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Preliminary Investigations of Saudi Fluorite for Radiation Dosimetry

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Abstract: The general dosimetric properties of local natural CaF_2 are investigated using the thermoluminescence technique. It shows very good dosimetric properties with low fading and linear dose response (4×10^{-2} - 10^4 Gy). In addition to that, the trap parameters such as activation energy , kinetic order, sensitivity and fading were undertaken to satisfy the feasibility of using the present sample as γ- ray dosimeter.

Keywords: TLD, γ- ray, Dosimetry, CaF_2 .

Introduction

The thermoluminescence (Tl) properties of naturally occurring materials have been the subject of several experimental investigations [1-6]. In recent years CaF_2 has been used extensively for thermoluminescence (Tl) dosimetry of ionizing radiation. Calcium fluoride, CaF_2, is naturally present as the mineral fluorite. The TL sensitivity of natural calcium fluoride was attributed to the traces of unidentified impurities [7]. A wide variety of impurities was found to change from sample to another. In using Tl dosimeters one of the main difficulties arises in the evaluation of the time occurrence of an anomalous exposure superposed on a normal one. This problem has been studied using CaF_2. Also, the simultaneous estimation of dose and time elapsed since exposures are based upon variations in the behavior of peaks in the glow curve [8]. Thus, it is important to have good knowledge of some of the kinetic parameters [9].

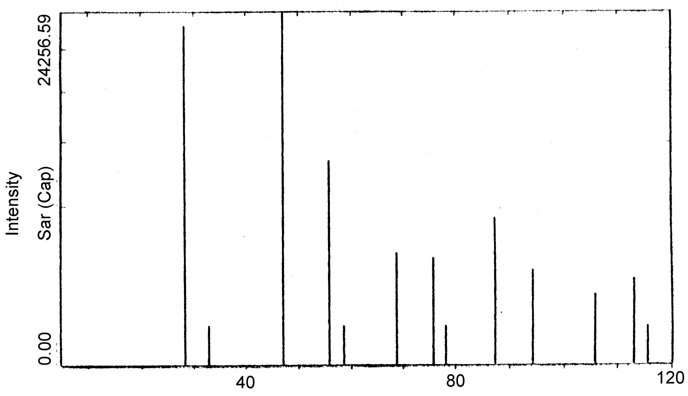
Fading is an important but often neglected factor in environmental radiation monitoring using Tl-detectors, although it is one of the major drawbacks of Tl-dosimetry. The fading effect has been thoroughly studied for different types of Tl-materials [10].

The aim of this work is to study the Tl-characteristics of natural CaF_2 after thermal treatments and to evaluate its activation energy.

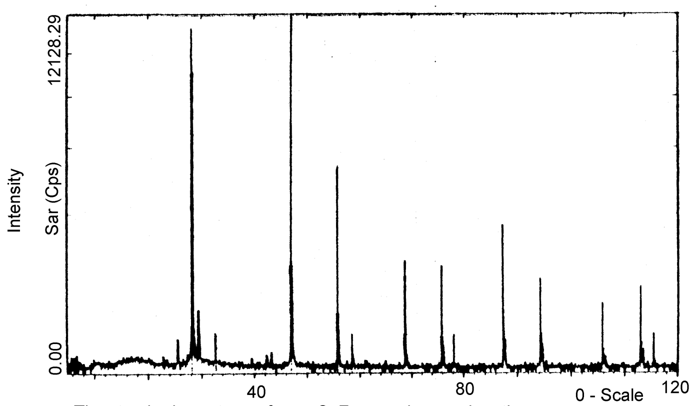
Based on these observations the widespread natural CaF can partially fulfill the requirements to be a good environmental monitoring dosimeters with the least cost.

Experimental Procedure

In the present work, natural calcium fluoride samples of crystalline form and light blue type are investigated as Tl-phosphor. The calcium fluoride content in the sample was found to be 99% of the whole sample [11]. To gain a rough estimate of the impurities in the samples, X-ray analysis was undertaken using X-ray Diffractometer D500 (SIEMENS), Fig.1. The operating voltage is 40 kV and the corresponding current is 35 mA. The major trace elements found are Na, Fe, Si, and S. The more intense impurity lines seen in Fig.1 are attributed to (Z_n + H_g) S . This result is obtained by means of a data acquisition program designed with the diffractometer by SIEMENS company.



The standard spectrum of pure CaF_2



The standard spectrum of pure CaF_2 superimposed on the spectrum of the natural sample

Fig. 1. Sample spectrometry analysis by X-ray diffractometer (SIEMENS D500).

