Structural and TL glow curve of GdAlO$_3$ perovskites

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Abstract. TL glow curve of any semiconductor is the patterns that mean when a material is suitable as Thermoluminescent (TL) material. Gadolinium aluminate (GdAlO$_3$) perovskites have several properties that can be propose it as a good host for thermoluminiscent materials. GdAlO$_3$ perovskite powder was synthesized by coprecipitation method and the powders were analyzed by characterization techniques. The Differential scanning calorimetry study showed changes in crystalline phases at 900 °C and 1084 °C during the calcination process. The first change of crystalline phase was identified by X rays diffractometry technique as a change from GdAlO$_3$ hexagonal to GdAlO$_3$ orthorhombic. TL glow curves of GdAlO$_3$ under ultraviolet (UV) 256 nm and beta radiation effects were observed as crystallite size was increased.

1. Introduction
Ceramic materials based in perovskite structure have several applications due to its simple crystal structure and electric, magnetic, piezoelectric, optical, catalytic and magneto resistive properties [1] [2] [3]. Gadolinium compounds are used as phosphors for color TV tubes, neutron absorption and control rod applications [3]. Gadolinium aluminate has good qualities as host phosphor materials because of chemical stability, high melting point, high thermal stability, low thermal expansion, high thermal conductivity, low cut off phonon energy (~580 cm$^{-1}$) and good transparency to infrared radiation [4]. Many synthesis methods have used to obtain perovskite materials, the most common is the solid-state method. Solid-state synthesis requires a huge amount of energy and its products have low quality about homogeneity and phase purity. In order to improve the efficiency of synthesis method is very common to use wet chemical method of synthesis [5]. Coprecipitation synthesis is a wet chemical method quite used by many authors to obtain perovskite structure materials [6] [7] [8].

Thermoluminescent dosimetry (TLD) is widely applied in the dose estimation of ionizing radiations (X rays, gamma rays, ion beams, etc.). A material to be used as TLD needs the following properties: (i) a comparatively simple glow curve having a single peak with its temperature less than 200 °C; (ii) same TL response for all energies of ionizing radiation; high sensitivity that comprises both a high efficiency of light emission and a low threshold dose; (iii) low fading, good linearity of the TL signal in the specific useful range of radiation dose; (iv) an effective atomic number Zeff, which can be near to that of the biological tissue [9]. The aim of the present research was to study TL glow as a function of calcination temperature, crystal phase and powders size in order to check if it useful application as host of TLD materials.

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2. Methods and materials

Powders of GdAlO$_3$ were obtained by coprecipitation method. Gd$_2$O$_3$ (99.9 % purity, Alfa Aesar), Al(NO$_3$)$_3$·9H$_2$O (98.6 % purity, J.T. Baker) were starting materials. Gd$_2$O$_3$ was dissolved in HNO$_3$ (70%, Meyer). Solutions with correct stoichiometry were mixed in a beaker under magnetic stirring. The mixture was transported to another beaker with enough volume of NH$_4$OH (28 % purity, J.T. Baker) to keep pH equal 11, through peristaltic pump. The precipitated mixture at high pH was left for one hour under magnetic stirring. After one hour, the precipitate was filtered and washed in distilled water at 70 °C during one hour. The mixture was filtered again, and it submitted in an oven at 100 °C for 48 h for drying. After the dry process, the agglomerated was make powder trough manual grinding. Finally, powders were carried to calcination process. The calcination process started at room temperature using 5 °C/min of heating rate. The maximum temperature of calcination cycle remained constant during 5 h. In order to study the material behavior, different calcinations cycles were applied changing maximum temperatures: 900 °C, 1000 °C, 1100 °C, 1200 °C and 1400 °C.

TGA and DSC studies of powders before calcination process were carried out in a thermo balance (SDT Q600, TA Instruments) in dynamic air atmosphere. The weight loss as a function of temperature was recorded up to 1200 °C. The heating rate was 20 °C/min from ambient temperature to 1200 °C. The phase purity and crystallinity of the nanophosphors was examined by powder X-ray diffractometer equipment (Bruker D8 Advance) using Cu Kα radiation (1.541 Å). The step for 2θ was 0.02 and the step for time analysis was 0.6 s. TL glow curve of calcined powders was obtained using lxesygsmart, Freiberg Instruments, TL/OSL reader. The samples were exposed to beta radiation at 3.6 Gy. TL glow curve was also studied under 256 nm UV radiation effect.

3. Results and discussion

3.1. Thermal analysis of precursor powders

Figure 1 shows the studies of TGA and DSC of the powder before to receive calcination cycle.
TGA curve got characterize by five loss weight steps: room temperature to 175 °C identified as decomposition process of physisorbed water, from 175 °C to 400 °C occurred the bigger weight loss (~ 12 %) linked with the elimination of a big mass of structural water in material, from 400 °C to 580°C it showed a weight loss at about 8 %, which one was related with decomposition reactions of NO₃ [10], last two steps are lower meaning chemisorbed water loss. DSC curve showed two endotherms at 251 °C related with the first step in the TGA curve and 480 °C linked with the second step in TGA curve. DSC curve also showed two exotherms at 900 °C and 1084 °C typical of change of crystalline phase.

