KINETIC ANALYSIS OF THE THERMOLUMINESCENT GLOW CURVE OF AQUAMARINE ($Be_3Al_2(SiO_3)_6$)

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Abstract

Kinetic analysis of the thermoluminescent glow curve of aquamarine, cyan variety of beryl ($Be_3Al_2(SiO_3)_6$), is reported. Samples were irradiated at room temperature using a 90Sr/90Y β source at a rate of 0.10 Gys^{-1}. Measurements made at 1°C/s after irradiation from 1 to 100 Gy show a main peak at 75°C followed by three secondary peaks at 113, 188 and 306°C respectively. The dose response of the main peak is linear within the first 10 Gy but tends towards sub-linearity as the dose is further extended to 100 Gy. The peak fades with the delay between irradiation and measurement about 14% of its initial value 600 s after irradiation. Reproducibility analysis shows that the material reproduces its response under identical experimental conditions with an uncertainty of 0.8% after 10 Gy beta dose irradiation. The kinetic analysis of the glow curve was carried out using the curve fitting method. The results show that the main peak follows first order kinetics, its activation energy is of the order of 1 eV and the frequency factor is between 10^{12} and 10^{14} s^{-1}, while some secondary peaks follow general order kinetics.

1. Introduction

Beryl is a kind of hexagonal cyclosilicate ($Be_3Al_2Si_6O_{18}$) [1,2]. In the crystal structure of beryl, the occurrence of ion substitution is very common, giving rise to a great variety of colors. Beryl crystals can show colors such as green (emerald), blue (aquamarine), yellow (golden beryl or heliodor), pink (morganite) and colorless (goshenite) if they contain transition metal ions as impurity located in crystalline sites [2,3]. The green color of emerald is caused by Cr^{3+} ions in aluminum sites and when Mn^{3+} replaces Al^{3+}, morganite is formed [2,3]. Different concentrations of Fe^{2+} and Fe^{3+} ions in structural and interstitial positions of the crystal determine the color of Fe-containing beryls, from blue (aquamarine) to yellow-orange (heliodor) [2,3].

The first work on the response of natural beryl doped with transition metals was published by Chithambo et al. [3]. According to their results, Fe-doped beryl shows strong thermoluminescent emission between 300 and 400 nm. Recently "Thermoluminescence of aquamarine" is reported by Herrera et al [4]. They reported a prominent glow peak at 75°C and three secondary peaks at 113, 188 and 306 °C. According to their results, the peak follows first order kinetics, that its activation energy is of the order of 1 eV and that it has a frequency factor of ~ 10^{12} s^{-1}. Their work concentrates on the thermoluminescent study of the main peak of the aquamarine glow curve.

In this work the study of the kinetic parameters of the complete glow curve of aquamarine is reported. We use different methods of kinetic analysis to determine the kinetic parameters. In addition, some of its dosimetric characteristics such as dose response, thermal fading and reproducibility are reported.

2. Materials and methods

Measurements were made on commercially available aquamarine (African Gems and Minerals Inc., Cape Town, South Africa). The sample, prepared in coarse grain form, was used *as received* without any pre-measurement treatment. Experiments were performed using a RISØ TL/OSL DA-20 Luminescence Reader at Rhodes University, South Africa. The luminescence was detected by an EMI 9235QB photomultiplier tube through a 7 mm Hoya U-340 filter transmission band. Samples were irradiated at room temperature using a $^{90}Sr/^{90}Y$ β source at a rate of 0.10 Gys^{-1}. All measurements were carried out at a heating rate of 1°Cs^{-1} unless otherwise stated.