Heating was performed in a nitrogen atmosphere (600 Torr) and at a rate of 2.08 $^{o}Cs^{-1}$. Powdered samples were used (not selected for any particular grain size) and placed in a stainless steel boat for heating.

The irradiation was performed using a ^{60}Co gamma source delivering 1.97 Gys^{-1} . The dose rate at the center of the chamber was measured by ferrous sulphate dosimetry as per Quality Control Specification QC-16-3511 by NORDION INTERNATIONAL INC. Canada, Ontario. Accuracy of the estimated dose rate is ± 1.45 at the 95% confidence limits. For Tl measurements, the Harshaw 2080 Tl-reader was connected to a Pico-processor glow curve. An IBM personal computer equipped with a Harshaw system 2080/4000/SAAS TLD file Manager was used for processing and performing a complete analysis of Tl-glow curves. The maximum tray temperature was 400^{o}C with a heating rate of 5^{o}C /sec.

A relation between TL-Intensity (TLI) and the thermal treatment temperatures for CaF_2 samples from 150 – 350 mg at a fixed dose of 100 Gy was undertaken. At least five samples have been treated for every specific temperature. From this relation, it is found that the TLI increases with thermal treatment temperature (300^{o}C to 400^{o}C). The Tl- sensitivity decreases gradually up to 600^{o}C, beyond which a rapid decrease is observed. This decrease in sensitivity may be attributed to the partial change of the chemical compound from CaF_2 to CaO_2 which is not a TL-sensitive. Accordingly, the 400 ^{0}C is found to be the best thermal treatment temperature suitable to sensitize natural CaF_2 .

The study of the normalized Tl – intensity as a function of sample weight showed no variation in TLI with weight in the range 20 – 50 mg where the maximum TLI was obtained.

To study fading effect, one of the irradiated samples (100Gy) was measured immediately after irradiation and considered a reference, other samples were stored in a dark place at room temperature for different length of time up to a maximum storage time of 60 days until evaluating their relevant TLI.

Results and Discussion

The glow curve of the natural CaF_2 powder has four peaks at 48, 90, 160 and 200 ^{o}C as shown in Fig. 2. These peaks are sensitive to gamma-radiation doses and the most sensitive is the dosimetric peak at 48^{o}C.

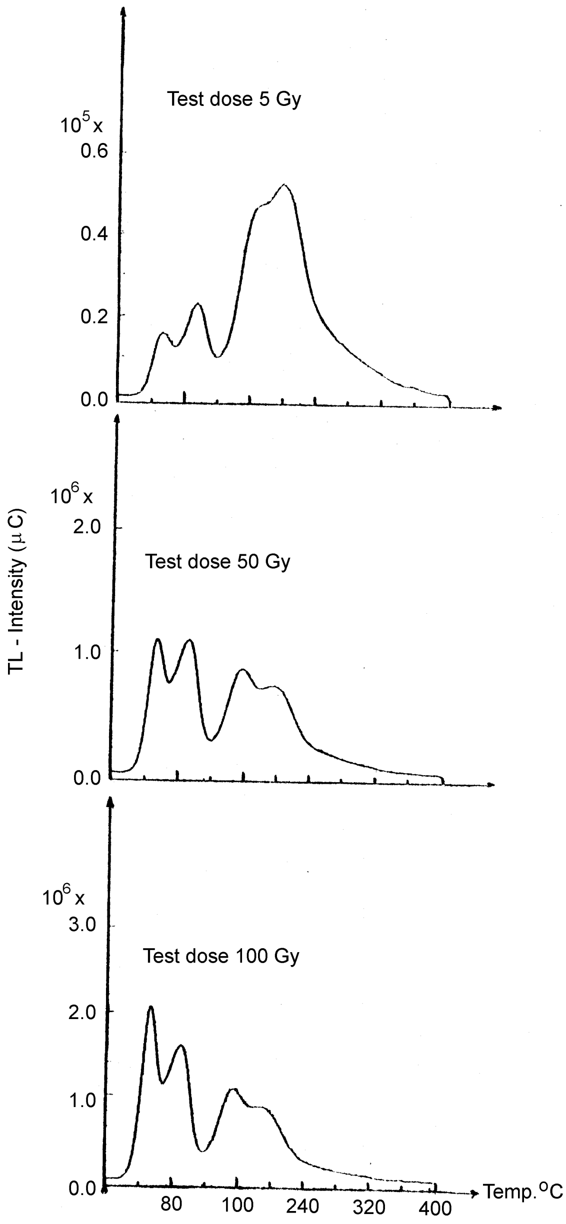


Fig. 2. Glow curve of CaF_2 irradiated with different γ-doses.

