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# Thermoluminescence kinetic parameters of $Bi_4Ge_3O_{12}$ single crystals

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**Abstract**

In this work, we present a detailed kinetic study of the thermoluminescence of $Bi_4Ge_3O_{12}$ (BGO) single crystals grown by the Czochralski technique. A single crystalline phase was confirmed through X-ray diffraction pattern analysis based on the Rietveld profile refinement method. The thermoluminescent (TL) glow curves were induced by UV or beta radiation and measured between 20 °C and 200 °C. The glow curves of BGO crystal presented two peaks at 61 °C and 90 °C for both kinds of radiation. The kinetic parameters, kinetic order (*b*), activation energy (*E*) and frequency factor (*s*), of the TL glow curves have been determined by four different methods. The lifetime of the peaks at room temperature was also determined and used to discuss the stability of the TL peaks at room temperature.


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## 1. Introduction

Bismuth germanate ($Bi_4Ge_3O_{12}$ or BGO) is known as a good scintillator material and radiation detector based on its intrinsic luminescence properties. It is widely used as a radiation detector in electromagnetic calorimeters, tomography systems for medicine and in check-light source for thermoluminescent systems [1,2]. It also possesses important applications in electro-optical, electro-mechanic and non-linear optical devices [3]. For all these applications, there is a great interest in the defect structure of the material. Thermoluminescence (TL) is a convenient technique to understand the charge trapping and detrapping mechanisms that result from the interaction of the radiation with the existing defects in material and that may interfere in the scintillator response.

Although several aspects of BGO thermoluminescence (TL) have been investigated in the last two decades [4–11], there are still some unclear points, for example, the number of TL peaks above room temperature. Melcher et al. reported three TL peaks at 65 °C, 115 °C and 150 °C (heating rate of 8 °C/s), though the first peak was not presented in the TL glow curves [4–6]. Similarly, Lecoq et al. observed TL peaks at 70 °C, 100 °C and 140 °C (measured under a heating rate of 5 °C/s) [7]. On the other hand, Sangeeta and Sabharwal related only a single TL peak at 96 °C (heating rate of 1 °C/s) for stoichiometric samples [8] and Raymond et al. observed two peaks at 135 °C and 185 °C (heating rate of 2.5 °C/s) [10].

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Concerning the activation energy, there is also a disagreement between the values found in the literature for the second TL peak, which vary from $(0.75 \pm 0.05)$ eV [6] to $(1.1 \pm 0.1)$ eV [10], and there is a lack of information about kinetic analysis of the other peaks.

The aim of this work is to present a fully detailed study of the trapping and detrapping mechanisms of bismuth germanate single crystals. The kinetic parameters, namely the activation energy, kinetic order and frequency factor, were determined through four different methods used to analyze the thermoluminescent data.

## 2. Experimental

### 2.1. Crystal growth

BGO single crystals were grown by the Czochralski technique from a stoichiometric mixture of $Bi_2O_3$ and $GeO_2$ powders (Alfa Aesar, grade purity 99.99%), using high purity cylindrical platinum crucibles with 40 mm diameter and 40 mm height. BGO seeds oriented along the [0 0 1] direction were held in a pure platinum seed holder and used to initiate the crystal growth. The runs were carried out in room atmosphere with pulling and rotation rates of 0.2 mm/h and 14 rpm, respectively. The growing temperature, measured at the bottom of the crucible, was 1120 °C. Transparent single crystals without inclusions were produced with typical sizes of 10 mm in radius and 20 mm in height. For the TL measurements, the crystal was cut in slices of $4 \times 4 \times 1$ mm$^3$ and polished with alumina powder.

### 2.2. X-ray diffraction

The structural investigation was made by powder X-ray diffraction analysis in a XRD – Rigaku Rotaflex RU-200B, using Cu K$\alpha$ radiation. The measurements were done at room temperature in step-scan mode, in the $2\theta$ range between 10° and 70°, with steps of 0.02° and acquisition time of 3 s. The diffraction pattern was analyzed according to the Rietveld profile refinement method using DBWS software [12].