3. Results

3.1 Glow curve features

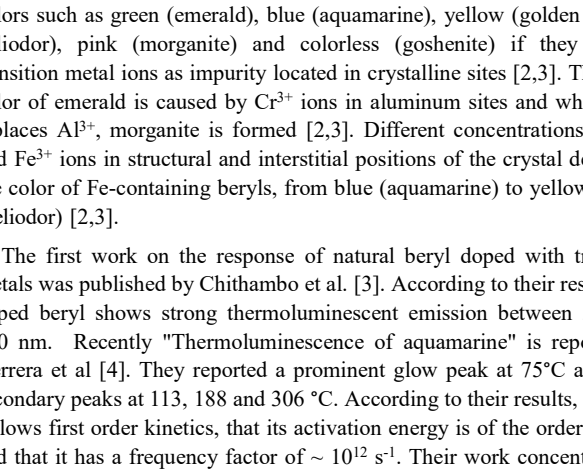

Fig. 1. A glow curves of aquamarine measured at 1 °C/s after irradiation to 10, 40 and 100 Gy. The high intensity main peak is at 74.9±0.8 °C. The inset shows the lower intensity peaks at 188 and 306°C respectively for the same dose.

40 Gy				
kinetic parameters	**Peak 1**	**Peak 2**	**Peak 3**	**Peak 4**
$T_M(K)$	347.15	390.15	416.15	464.15
b	1.29	1.40	1.39	1.29
E (eV)	1.02	1.45	1.56	1.53
s	6.58E+13	7.84E+17	5.20E+17	3.81E+15
FOM (%)	4.9			

Table 1. Deconvolution results for aquamarine irradiated to 40 Gy using the four-parameter logistic asymmetric function.

3.2 Dependence of peak position on dose & T_m-T_{stop} analysis for the main peak glow curve

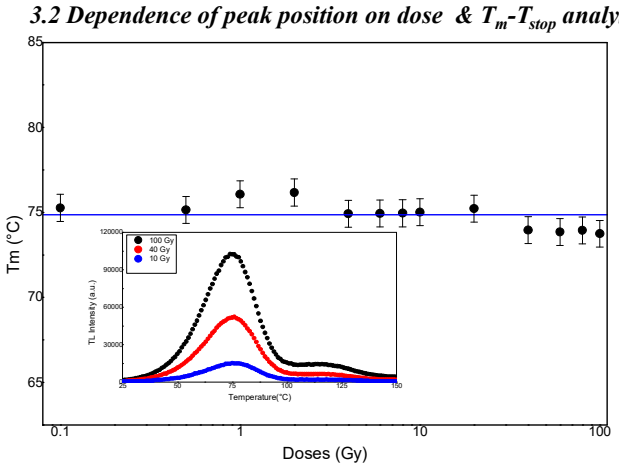

Fig. 2. Variation of position of the main peak with irradiation dose. The inset shows the Influence of irradiation dose on the main Peak for 8, 40 and 100 Gy. Since the position of the peak is independent of irradiation dose, as also shown in the inset, the main glow peak follows first-order kinetics.

3.3 Kinetic analysis: Initial rise method

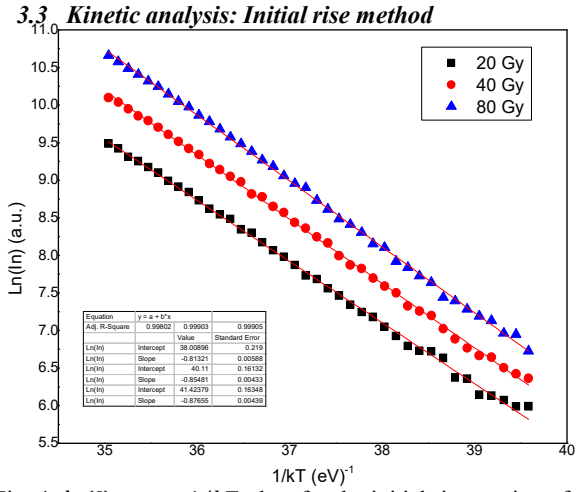

Fig. 4. $ln(I)$ versus $1/kT$ plots for the initial rise portion of the main peak Aquamarine corresponding to 20, 40 and 80 Gy beta doses. The values of activation energy corresponding to 20, 40 and 80 Gy irradiated samples were calculated as (0.81 ± 0.01), (0.86 ± 0.01) and (0.88 ± 0.01) eV respectively.