Figures 3 and 4 show the dose response curves of the sample which were annealed at 400°C for 30 min. and irradiated with different γ-ray doses. It is clear from these figures that the linearity is indeed present up to nearly 10^4 Gy above which Tl saturation occurs. Fig.4 also shows that the most sensitive peak is that at 48 °C. Our present study also reveals that the best annealing course to perform a regeneration process for our sample to make it ready to be used again as a new dosimeter is 400 °C /20 min. Also, the relation between post-irradiation annealing time of samples and its TLI was studied at different temperature and doses. It is found that 40°C /5 min. is the best post-irradiation annealing course prior to Tl evaluation to eliminate the shallow traps error effect. The used oven is a TLD programmed annealing furnace from HARSHAW/FILTROL Company.

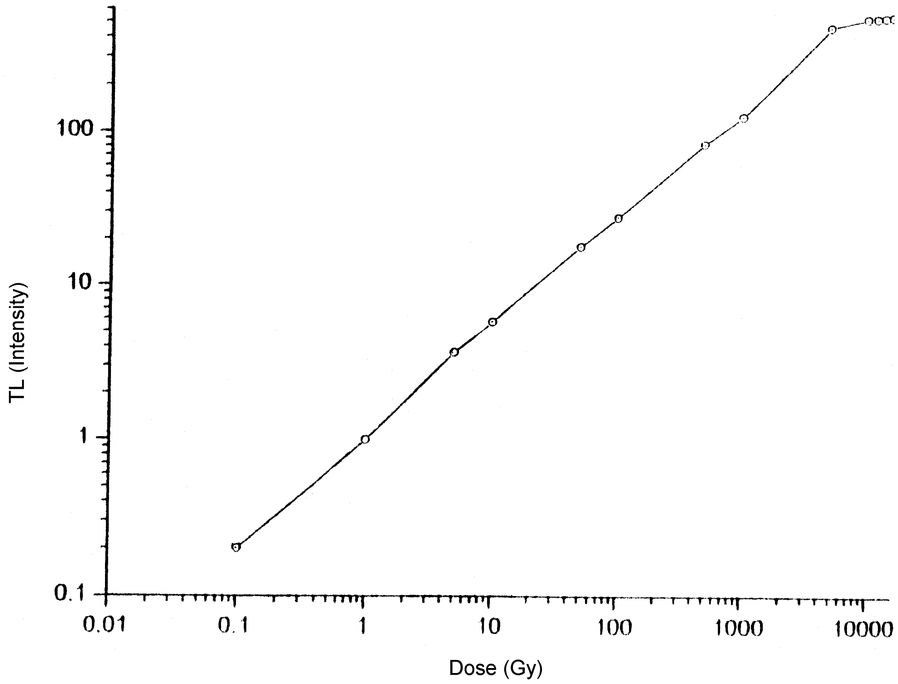


Fig. 3. The total TLI response as afunction of the dose.

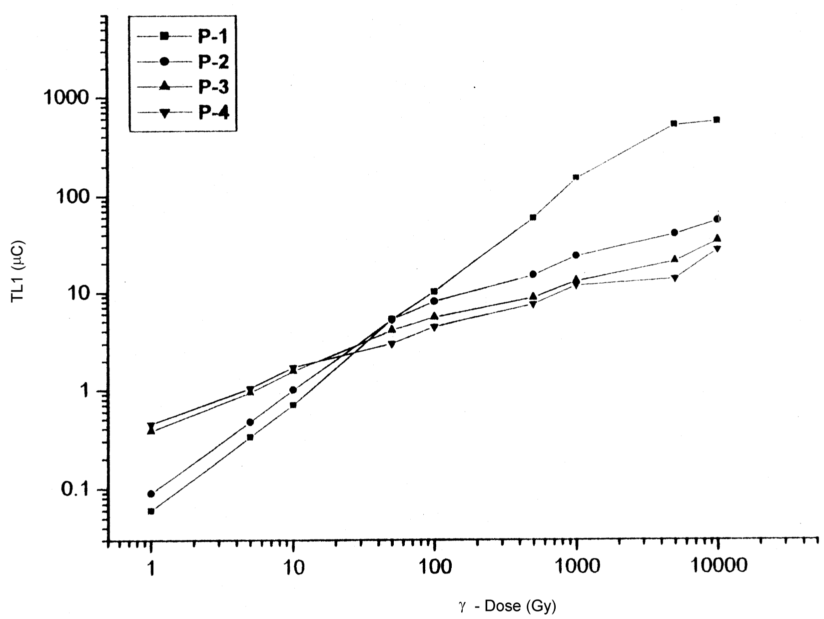


Fig. 4. The TLI response as a function of the dose for the different peaks appeared in the glow curve.