### 2.3. Thermoluminescence

Thermoluminescence measurements were performed from 20 °C up to 200 °C. The sample holder was kept below room temperature (at about 15 °C) using cooled gas flow and was heated up using a computer controlled heating program. The light was collected just above the sample using a Hamamatsu R928 photo-multiplier tube (PMT). Heating rates from 1 °C/s to 6 °C/s were employed. The irradiations of the samples prior to the TL measurements were done using a $^{90}Sr/^{90}Y$ β-rays source or UV light from an Hg lamp without the glass bulb. During the irradiation, the sample temperature was kept at 0 °C to prevent any decay of the TL peaks near room temperature. The TL curves were acquired just after the exposure to β-rays or to UV light.

## 3. Results

The powder X-ray diffraction pattern of the BGO crystal is shown in Fig. 1. The dots represent the experimental points and the solid line the refined spectra that was obtained using, as starting parameters, the Radaev et al. [13] lattice constants and atomic positions and a pseudo-Voight function for the XRD profiles. The bottom part of the figure displays the difference pattern indicating that a quite good structural refinement was achieved, with a reliability parameter $R_{wp}/R_{exp} = 3.5$. No other crystalline phase, except for the 4:3:12 one, was detected. Table 1 lists the calculated lattice parameter, cell volume and crystal density, compared to the Radaev et al. values [13].

Fig. 2 presents the TL glow curves from 20 °C up to 200 °C of the BGO samples irradiated with UV light and β-rays. The measurements were performed following a linear heating program with 1 °C/s. Both glow curves are very similar displaying two TL peaks at 61 °C and 90 °C. The

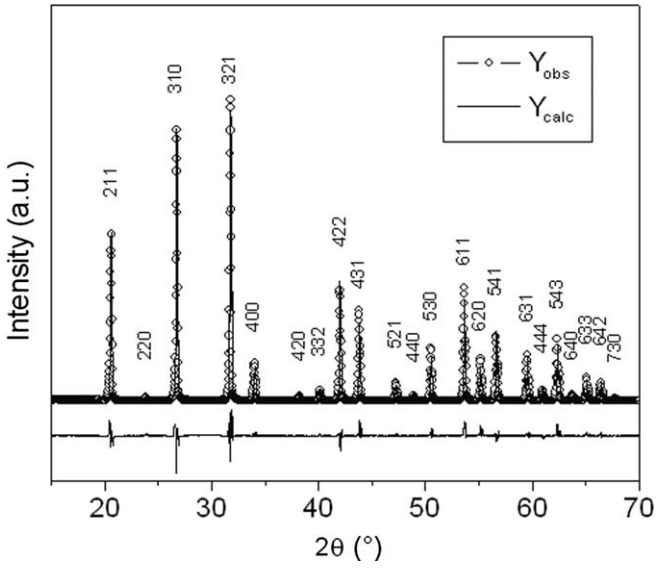


Fig. 1. Experimental and simulated powder XRD pattern of the BGO obtained using the Rietveld refinement. The difference plot is shown at the bottom of the graph. The crystallographic planes were indexed using [13].

Table 1
Refined lattice parameter of the $Bi_4Ge_3O_{12}$ obtained from the powder X-ray diffraction pattern, as compared to Radaev et al. [13]

| | $Bi_4Ge_3O_{12}$ – Cubic, space group $I\bar{4}3d$ | | | | |
|---|---|---|---|---|---|
| | $a$ (Å) | $V$ (Å$^3$) | Density (g/cm$^3$) | $R_p$ | $R_{wp}/R_{exp}$ |
| Present work | 10.5101 | 1161.0 | 7.13 | 11.3 | 3.5 |
| [13] | 10.524 | 1165.6 | 7.08 | | |
| % Difference | −0.13 | −0.40 | 0.71 | | |

The calculated cell volumes and crystal density and the reliability coefficients are also shown.