4. Powder X-ray diffraction

Figure 2 shows DRX results in sequence of powders obtained by different calcination cycles.

![DRX patterns of powders obtained to different calcined temperatures](image)

Figure 2. DRX patrons of powders obtained to different calcined temperatures. ■ GdAlO₃ hexagonal, ● Gd₄Al₂O₉ monoclinic, ▲ GdAlO₃ orthorhombic.

The patterns of DRX at 100 °C did not shows any crystalline peak. Powders calcined at 900 °C show visible peaks that were identified as GdAlO₃ hexagonal phase (PDF 04-006-5198) and Gd₄Al₂O₉ monoclinic phase (PDF 00-046-0396). As can be seen in figure 2 after 1000 °C a change of crystalline phase from GdAlO₃ hexagonal to GdAlO₃ orthorhombic was observed, this result is agreement with DSC study. The phase Gd₄Al₂O₉ monoclinic coexisted with principal phase GdAlO₃ before 1400 °C. The phase Gd₄Al₂O₉ monoclinic did not be desired because the study was focused in obtain a pure phase of GdAlO₃. It was eliminated at 1400 °C of calcination temperature. Therefore, the most recommended calcination temperature to obtain pure GdAlO₃ orthorhombic crystalline phase with coprecipitation synthesis method was 1400 °C.
In order to determine the crystallite size $D$ as a function of calcination temperature the Scherer formula was used [9] [11]:

$$D = \frac{K \lambda}{\beta \cos \theta} \tag{1}$$

where $K$ is a constant equal to 0.94 [11], $\lambda$ is the wavelength of X rays used in DRX analysis, $\beta$ is full width at half maximum of principal peak and $\theta$ is the position of principal peak. The calculus was done for curves with maximum calcination temperature greater or equal than 1000 °C. The principal peaks for these curves were localized in $2\theta \approx 34^\circ$. The fitting function selected for the calculus of $\beta$ parameter was the Gaussian function. Table 1 shows the results of $D$ calculated by Scherrer formula. The respective errors were determined by propagation errors.

| $T$ (°C) | $D$ (nm) | $E(D)$ |
|---------|--------|--------|
| 1000    | 30.39  | 0.002  |
| 1100    | 32.79  | 0.002  |
| 1200    | 39.99  | 0.002  |
| 1400    | 40.64  | 0.002  |

The results of crystallite sizes showed a tendency to increase, as calcination temperature was increased.

4.1. Thermoluminescent glow curve

The research got to focus to analyze thermoluminescent properties of GdAlO$_3$ as a potential applications as host TLD materials. Figure 3 shows the glow curve response to beta radiation during 60 s of powders analyzed.

![Figure 3. TL response of powders at different maximum calcination temperatures exposed to beta radiation during 60 s.](image-url)
TL response to beta radiation was similar by 900 °C, 1000 °C and 1100 °C calcination temperature curves. TL glow peak centered at 100 °C is observed for all samples, however, this peak is increasing of intensity as calcinated temperature is increasing. A second peak is observed for samples calcined at 1200 °C, which is increased also as calcination temperature is increased. Powders calcined at 1400 °C exhibited well defined four peaks centered at 100 °C, 180 °C, 280 °C and 320 °C. The intensity and number of point defects increased with calcination temperature. The material became more sensible with increasing crystallite size. This behavior suggests a detail studies on TL properties of semiconductor material based on GaAlO$_3$.

The material was more sensible when the calcination temperature raised to 1400 °C. Thus, powders calcined at 1400 °C were exposed to UV radiation (256 nm) for 5 s period with the objective to analyze its TL behavior under radiation composed by photons. Figure 4 illustrates TL response of powder calcinated at 1400 °C.

![Figure 4. TL response of powders calcined at 1400 °C exposed to UV radiation during 5 s.](image)

TL response under UV radiation was characterized by three well defined maximums at 99 °C, 191 °C and 289 °C. The material was sensible to UV radiation too. Results indicated GdAlO$_3$ had a quite intense TL response and can be a potential efficient host to TLD materials.

5. Conclusions
GdAlO$_3$ perovskite powders were synthesized by coprecipitation method. DSC study showed changes in crystalline phases at 900 °C and 1084 °C during calcination process. The first change of the crystalline phase was identified by DRX technique as a change from GdAlO$_3$ hexagonal to GdAlO$_3$ orthorhombic.

The unwanted phase Gd$_4$Al$_2$O$_9$ monoclinic phase was eliminated at 1400 °C of calcination temperature. The results of crystallite sizes showed a tendency to increase, as the calcination temperature is increasing. TL glow curve of GdAlO$_3$ powders was obtained as a function of calcination temperature. TL glow curve was obtained with the expectation at 1400 °C of calcination temperature, which is good candidate for a detailed study for TL properties.

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