harshaw TLD Reader at Institute for Materials Science, VAST. The preparation and luminescence research were implemented in Institute of Reasearch and Development of High Technology, Duy Tan University, Da Nang, Vietnam.

III. RESULTS AND DISCUSSION

III.1. Structure and particle size

The powder XRD patterns of Y_2O_3:Eu^{3+} (5 mol%) sample, which was synthesized by combustion method with EDTA-Na_2 as fuel, annealed at 350˚C and 700˚C/ 1h are shown in Fig. 1. The appearance of all prominent diffraction peaks of the planes (222), (321) (411), (420) (332), (422), (440) and (145) coincides with the cubic yttrium oxide phase (JCPDS No 41 -1105). The particle sizes of materials were calculated to be in the range of 24 nm for 350˚C, 26 nm for 700˚C annealed sample.

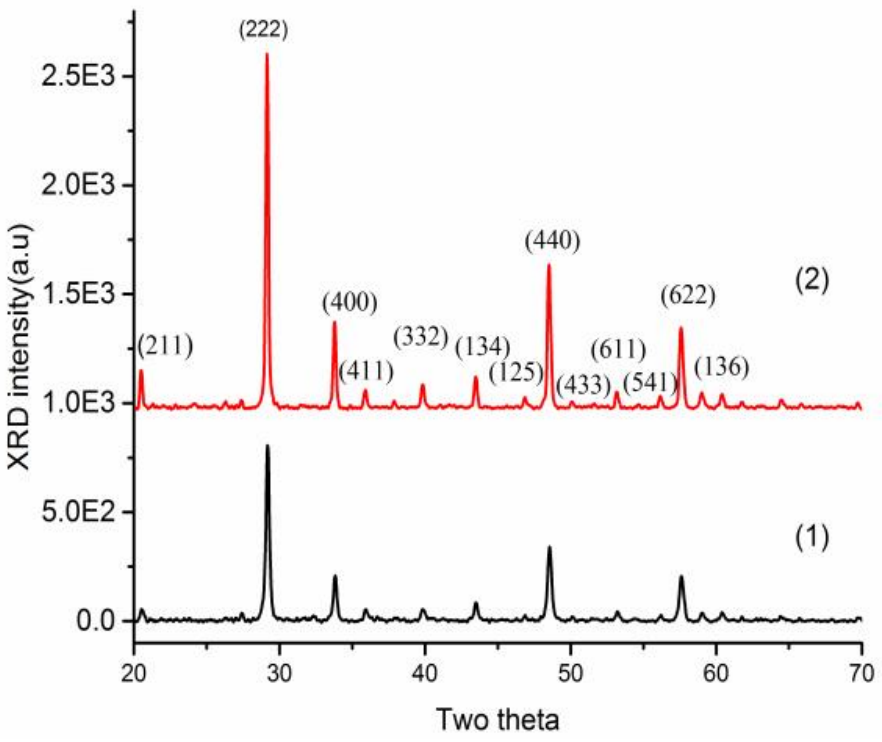

Fig. 1. XRD patterns of Y_2O_3:Eu^{3+} 5 mol%, EDTA-Na_2, treated at 350˚C/ 1h (1), 700˚C/1h (2).

Figure 2 presents the XRD patterns of Gd_2O_3:Er^{3+}0.5 mol%, annealed at 350˚C and 700˚C in 1h. According to the JCPDS No 42 – 1465 reference it is clear that the nanophosphors are in the pure monoclinic phase.

Similar results were obtained for Gd_2O_3:x Eu^{3+} ($x = 5,7,9$ mol%) phosphors, as it was reported in our recent paper [9]. Sintering the phosphors at 350˚C/1h, 700˚C/1h (Fig. 1 and Fig. 2) and increasing the activator concentration [9] did not change the crystalline monoclinic phase of the two prepared nanophosphors. It was in good agreement with observation given by other researches [2,3,8,10,11]. The main crystallite sizes of Gd_2O_3: Eu^{3+} 7 mol% and Gd_2O_3:Er $^{3+}$ 0.5 mol% were 24 nm and 32.5 nm, respectively.

