DOSIMETRIC FEATURES OF NATURAL FLUORITE FROM ROMANIA

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Abstract. *Thermoluminescent dosimetric features of two batches of fluorite from Romania (Cavnic and Tulcea) are presented. An initial thermal treatment at 600^0C for 60 min. to cleaning of natural dose has been performed. All samples showed the same glow curve structure with three prominent peaks located at 100^0, 180^0 and 280^0C at a heating rate of 5^0C/s. An attempt was made to determine the kinetic parameters of TL glow curve. The activation energy E ~ 1.31 eV (Tulcea batch) of the dosimetric peak and the kinetic order b=2 were obtained. The dose response of CaF_2:nat from Tulcea to gamma-rays is linear in the range 2 Gy to $5\cdot10^3$Gy, where saturation effects became pronounced. A thermal fading of 18% during 30 days was observed.*

Keywords: *fluorite, thermoluminescence, glow curve, activation energy, thermal fading*

1. INTRODUCTION

Fluorite is CaF_2 mineral which is found in many geological deposits occurring in Germany, Austria, Switzerland England, Norway, France, China, Mexico, Russia, Spain, Iran, Romania, United States and other countries. Fluorite samples have extremely variable colors and many times can be an intense purple, blue, green or yellow; also colorless, reddish orange, pink, white and brown depending on their origin and impurity content.

Another property of fluorite is its thermoluminescence (TL). This is the property of a substance to emit light when heated, when the substance has previously exposed to ionizing radiation. The emitted amount of light is proportional to the irradiated dose.

During the early years, fluorite was studied under the dosimetric point of view in Germany and Switzerland [1, 2]. This mineral has been also studied in Belgium M. B. L. E. (Manufacture Belge de Lampes et de Materiel Electronique S/A, Brussels) laboratories [3-6] and by various other researchers [7-9].

In the last twenty years, several reports dealing with the thermoluminescence studies of fluorite are also available in the literature [10-16].

The aim of present paper is to investigate TL features of some fluorite minerals from Romania. The results obtained have been compared with those found in the literature for other fluorites.

2. EXPERIMENTAL

Five different fluorite samples were selected for this study. All samples come from Facluty of Geology and Geophysics in University of Bucharest and were purchased from Romania (Cavnic and Tulcea), Germany (Freiberg and Arnaberg) and United Kingdom (Derbishire). Samples were hand crushed in an agate martor. The grain size was selected to be 80-150 μm. Granularity of the samples used was measured by means of sieves.

Two annealing treatments were necessary to be applied to powdered natural calcium fluoride samples: 600^0C for 1 h to empty the TL traps filled during geological time and 400^0C for 0.5 h to sensitize the dosimetric material.

For irradiations, ^{137}Cs GAMMATOR M-38-2 equipment was employed. The irradiations were performed at room temperature, normal pressure and humidity at a dose rate of 0.4 KGy/h.

For the thermoluminescence measurements (LTM Fimel apparatus) 4 mg of samples in the form of loose powder were used. The thermoluminescence glow curves of the investigated samples were obtained on the temperature range between room temperature and 450^0C. The linear heating rate was set at 5^0C/s and all measurements were taken in ambient temperature.

3. RESULTS AND DISCUSSION

Fig. 1. shows the three peaks TL glow curve of Romanian fluorite samples after γ-dose of 65 Gy.