3.4 Kinetic analysis: Curve fitting technique

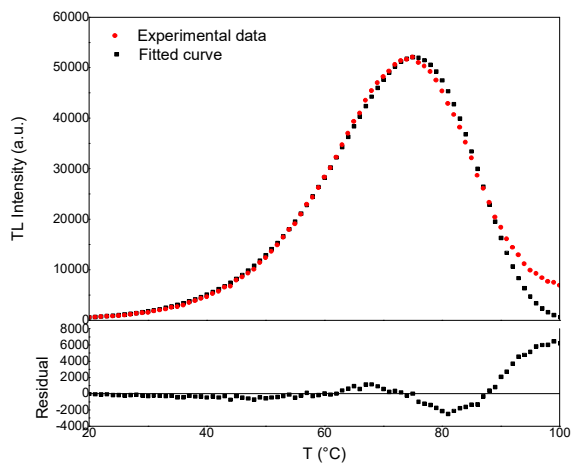

Fig. 5. Results of curve fitting for the main peak in Aquamarine irradiated to 40 Gy, the value of activation energy is (0.96 ± 0.01) eV; the order of kinetics (b) is 1.27 ± 0.01 and frequency factors is 7.60 x 10^{12} s^{-1}.

3.5 Deconvolution of the aquamarine glow curve using the logistic asymmetric function.

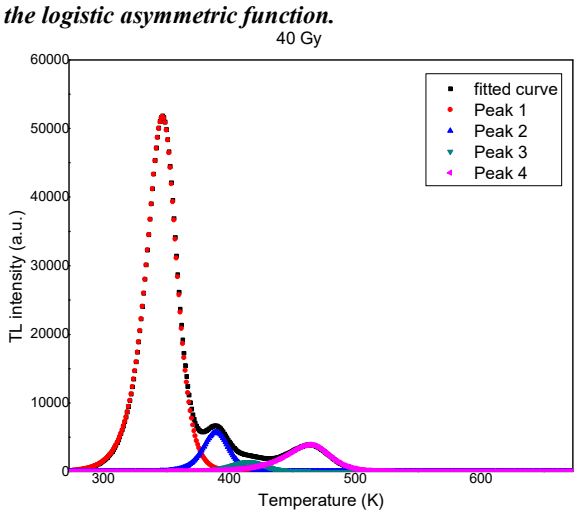

Fig. 6. Deconvolution of the glow curve of aquamarine, irradiated to 40 Gy of β dose and read out at 1 °C/s, using the four-parameter logistic asymmetric function. Fig. shows 4 signals present in the glow curve between 273 and 500 K located at 347, 390, 416 and 464 K respectively. The third TL signal is not observed experimentally. TL peak located at 575 K is not reported due to its low intensity. The results are shown in Table 1.

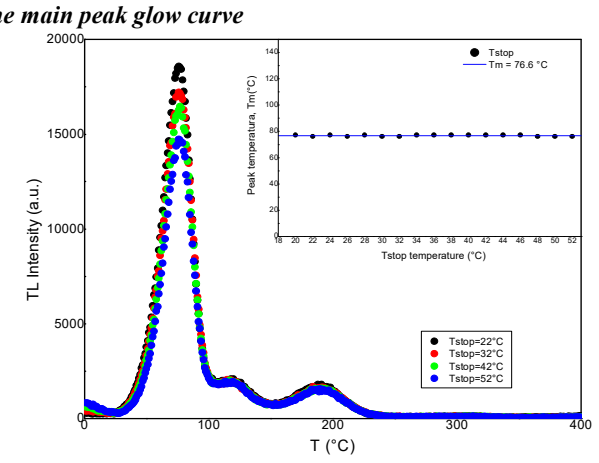

Fig. 3. Main peak after an irradiation to 10 Gy. Tstop between 22°C and 52°C. The inset shows the Tm-Tstop plot, see that the position of the main peak is independent of the Tstop preheating temperature, indicating that the main peak follows first-order kinetics.

