**KINETIC CHARACTERIZATION OF GAG: CE PHOSPHOR**

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**Abstract**

Thermoluminescence (TL) kinetic characterization of cerium (Ce3+) doped gadolinium aluminum garnet (GAG) prepared by wet chemical synthesis method are presented in this study. Thermoluminescence glow curve of GAG phosphor after UV irradiated has two peaks at about 350 and 501 K with a heating rate of 2 Ks-1. Thermoluminescence kinetic parameters such as order of kinetics, frequency factor and activation energy associated with the main glow peak of the GAG:Ce phosphor have been calculated using various heating rates (VHR) computerized glow curve deconvulation (CGCD) and peak shape (PS) methods in this study. The activation energies obtained by VHR, PS and CGCD methods are calculated to be 1.24, 1.11 and 1.14 eV, respectively. The frequency factors attained by these methods were found as 3.41x1011, 1.80x1010 and 2.63x1010 s-1, respectively. Results acquired using all methods are discussed and compared.

**Keywords:** Gadolinium aluminum garnet, Thermoluminescence, Kinetic parameter

**1. INTRODUCTION**

Garnet crystal is commonly used at high temperatures due to their high chemical and thermal stability. Moreover, it is used in the solid-state laser host materials, the refractory coating fillers, magnetic materials, and phosphor powders [1-3]. The optical properties of Ce-activated garnet series used in white light emitting diodes have been remarkable in recent years [4]. Gadolinium aluminate is nowadays being investigated quite interesting as a material for, electronic, optical, magnetic and structural applications [5]. Information on the luminescence properties of cerium doped gadolinium aluminum garnet is limited to a few studies. Studies were performed with related to gadolinium aluminum garnet preparation methods [1-7].

The recent increase in solar ultraviolet (UV) radiation reaching the Earth's surface due to the depletion of stratospheric ozone has been a major concern, due to the harmful effects on living organisms associated to the UVB (320–290 nm) and UVA (400–320 nm) components of the solar spectrum. Additionally, UVB may have several adverse influences on planktons in sea ecosystem [8,9].

Thermoluminescence dosimeters have some superior characteristics such as their availability, being cheap and easy to use in the determination of exposed dose to living organisms. Recently, studies related to UV radiation measurement by thermoluminescent dosimeters were increased due to being cheap and easy technique in the UV measurement. This has led us to examine the usability of GAG:Ce phosphor in the measurement of UV radiation dose. The determination of the trapping parameters from thermoluminescence glow curves is an important research subject to improve the properties of the material as dosimetric usage.

In the present study, cerium-doped gadolinium aluminate phosphor prepared by a wet chemical synthesis route was used. In this work, the thermoluminescence kinetic characterization was investigated cerium-doped gadolinium aluminate phosphor after UV irradiation. It was observed that glow curve of the phosphor was consisted of two peaks at about 80 and 230 ̊C. The kinetic parameters such as kinetic order (b), activation energy (E), and frequency factor (s) were calculated using various heating rates (VHR), Chen peak shape methods and computerized glow curve analysis (GCGD) methods were used.

 **2. MATERIAL AND METHODS**

The cerium-doped gadolinium aluminate phosphor used in this study was synthesized by wet-chemical route via the reagent simultaneous addition technique (WCS-SimAdd ) technique. In order to prepare GAG:Ce phosphor was synthesized without NH4Cl as a flux. All experimental details can be found in our earlier works [10]. Prior to irradiation with the wavelength of 311 nm Philips UV 100 lamp was used for TL measurements. TL glow curves were recorded by Harshaw 3500 TL reader.

Kinetic parameters such as kinetic order, activation energy and the frequency factor have a remarkable influence on the thermoluminescence characterization of a phosphor. Hence, knowledge of these parameters has critical importance for understanding the thermoluminescence phenomenon in the phosphor, and there have been many methods for determining these parameters experimentally [11].

In this study peak shape (PS), various heating rates (VHR) and computerized glow curve deconvulation (CGCD) methods were used to analyze the kinetic characterization for GAG:Ce phosphors.