Figure 5 shows the variation of total Tl fading of irradiated sample with the storage time in dark. The intensity follows a slow build up about 2 % from the beginning time of storage till 6 days after which signal fading starts attaining 92 % of the residual TL signal after 40 days of storage. The slow build up during the first 6 days may be due to the transfer of charge carriers between different traps after which the fading process exceeds this effect to reach the steady condition. It is well known that if the trapped electrons can pick up enough energy they are re-excited back to the conduction band. Also, the shallow traps are somewhat unstable even at ordinary room temperature [12,13].

To calculate the activation energy E from the Tl-glow curve, a very simple method was previously given [14,15], using the symmetry of the glow peak shown in Fig. 6. They considered that the symmetry factors μ_g is not sensitive to changes in the activation energy E and frequency factor s.The order of the kinetics for each peak was estimated making use of the symmetry factor μ_g, which is equal to $\frac{\delta}{\omega}$, where δ is the half width at high temperature and ω is the total width of the glow peak. $\mu_g < 0.5$ for first order kinetics and $\mu_g \geq 0.5$ for second order kinetics. They applied this method on NaCl and KCl crystals using the following equations [15]:

$$E_1 = \frac{1.72KT_m^2}{\tau}(1-2.98\Delta) \text{ ……………for the first order and}$$

$$E_2 = \frac{2KT_m^2}{\tau}(1-3\Delta) \text{ ……………….. for the second order.}$$

Δ is a correction factor which is equal to $\frac{2KT_m}{E}$,

T_m is the maximum glow peak temperature, τ is the full width at low temperature and K is the Boltzmann's constant in eV/ ^oK . Furthermore, the kinetic parameters of the CaF_2 :Tm (TLD-300) dosimeter were determined experimentally using the same peak shape method taking into consideration that μ_g is not sensitive too to changes in E and S, [9]. The peak-shape methods used in this study were those of reference 14 and 15 as described above where the activation energy has been carried out for the four peaks which appeared in the glow curve (Fig.2). To have a good resolved peak and hence good peak parameters one has to apply either a well designed mathematical program or the partial annealing method [9]. The criterion used in the second method involved beside the erase of the first peaks, eliminating their influence in the remaining peaks. In this work, we have applied a mathematical program along with the partial annealing method to ensure high confidence in the results.

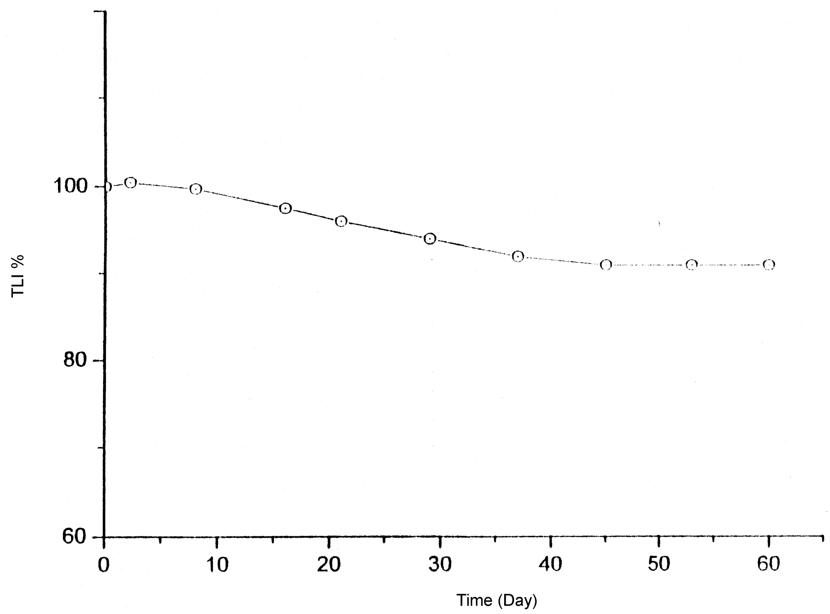


Fig. 5. TL - Fading of irradieted natural CaF_2 with respect to the variation of storage time in dark.

