The effects of pre-irradiation heat treatment and heating rate on the thermoluminescence glow peaks of natural CaF$_2$

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In this article, we have investigated the effects of pre-irradiation heat treatments on the thermoluminescence (TL) glow peaks of natural fluorite (CaF₂) collected from the central Anatolia region of Turkey. A typical TL glow curve of phosphor consists of four clear glow peaks with maximum intensities occurring at temperatures around 100°C, 120°C, 190°C and 290°C for a sample irradiated to a dose of 48 Gy and readout at a heating rate of 1°C/s. It was observed that the intensities of all the TL glow peaks are strongly sensitive to annealing temperatures and durations. Annealing at 450°C for 15 min was found to be the best for reproducibility of experimental results. The dose–responses of individual TL peaks of this material were also examined after annealing at 450°C for 15 min by β-irradiation to doses between 0.04 Gy and ≈10.4 kGy. It was observed that the total area and peak heights of all glow peaks showed similar trends with increasing radiation dose; first, they increased linearly up to ≈50 Gy and then saturation effects began above this dose value. The effect of heating rate on the TL glow peaks of the mineral was also studied and it was observed that the intensities of glow peaks are differently affected with variation in heating rate.

Keywords: thermoluminescence; natural fluorite; heating rate; dosimetric properties; annealing temperature

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1. Introduction

Thermoluminescent dosimeter materials, including natural and artificial, have been investigated for routine applications in environmental and personnel dosimetry (1). The aim of many studies, apart from investigating the possibility of employing these phosphors for dosimetry purposes, was also to understand the trap structure and defects in them (2, 3). CaF₂ has attracted a lot of attention and has been found attractive for radiation dosimetry in both natural and synthetic forms after doping with Dy, Mn or Tm (4–7). For thermoluminescence (TL) application in dosimetry, average absorbed dose is usually estimated from a previously established dependence of the TL glow-peak-integrated TL intensity or the maximum intensity on radiation dose (8, 9). However,
it is well known that the integrated intensity and the maximum intensity of dosimetric peaks of some TL materials (i.e. TLD-100) changes with variations in pre-irradiation heat treatments and heating rates (10). Therefore, in the development of new TL materials for dosimetry purposes, efforts have been made to understand the effects of heat treatments on the glow peaks of the materials (9–17). For example, Kharita et al. (17) used annealing temperatures between 150°C and 750°C for a duration of 1 h and observed the effect of the annealing temperature on the intensity of TL peaks of powder natural fluorite samples from Cornwall, England. The results have shown that the TL response does not change for annealing temperatures up to 450°C. But, it was observed that the signal decreased rapidly at higher temperatures. In this article, the effects of pre-irradiation heat treatments on the TL glow peaks of natural fluorite CaF₂ collected from the central Anatolia region of Turkey and some dosimetric properties are investigated in detail.

2. Experimental

Samples of the colorless natural fluorite crystal were collected from Kırşehir in the region of Central Anatolia in Turkey. The samples were taken from ingots about 2 mm thick in size, from a good optical quality surface with typical dimensions of 4 × 6 mm². The crystalline structures and chemical analyses of the samples without annealing or after annealing at 500 and 550°C for 1 h were checked by X-ray diffraction (XRD) technique using a Bruker AXS D8 Advance model X-ray diffractometer and X-ray fluorescence technique using a Panalytical Axios Advanced model X-ray fluorescence spectrometer (WD/XRF), respectively.

For TL analysis, the samples were first annealed at temperatures ranging from 300°C to 650°C with an increment of 50°C for 1 h to observe the effect of pre-irradiation heat treatment on the intensity of glow peaks. All annealing treatments were performed with a specially designed microprocessor-controlled electrical oven, which is able to control the temperature within ±1°C. Sample was irradiated at room temperature using the β-rays from a calibrated 90Sr–90Y source (≈0.04 Gy/s). The irradiated sample was readout in N₂ atmosphere with a Harshaw QS 3500 manual type reader that was interfaced to a PC where the signals were stored and analyzed. Glow curves were measured at a linear heating rate of 1°C/s during the investigation of the effects of pre-irradiation heat treatments on the intensity of TL glow peaks. Otherwise, the effects of heating rates were investigated using heating rates from 1 to 10°C/s.