The VHR method arises from recording the maximum temperatures of the glow peak with different heating rates. The maximum temperature Tm is associated with the heating rate *β*, this relation could be described in equation (1) as VHR method:

 (1)

where k is Boltzmann’s constant, Tm is the maximum temperature of glow peak , E is the activation energy (eV) and s is the frequency factor (s-1). After recording Tm with a number of different heating rates, E could be calculated from the slope of the straight line obtained from the plot of the ln (T2m/ *β*) versus 1/Tm. The intercept of the slope this plot gives the value of s [12, 13]. Kitis and Tuyn proposed a model to correct for the temperature lag based on TSL measurements [14]. This model is given as an equation (2):

 (2)

where *c* is a constant and Tma and Tmb are the maximum temperatures of glow peaks with heating rates βa and βb, respectively.

**3. RESULTS AND DISCUSSION**

The dose response of a dosimeter should have linear or a well known function to be used in dosimetric purpose. TL glow curves of the GAG:Ce phosphor were recorded after UV irradiation 1, 5, 10 and 20 minutes (Figure 1). The high temperature peak shifts when irradiation dose of the phosphor increases. Therefore, this result states about the knowledge about the kinetic order of the peak not being a first order.



**Figure 1.** TL glow curves of the GAG:Ce phosphor exposed to UV irradiation at different duration.

The glow curve of the GAG:Ce phosphor is well defined so the various heating rate method was applied for kinetic characterization for the phosphor. Glow curves GAG:Ce phosphor after 5 minutes of UV irradiation are corrected using 1, 2, 5, 10, 20 and 40 K / s heating rates (Figure 2). If the glow curves are investigated, the maximum peak temperatures were shifted to the rising side with increasing heating rate. This is an expected phenomenon.

The kinetic parameters are calculated by taking into consideration of the shifts in VHR method. However, the obtained result requires some corrections due to the occurrence of some systematic errors during thermoluminescence measurements. It has been well established that temperature lag (TLA) and thermal gradient (TG) have an important role in the kinetic parameter analysis [15-19]. The TLA of all measurements are evaluated using the method recommended by Kitis and Tuyn [20, 21].

 

 **Figure 2.** Glow curves of GAG:Ce irradiated with a UV. The glow curves were recorded at different heating rates, namely 1, 2, 5, 10, 20 and 40 °Cs-1 respectively.

As a result of the measurement, the graph of ln (T2m/β) corresponds to (1/Tm) the maximum temperature values obtained from the glow peaks was plotted for each heating rate (Figure 3). This graph should be a straight line since heating rates in the system is linear. Data (🞏) correspond to the peak temperatures as attained from experiments and data (⯆) to the peak temperatures corrected for the temperature lag in figure 3. A plot of ln (T2m/β) against 1*/T*m, where *β* is the heating rate, should give a straight line. The activation energy is determined from the slope of these lines and frequency factor is attained from the intercept. According to this method E and s parameters are calculated as 1.24 eV and 3.41x10+11 s-1, respectively.

The Peak Shape method developed by Chen, which takes into account the peak shape or geometrical properties of a well known method of TL glow curve analysis, has been applied [22]. According to this method, the average activation energy (E) was found to be 1.11 eV and average frequency factor (s) 1.80x10+10 s-1 according to the peak shape method of high temperature peak (501 K) which can be taken as a dosimetric peak.

**Table 1.** The kinetic parameters of the glow peak about 501 K measured by 2 K.s-1 of GAG:Ce phosphor attained by PS methods.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| PS Method | Activation Energy (E) | (eV) | Frequency Factor (s) | (s-1) |
| Eδ | 1.13 | sδ | 2.57x1010 |
| Eτ | 1.09 | sτ | 9.85x109 |
| Eω | 1.11 | sω | 1.83x1010 |

Glow curve deconvulation analysis of the phosphor GAG:Ce after exposing to UV irradiation by using the deconvulation program [23] was indicated in Figure 4. The most appropriate deconvoluted peak was taken into consideration by deciding the figure of merits (FOM). The physically calculated kinetic parameter by using FOM was in between 0.0% and 2.5% [24]. The FOM value of the current deconvulation process of the GAG:Ce glow curve was found as 2.05%. As a result of analysis, it was observed that the glow curve is composed of four peaks at about 351, 452, 501 and 575 K. Although, phosphor has composed of four peaks, only the peak 3 could be used as a dosimetric. The kinetic parameters for all the above peaks were also calculated and are summarized in Table 2. The activation energy and frequency factors of the main peak at 501 K were obtained as 1.14 eV and 2.63x10+10 s-1 respectively. The kinetic order of the peak was founded as the general order.