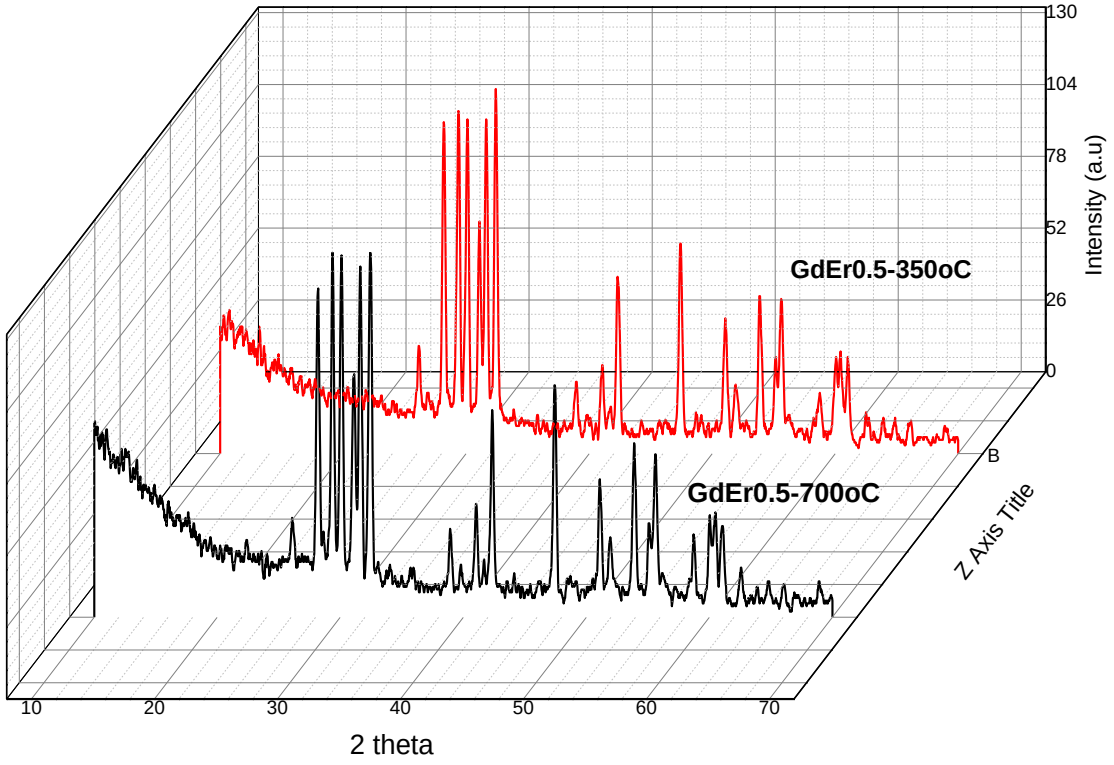

Fig. 2. X-ray diffraction pattern of Gd_2O_3: Er^{3+} (0.5 mol%) prepared by gel-combustion method with EDTA-Na_2 as fuel, annealling at 350˚C and 700˚C in 1 h.

The incorporation of the rare earth ions in the Gd_2O_3, Y_2O_3 host lattice, one of the most important parameters, has been confirmed by studies of the energy dispersion spectrum (EDS), photoluminescence (PL) spectrum and photoluminescence excitation (PLE) spectrum as reported in our paper [9]. The obtained results proved to the success of the synthesis process.

III.2. Thermoluminescence process

Thermoluminescence (TL) is the emission of light from an insulator or semiconductor material, which was previously irradiated by ionizing radiation, when it is heated. The TL glow curve of the sample recorded during sample heating process is related to traps locating at different energy levels in the band gap of material. The characters of the glow peaks such as positions, shapes and intensities are depended on different parameters of the trapping states responsible for the TL, among them the activation energy E, the frequency factor s and the order of the kinetics

associated with the glow peaks are the most important parameters. Recent studies on luminescent nanomaterials indicated their applicability in dosimetry of ionizing radiation, especially for the measurement of high doses [4, 8, 12]. In the present work, the thermoluminescence properties induced by UV radiation of Y_2O_3: Eu^{3+}, Gd_2O_3: Eu^{3+} and Gd_2O_3: Er^{3+} nanophosphors fabricated by the above presented procedure have been investigated. D2 lamp is used as UV source for irradiation of samples.