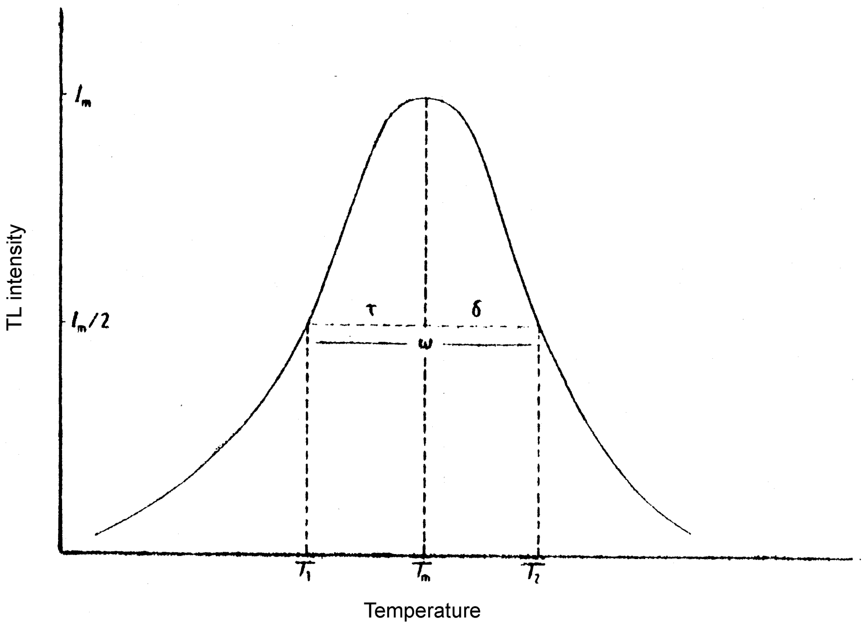


Fig. 6. An isolated glow peak with the parameters $\omega = T_2 - T_1$, $\tau = T_m - T_1$ and $\delta = T_2 - T_m$ where T_m is the temperature of the maximum and T_1 and T_2 are the low and high half-intensity temperatures respectively.

The calculated activation energy values using the above method are given in Table 1. From this Table, one can observe that E >1.0 and $\mu_g < 0.5$, which means that this sample is a good dosimeter and has first kinetic order.

Table 1. The four peaks parameters of the CaF_2 glow curve

	T_m (K)	**E_1 (eV)**	**E_2 (eV)**	δ	τ	μ_g	Δ
P1	321	1.04	1.18	9.01	2.90	0.41	0.048
P2	363	1.36	1.55	9.20	2.81	0.42	0.042
P3	433	1.35	1.53	14.43	8.11	0.44	0.048
P4	473	1.32	1.50	18.20	1.90	0.45	0.049

In general, the obtained values of activation energies proves that the effect of normal climate conditions on fading effect is nearly negligible. In other words, the traps are deep enough to result in sufficient stability at room temperature (half-lives of the trapped electrons of at least several months) which is of dosimeteric interest [16].

Conclusion

Natural calcium fluoride is sensitive to γ-radiation through a useful dose range (0.04-10^4 Gy). It can be sensitized by thermal treatment at 400^{o}C for 30 min..For pre and post irradiation, the best course of thermal annealing was found to be 400^{o}C / 20 min. and 40^{o}C/5 min. respectively. Under normal environmental conditions, CaF_2 Tl dosimeters suffer from 10% signal fading after two months (60 days) post irradiation storage. Furthermore, the results show that this type of samples is of the first order kinetics and has an activation energy more than 1.0 eV This result leads to a conclusion that the natural CaF_2 phosphor is suitable for practical and environmental dosimetry.

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دراسات أولية عن الفلورايت السعودي كمقياس للجرعات الإشعاعية

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ملخص البحث. تمت دراسة خواص الوميض الحراري لعينات من فلوريد الكالسيوم الطبيعي المحلي قبل تعرضها لسلسلة من الجرعات الإشعاعية وبعدها بواسطة مصدر كوبالت - ٦٠ مع المعالجة الحرارية لها.

وقد بينت الدراسة إمكانية استخدام هذه العينات عمليا كمقياس للجرعات الإشعاعية في المدى ٤ × ١٠$^{-٢}$ - ١٠^{٤} جراي. بالإضافة إلى ذلك تمت دراسة بعض البارامترات الأخرى مثل طاقة التنشيط ، الرتبة الحركية، الحساسية وتأثير الزمن على قدرتها في الاحتفاظ بالجرعة حتى يتم تحقيق الشروط اللازمة لاستخدام العينات لقياس الجرعات الإشعاعية الناتجة عن إشعاعات جاما.