**Table 2.** The kinetic parameters of the glow curve of GAG:Ce phosphors were obtained in CGCD analysis.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Peak** | **Im** | **Tm (K)** | **E (eV)** | **b** | **S (s-1)** |
| 1 | 1362844 | 351 | 0.80 | 2 | 3.51 x10+10 |
| 2 | 348461 | 452 | 0.85 | 1.87 | 2.05 x10+8 |
| 3 | 12312130 | 501 | 1.14 | 1.31 | 2.63x10+10 |
| 4 | 98729 | 575 | 1.26 | 2 | 8.39 x10+9 |

**4. CONCLUSION**

Investigation of thermoluminescence properties of cerium-doped gadolinium aluminate phosphor subject is an original work. Our literature review shows that so far no work has been done in the thermoluminescence kinetic characterization studies of cerium doped gadolinium aluminum garnet phosphor. Keeping this in view, an attempt is made to study about the thermoluminescence properties of this material. The kinetic parameters of Ce doped gadolinium aluminum garnet phosphor were analyzed using the VHR, Chen’s peak shape and computerized glow curve deconvulation methods. The obtained E, s and b parameters determined by all methods were found in good agreement. The results show that the main dosimetric peak of GAG:Ce phosphor being at 501 K have a general order kinetic model. A whole knowledge of the thermoluminescence processes, determining the kinetic parameters is worth further investigation in order to design the most suitable dosimeter suitable for UVB.

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**REFERENCES**

**[1]** Surresh, G., Seenivasan, G., Krishnaiah, M.V., Murti, P.S., Investigation of the thermal conductivity of selected compounds of gadolinium and lanthanum, Journal of Nuclear Materials, 249, 259-261, 1997.

**[2]** Cizauskaite, S., Reichlova, V., Nenartaviciene, G., Beganskiene, A., Pinkas, J., Kareiva, A., Sol–gel preparation and characterization of gadolinium aluminate, Materials Chemistry and Physics, 102, 105-110, 2007.

**[3]** Chiang, C.C., Tsai, M.S. and Hona, M.H., Preparation of Cerium-Activated GAG Phosphor Powders Influence of Co-doping on Crystallinity and Luminescent Properties, Journal of The Electrochemical Society, 154, 10, J326-J329, 2007.

**[4]** Marius, M., Popovici, E.J., Barbu-Tudoran, L., Indrea, E., Mesaros, A., Cerium-doped yttrium aluminate based phosphors prepared by wet-chemical synthesis route: Modulation of the luminescence color by changing the host-lattice composition, Ceramics International, 40, 6233–6239, 2014.

**[5]** Matos, M.G., Calefi, P.S., Ciuffi, K.J., Nassar, E.J., Synthesis and luminescent properties of gadolinium aluminates phosphors, Inorganica Chimica Acta, 375, 63–69, 2011.

**[6]** Dotsenko,V.P., Berezovskaya, I.V., Voloshinovskii, A.S., Zadneprovski, B.I., Efryushina, N.P., Luminescence properties and electronic structure of Ce3+-dopedgadolinium aluminum garnet, Materials Research Bulletin, 64, 151–155, 2015.

**[7]** Popovici, E.J., Morar, M., Bica, E., Perhaita, I., Cadis, A.I., Indrea, E., Barbu-Tudoran, L., Synthesis and characterization of cerium doped yttrium-gadolinium aluminate phosphors by wet-chemical synthesis route, Journal of Optoelectronics and Advanced Materials, 13, 617–624, 201