Fig. 3 shows the TL- glow curve for Y_2O_3: Eu^{3+} (5 mol%) annealed at 700˚C/1h nanophosphor, recorded from 50˚C to 400˚C at a linear heating rate 2˚C/sec after 5, 10, 15, 20, 25 and 30 minutes exposure to D2 lamp UV source. It is observed that this glow curve consists of a broad peak extending from 75˚C to 350˚C. Applying the TLAnal software for deconvolution of the glow curve of the sample UV irradiated in 5 minutes, we know that this peak was formed by some overlap peaks, among them one prominent peak located at 167˚C (440 K) was found. The TL intensity of this intense peak increased regularly with UV exposure time.

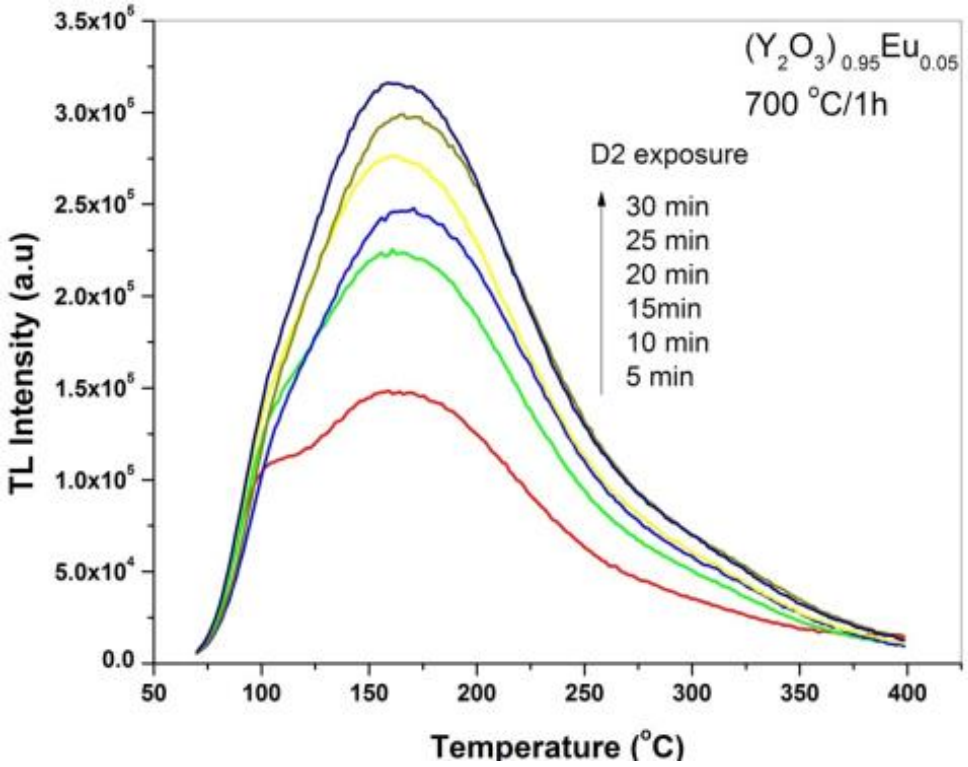

Fig. 3. TL glow curve of Y_2O_3 : Eu $^{3+}$5 mol%

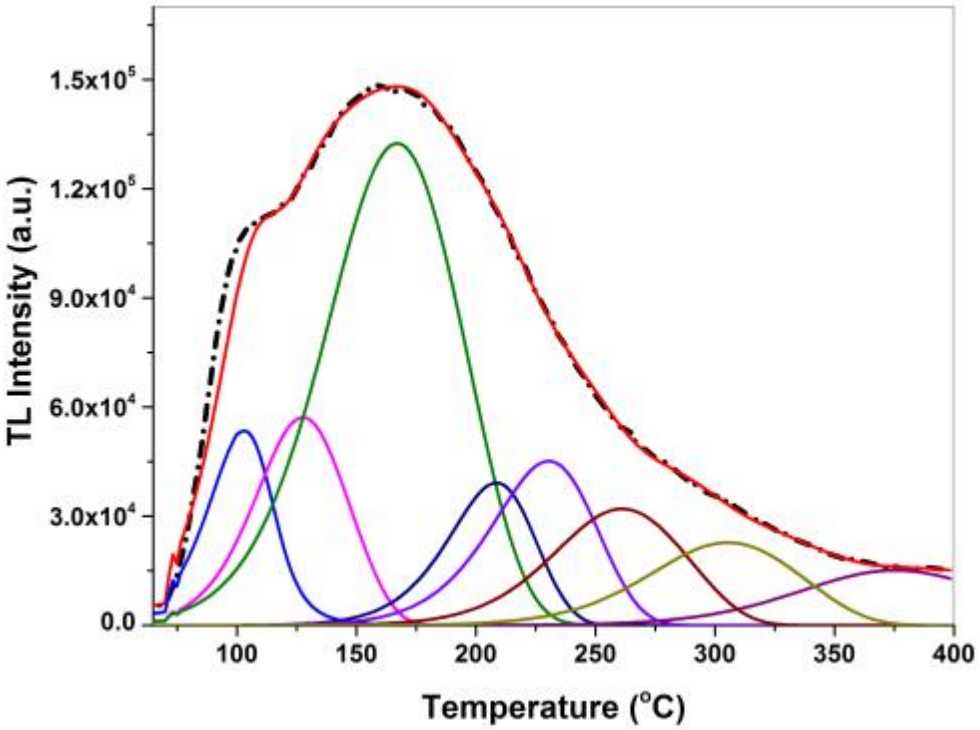

Fig. 4. Deconvoluted curve of Y_2O_3: Eu $^{3+}$0.5 mol%, annealed at 350 ˚C / 1h, irradiated by D2 lamp in 5 min., using TLAnal software.

Fig. 5 and Fig. 6 present the TL glow curves of Gd_2O_3:Er^{3+} (0.5 mol%) and Gd_2O_3:Eu^{3+} (7 mol%) for different exposure times to D2 lamp, respectively. In both cases, the glow curve consists of several overlap peaks. After performing deconvolution of the glow curves one can observe two main peaks located at 371 K, 456 K in the glow curve of Gd_2O_3:Er^{3+} (0.5 mol%), annealed at 350˚C/ 1 h, irradiated to UV in 5 minutes and at 393 K, 498 K in the glow curve of Gd_2O_3: Eu^{3+}(7 mol%) treated at the same conditions.

As mentioned above, the photoluminescence and thermoluminescence behavior of a sample depends on many factors such as the crystal structure, band gap, synthesis process, crystal size, lattice imperfections and mainly the effects of impurities of solids [1, 2, 6, 13]. When a phosphor sample was irradiated by UV radiation, its TL response mainly generates from the surface traps, which are created during the sample processing [5]. In the case of Y_2O_3:Eu^{3+} (5 mol%) phosphor prepared by combustion method with EDTA-Na_2 as fuel at 350˚C, the exsistence of an intense single glow peak indicates that a major single defect might be formed because of UV irradiation [8]. The TL signals of Gd_2O_3:Eu^{3+} va Gd_2O_3:Er^{3+} nanophosphors demonstrate that there are two major trapping sites in the sample structure, which are dependent on the sample preparation condition and doping concentration [8]. Consideration in detail of the TL glow curves of Gd_2O_3: Er $^{3+}$0.5 mol% presented in Fig. 5 indicates that the intensity of the low temperature peak (371 K) reaches the highest value only after UV exposure for 5 min and is higher than that of the second peak (456 K). This value is almost unchanged when we increase the irradiation time, it seems to be saturated.