3.6 Dosimetric features: Fading

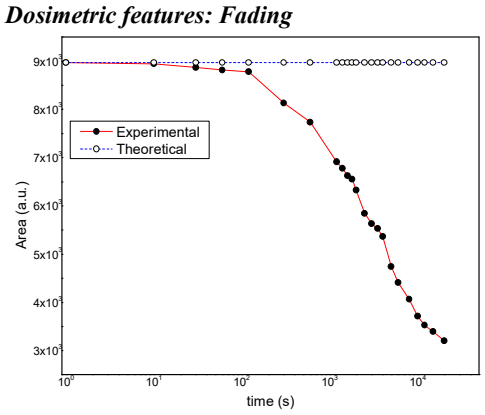

Fig. 7. Variation of the peak area of the main peak with delay time. The solid line through the data points shows a plot of peak area of the main peak of aquamarine sample with storage time. The peak intensity drops 14% of its initial value 600 s after irradiation, 35% of the initial value 2500 s after irradiation and reaches 64% of the signal fading 20000 s after irradiation.

3.7 Dosimetric features: Dose Response

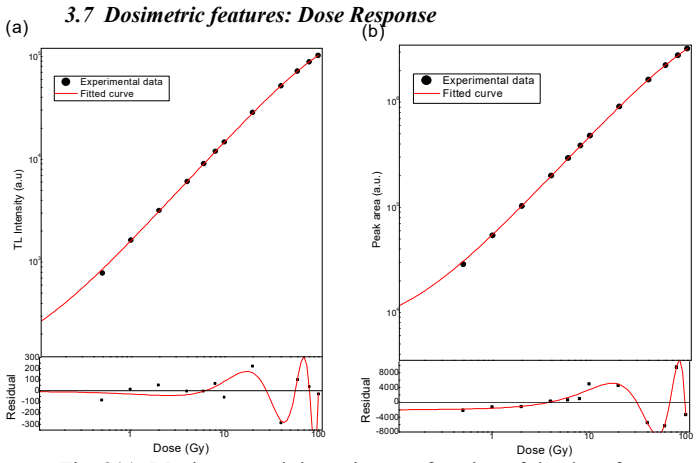

Fig. 8(a). Maximum peak intensity as a function of the dose from 0.1 to 100 Gy. (b) Area of the main peak of the glow curve as a function of the dose from 0.1 to 100 Gy. In both cases, a linear behavior is observed from 0.5 Gy to 20 Gy, followed by a sublinear behavior to 100 Gy.

4. Conclusions

The effect of dose on the kinetic parameters of the main peak of the glow curve of the beryl variety known as aquamarine (Be3Al2(SiO3)6) has been studied. The high intensity main peak is at 74.9±0.8 °C. There are three secondary peaks at 113, 188 and 306 °C. The position (T_M) of the main peak is independent of dose at 74.9±0.8 °C from 0.1 to 100 Gy. Kinetic analysis of the main peak performed using the initial rise and curve fitting methods show that the peak follows first order kinetics, its activation energy is of the order of 1 eV and has a frequency factor of ~ 10^{12} s-1. Deconvolution of the glow curve shows that the order parameter (1.29) of the main peak (347 K) suggests a first order kinetics, while the order parameter (1.40) for the second peak (390 K) evidences a mixed order kinetics.

The dose response of the main peak is linear behavior from 0.5 Gy to 20 Gy, followed by a sublinear behavior to 100. For fading analysis, delays from 0 to 20000 s after irradiation to 10 Gy were used. To be used as a dosimeter the material presents a high fading (35% of the initial value 2500 s after irradiation). The high fading observed may be due to the main peak being at a temperature relatively close to room temperature (75°C). Reproducibility analysis shows that the material properly replicates its response under identical experimental conditions (0.85% uncertainty for 40 Gy dose).

Referencias

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