3. Results

The XRD patterns of the studied sample were examined without annealing and it was observed that there is no remarkable change on the XRD patterns of the studied samples. It may therefore be concluded that annealing in the temperature range considered in this article has no effect on the crystal structure of the natural fluorite. Similarly, XRF results did not show any dependence of the fluorite crystal structure on annealing temperature.

It is well known that many natural minerals have natural TL due to the natural radiation in the environment, and if the natural TL is removed using appropriate annealing temperature, it can affect the results of subsequent irradiation. The CaF₂ used in this study has natural TL, the glow curve of which is shown in Figure 1. The natural TL intensity was obtained from natural CaF₂, which was directly taken from the nature. The background signal was determined making the TL readout again. The natural TL was found to be completely removed by annealing the sample at 450°C for 15 min.
The glow curves after annealing the sample at different temperatures ranging from 300 °C to 650 °C for 1 h at an increment of 50 °C are shown in Figure 2. Each annealed sample was irradiated to a dose of approximately 48 Gy before the TL readout. It was observed that the TL properties of the natural CaF₂ do not change for annealing temperatures of less than 400 °C. On the other hand, as shown in Figure 2, the TL sensitivity of natural fluorite is significantly changed after annealing at temperatures above 400 °C. All the TL glow peaks have their maximum intensity at an annealing temperature of 450 °C. The variations of integrated TL intensities of each of the glow peaks of the natural CaF₂ with the annealing temperature are shown in Figure 3. Previous analysis of the glow curve of this sample (7) showed that the glow curve has six glow peaks between room temperature and 400 °C. With reference to the glow curves in Figure 2, the first two peaks (P₁ and P₂) appear at temperatures around 100 °C and 120 °C, the third peak (P₃) around 185 °C, while peaks four to six (P₄–P₆) are highly overlapping peaks and appear around 300 °C in Figure 2. Figure 3 shows that the integrated peak intensities of P₁ + P₂, P₃, and P₄ + P₅ + P₆ are qualitatively similar to one another with changes in annealing temperature. All the glow peak areas first increased with increasing annealing temperature up to 450 °C and then started to decrease above this temperature.

The results of the investigations carried out on the dependence of TL response on annealing duration showed that for annealing temperatures below 400 °C, TL response is independent of the duration of annealing. On the other hand, it was observed that the responses of all glow peaks increased up to 15 min at 450 °C and then they became approximately constant after 15 min up
The TL response of glow peaks of natural CaF$_2$ as a function of annealing temperature for 1 h (dose level ($D$) $\approx$ 48 Gy). The intensities are normalized with that of the sample annealed at 400 $^{\circ}$C.

to 1 h. When the annealing temperature is beyond 450 $^{\circ}$C, it was observed that the sensitivities of all glow peaks always decrease with increasing annealing time.

The dose response of natural CaF$_2$ was studied between 0.04 and $\approx$10.4 kGy using $\beta$-rays after the application of pre-irradiation heat treatment at 450 $^{\circ}$C for 15 min. Selected glow curves of natural CaF$_2$ after different dose levels are illustrated in Figure 4. The experimental observations have obviously shown that there were no significant changes in the shape of the glow curves of
natural CaF₂ with increasing dose levels. The only change is that the peak temperature ($T_m$) of the dosimetric peak of natural CaF₂ slightly shifts to lower temperatures as the dose is increased to a very high value. A plot of the integrated TL intensities of peaks $P_1 + P_2$, $P_3$ and $P_4 + P_5 + P_6$ is shown in Figure 5. In the given study, it is clearly seen that the dose–response curves of peaks $P_1 + P_2$, $P_3$ and $P_4 + P_5 + P_6$ exhibit linearity up to $\approx 50$ Gy and then saturation effects start for all peaks. In most natural CaF₂ samples, it was found that the dose–response curve is linear up to approximately $10^4$ R; saturation and nonlinearity usually occurs in the range $10^4–10^5$ R ($I$). In addition, many published studies have shown that the various peaks in natural CaF₂ saturate at different dose levels, and some of the peaks are supralinear above $10^3$ R ($4$, $18$).