Further increasing of irradiation time causes continuous increasing of the intensity of the higher temperature peak (456 K) up to 25 minutes of UV exposure. From this analysis we can assume that for UV exposure time from 5 min up to 25 min, [almost only] the trapping sites, which are responsible for the second, higher temperature peak, are filled up.

In Figures. 6 and 7, we can see that the intensity of the glow peak located at 498 K increases faster than that of the glow peak located at 393 K when the exposure time increased. The relationship between the TL signal intensity and the UV exposure time of Gd_2O_3: Eu 7 mol%, calculated from the total area of its glow curve, was plotted in Fig. 8. We note that the TL intensity of the sample increased linearly up to 15 minutes of UV exposure.

In the present work, an effort to prevent the surface of nanophosphors by coating it with silica by common sol-gel method using Tetraethoxysilane (TEOS) as precursor [14–16] has been performed. It was observed that the presence of the SiO_2 coating out-layer on the surface of sample improves the shape and symmetry of the glow curve as it can be seen when we compare Fig. 5 to Fig. 9. The reason of this is the certain defects can be reduced during surface coating and therefore reduce their influence on TL signal of the glow peak. The effect is still under investigation.

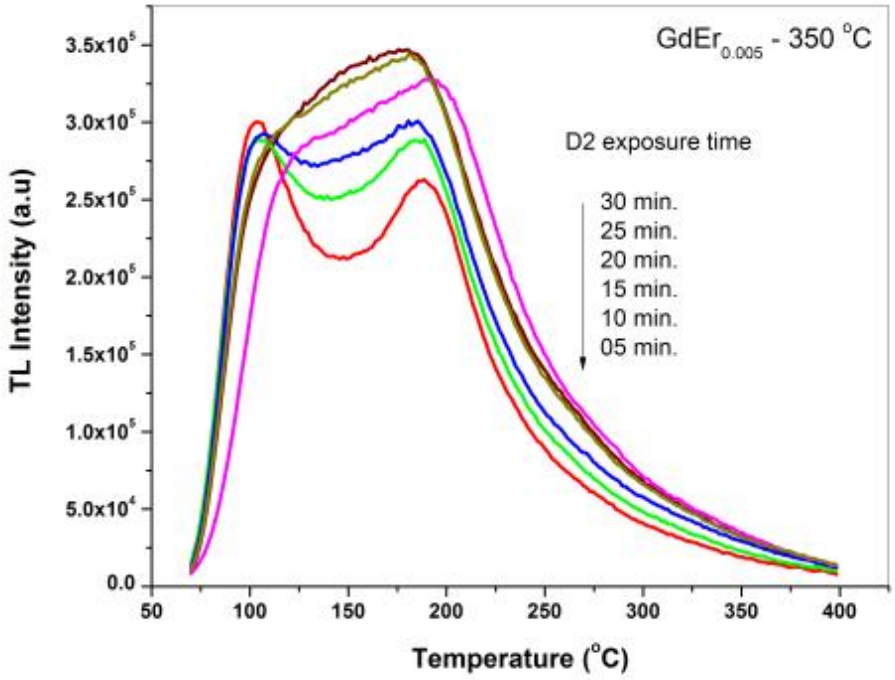

Fig. 5. TL glow curves for Gd_2O_3:Er^{3+}0.5 mol% for different UV exposure time with heating rate 2˚C/s.