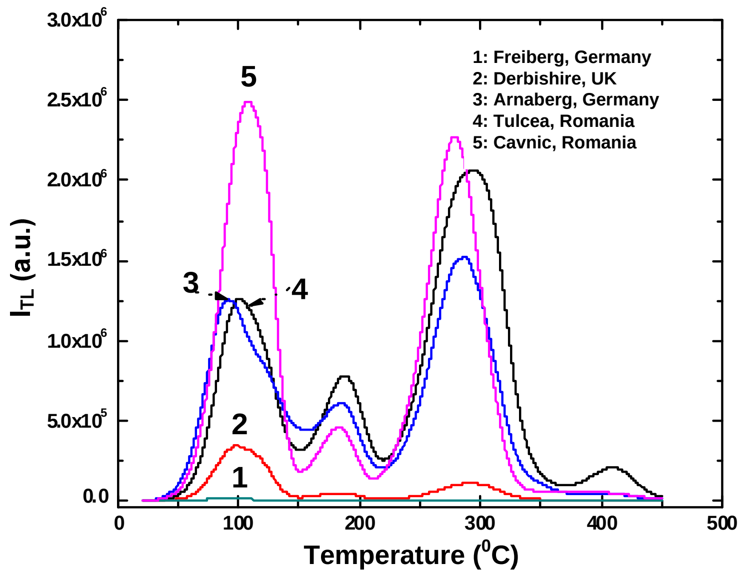

Fig. 1. Glow curves of the studied natural fluorites.

The first peak located at 100^0C is not proper for dosimetry because is fade-out rapidly at room temperature. The second glow peak around 180^0C is not quite intense signal and very stable peak at ~ 280^0C is considered dosimetric peak. The integrated light emitted under dosimetric peak represents ~52% for Romanian samples, 41% for German samples and 25% for English sample from the total thermoluminescence. This glow curve structure has the same glow peaks as those reported by other scientists [10, 12, 13, 17].

Various authors have indicated the importance of rare earth ions as Ce^{3+}, Dy^{3+} and Sm^{3+} as the major agents for trapping and recombination processes of natural fluorite [17-19]. The dosimetric TL peak, appearing at ~ 280^{0}C is attributed to the reduction-oxidation process involving Ce^{3+} i. e [17]:

$$Ce^{3+} \xrightarrow{\text{irradiation}} Ce^{2+} \xrightarrow{\text{heating}} Ce^{3+}$$

with the emission in the 320 – 340 nm band.

The TL response of Romanian fluorite samples was studied in the dose range from 2 to 10^3Gy showing a linear response as shown in figure 2. For doses higher than 1KGy, the TL response presented a sublinearity effect start tending to the saturation.

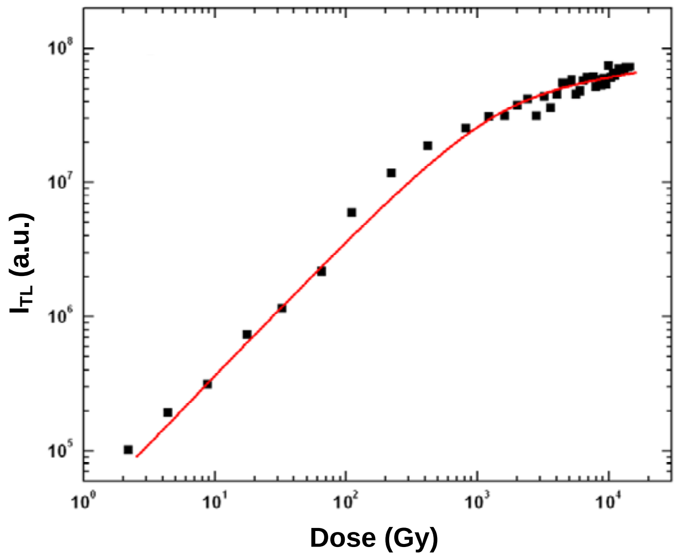

Fig. 2. Dose response of the dosimetric TL peak intensity for the Romanian fluorite sample (Tulcea) irradiated with gamma rays (^{137}Cs).