Glow curves of the sample acquired at different heating rates are presented in Figure 6. As seen in this figure, the peak temperatures of all the glow peaks in the glow curves of natural CaF₂ are shifting toward the higher temperature side as the heating rate increases and also their intensities are continuously decreasing. Ogundare et al. ($9$) have studied the effect of varying heating rates on the integrated TL intensity, peak height and temperature of the two high-temperature glow peaks in Nigerian fluorite. Their study showed that the integrated TL intensity of Nigerian fluorite decreases with increasing heating rate. The observed variations in the integrated peak areas of glow peaks of natural CaF₂ with heating rate are shown in Figure 7. In this figure, the TL responses of glow peaks are normalized at the lower heating rate ($1{^\circ}C/s$). It is very interesting that the influence of the heating rates on the intensities of all glow peaks are not approximately equal to each other. As seen, the decrease in the peak areas of glow peaks $P_1 + P_2$ and $P_4 + P_5 + P_6$ is

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**Figure 5.** The dose–response curves of glow peaks of natural CaF₂ determined by the peak area method.

**Figure 6.** Selected glow curves of natural CaF₂ measured at different heating rates from $1{^\circ}C/s$ to $10{^\circ}C/s$ ($D \approx 48$ Gy).
of the order of 20%, while there is no considerable decrease in the peak intensity of glow peak P3 with increasing heating rate from 1 °C/s to 10 °C/s.

4. Conclusion

The results in this work indicate that the TL glow peaks of natural fluorite are very sensitive to annealing temperatures and durations. All TL glow peaks have the highest sensitivity after annealing at 450 °C for 15 min and hence this is recommended as the pre-irradiation thermal process that will ensure reproducibility of experimental results. As already mentioned, the results of XRD and XRF have shown that there is no effect of annealing between 300 °C and 650 °C on the crystal structure of the samples. However, the TL responses of the sample TL are highly affected after annealing above 400 °C (Figure 2). These results indicate that the variations in the intensity of the TL glow curves are not due to phase transition in the crystal structure of samples after annealing but most probably are due to the change in the number of trapping or recombination centers. It is obviously seen that the pre-irradiation heat treatments affect the sensitivity of all glow peaks of the tested natural CaF₂, and much more research by different techniques is necessary to understand the causes of these sensitivity changes after annealing.

The experimental results of dose–response studies have shown that there were no significant changes in the shape of the glow curves of natural CaF₂ with increasing dose levels. However, the positions of lower temperature glow peaks below 250 °C do not shift toward lower or higher temperature sides with increasing dose levels, while the $T_m$ of the high-temperature glow peak above 250 °C slightly shifts to the low-temperature side. Furthermore, the dose–responses of all glow peaks ($P_1 + P_2$, $P_3$ and $P_4 + P_5 + P_6$) show a similar behavior. They first follow linearity up to $\approx 50$ Gy and then saturation effects start above this dose level. The dependence of TL response on heating rate showed that integrated peak intensities of glow peaks $P_1 + P_2$ and $P_4 + P_5 + P_6$ decreased with increasing heating rate and indicated thermal quenching (19). In this article, it has been shown that the integrated peak intensities of glow peaks $P_1 + P_2$ and $P_4 + P_5 + P_6$ continuously decrease with increasing heating rate. On the other hand, there is no effect of heating rate on the intensity of glow peak P3.

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