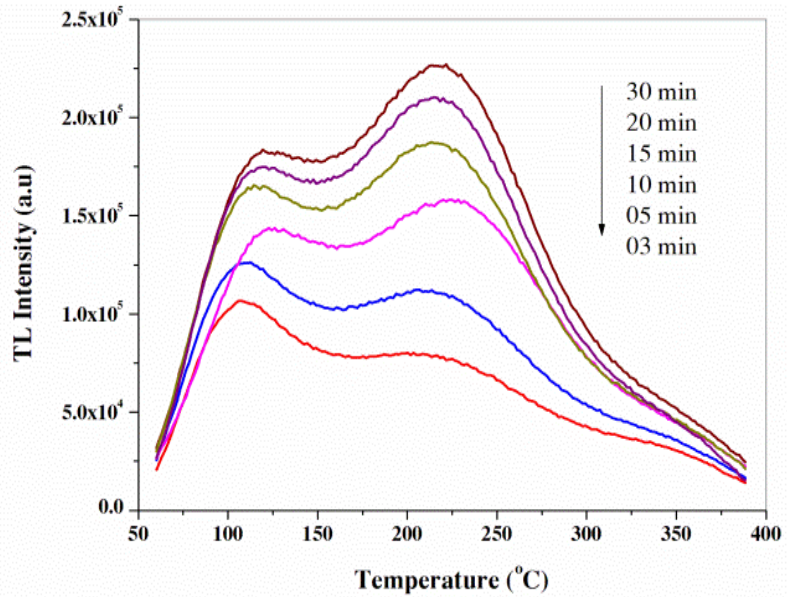

Fig. 6. TL glow curves of Gd_2O_3:Eu^{3+} 7 mol% for different UV exposure time with heating rate 2˚C/s.

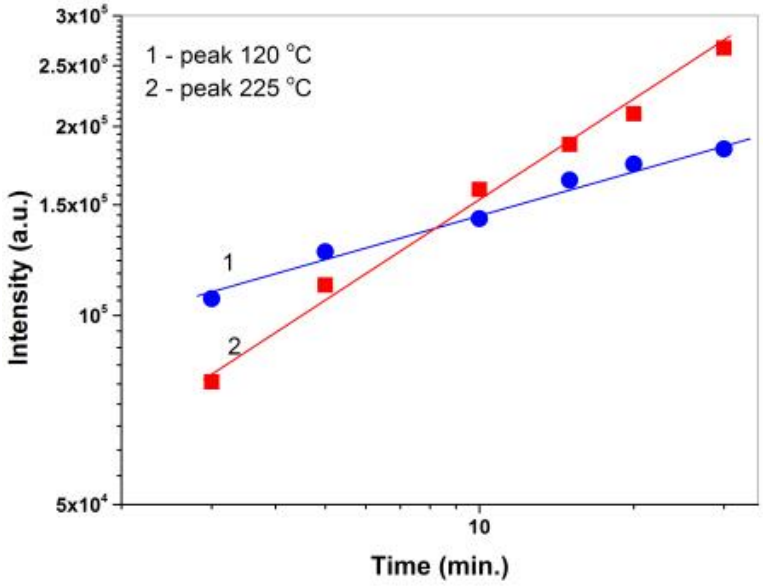

Fig. 7. Dependence of the TL intensity of peaks 120˚C (393 K) and 225˚C (498 K) on the UV irradiation time of Gd_2O_3:Eu^{3+}7 mol%.

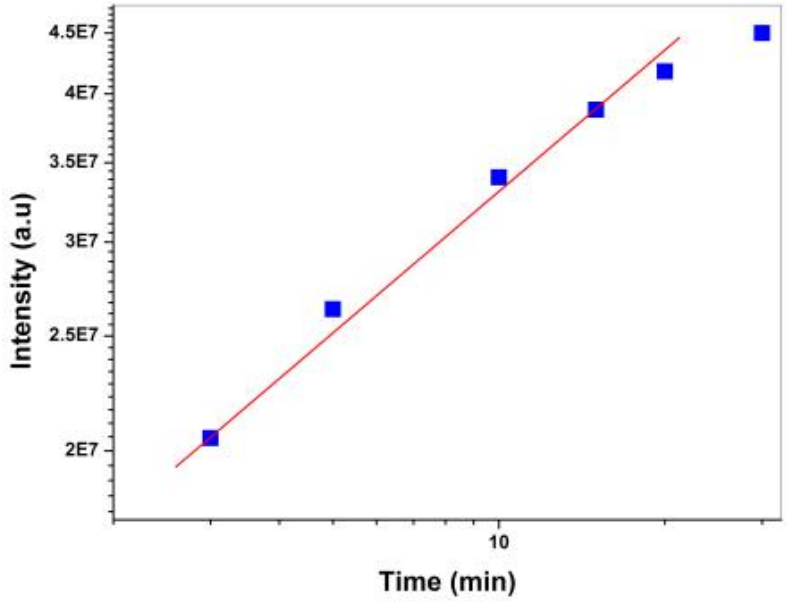

Fig. 8. Variation of glow peaks intensity of Gd_2O_3:Eu^{3+} 7 mol% with UV exposure times, calculated from the total area of sample's glow curve.