In order to analize the reproducibility of the TL signal, the effect of the reuse of the dosimeter was studied, performing six successive cycles of irradiation – reading; the intensities of the peak at 280^{0}C were observed as a function of the cycle number. The scatter of the results was less than 5.8%. For finding the kinetic parameters of TL main peaks, the geometrical factor (μ_g), Balarin's factor (γ) and the kinetic order (b) were calculated by means of the following expressions [20, 21]:

$$\mu_g = \frac{T_2 - T_m}{T_2 - T_1} \quad (1)$$

$$\gamma = \frac{T_2 - T_m}{T_m - T_1} \quad (2)$$

$$b = 0{,}0563 \cdot 10^{2{,}95\mu_g} \quad (3)$$

where T_m is the maximum temperature of the TL peak, T_1 and T_2 are the temperatures at the half-widths of the peak, $T_1 < T_2$. If $\mu_g = 0.42$, the kinetics is of the first order (b = 1) while $\mu_g = 0.52$ corresponds to the second order kinetics (b = 2).

The Balarin's parameter ranges from 0.7 to 0.8 for a first order kinetics and from 1.05 to 1.20 for a second order kinetics. Tables 1 and 2 summarize these parameters and the obtained values were applied to determine the activation energy (or trap depth), E. A close scrutiny of our results reveals that we obtained intermediate order kinetics.

According to Adam and Katriel [24], E = 1.71 eV but Frank and Stolz [25] reported E = 1.34 eV. The reasons for such differing values include difference in the origin of the fluorite, use of different heating rates for the acquisition of glow curves, use of different annealing procedures and so on [14].

Table 1. The kinetic parameters of TL dosimetric peaks for Romanian fluorite samples

Sample	μ_g	**b**	γ
Cavnic	0.49	1.57	0.96
Tulcea	0.50	1.68	1.00

Table 2. The trap depth for Romanian fluorite samples based on second-order glow curve analysis

Sample	Activation energy (trap depth) method, E (eV)					Mean (eV)
	Gross-Weiner modified by Chen [22]	Chen [20]	Lushchik modified by Chen [20]	Kelly-Laubitz [23]	Balarin [21]	
Cavnic	1.48	1.59	1.65	1.73	1.57	**1.60**
Tulcea	1.23	1.28	1.33	1.46	1.28	**1.31**

Under normal environmental conditions the Romanian natural fluorites suffer from 18% signal fading after one month (30 days) post irradiation storage (Fig. 3).

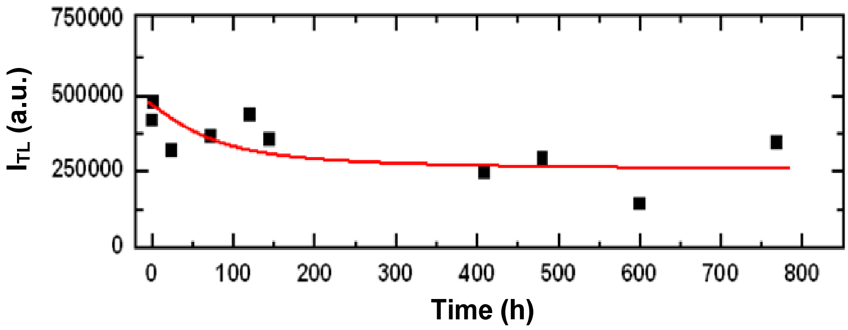

Fig. 3. TL decay for dosimetric peak over a storage period of 30 days at room temperature for Romanian natural fluorite (Cavnic).

The basic disadvantage of fluorite is its poorer response vs radiation energy: CaF_2 containing high – atomic number ($\overline{Z}_{ef} = 16.3$), material will exhibit much greater response at photon energies below 100KeV than at higher energies. Permanent efforts have to be made to improve our understanding of the influence of various parameters on the characteristics of thermoluminescence systems.

4. CONCLUSIONS

Romanian natural calcium fluoride showed some good dosimetric features such as: suitable glow curve structure, significant range of linearity, low fading, reproducibility in response etc.

The kinetic parameters of the dosimetric peak at 280^0C in two Romanian fluorite samples have been determined. The results emphasized that the traps obey the intermediate order kinetics and has an activation energy of 1.31 eV (Tulcea sample) and 1.60 eV (Cavnic sample), respectively.

Romanian natural calcium fluoride is suitable for practical and environmental dosimetry.

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