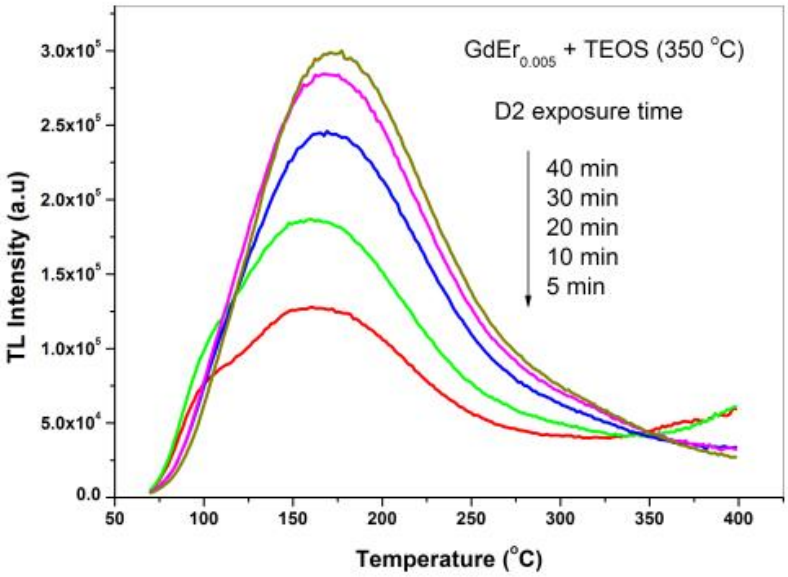

Fig. 9. TL glow curves of Gd_2O_3:Er^{3+}0.5mol%@ SiO_2 0.1 wt% induced by UV radiation from 5 to 40 minutes.

III.3. Kinetic parameters

The kinetic parameters of trapping states have been calculated by combining the results of deconvolution of glow curves using TLAnal software and the peak shape method. The results are

listed in Table 1. Normally, the low temperature peaks with small activation energy E are less sensitive and unstable. They cannot be able to use in dose determination.

Table 1. Calculated kinetic parameters of prominent glow peaks of samples, UV irradiated for 5 minutes at room temperature.

Samples	$Tmax$ (K)	E (eV)	S (s^{-1})	b
Y_2O_3:Eu^{3+}5 mol%	440	0.68	3.3×10^{10}	1.3
Gd_2O_3:Eu^{3+} 7 mol%	393	0.58	2.6×10^{9}	1.6
	498	0.8	2.6×10^{9}	1.6
Gd_2O_3:Er^{3+}0.5 mol%	371	0.69	6.5×10^{9}	1.6
	456	0.77	1.0×10^{12}	1.4
Gd_2O_3:Er^{3+}0.5 mol% 350˚C/1h@ SiO_2 0.1 wt%	450	0.75	9.4×10^{10}	1.5

Tmax is the temperature of the maximum TL peak, E is the activation energy, S is the frequency factor and b is the order of kinetics.

IV. CONCLUSIONS

The gel - combustion method using EDTA-Na_2 as organic agent has successfully been applied for fabrication of Y_2O_3:Eu^{3+}, Gd_2O_3:Eu^{3+} and Gd_2O_3:Er^{3+} nanophosphors. The thermoluminescence properties of the obtained samples were investigated for UV irradiation. It is observed that the materials seem to be sensitive enough to UV radiation. A very low irradiation UV dose (1-3 min. UV exposure by D2 lamp) can induce TL effect in the investigated samples. Coating the surface of the nanophosphor with a silica layer may improve the quality of the surface, reduces the certain defects, and thus may make a positive impact on the thermoluminescent behavior of the phosphor sample. These nanophosphors may have the potential application in UV light dosimetry. Further studies are being continued.

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