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The investigation of usage of fluorapatite mineral ($Ca_5F(PO_4)_3$) in tooth enamel under the different pre-irradiation thermal treatments

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ABSTRACT

Fluorapatite $Ca_5F(PO_4)_3$ is a kind of important thermoluminescence dosimeter (TLD) material, because the effective atomic number of fluorapatite is close to that of human bones and teeth. In the present study, thermoluminescence (TL) properties of fluorapatite mineral in tooth enamel under the different annealing temperatures with various annealing times were investigated. This study reveals that the fluorapatite in tooth enamel exhibits TL properties. Annealing of the sample affects extremely the TL glow curve and causes a huge enhancement in the sensitization of TL peak. The sample annealed at 1000 °C about 120 min gives best TL peak intensity (150 factors than un-annealed sample) and has a distinct peak around 230 °C. Also, the best reproducibility was observed for 1000 °C annealed sample temperature while un-annealed sample shows the worst reproducibility. Moreover, a good linearity in dose response is observed in the samples annealed at 400 °C and 700 °C.

1. Introduction

Tooth enamel is the hardest part of tooth and protects the dentine. In terms of its weight, it consists of 95% inorganic minerals, 1% organic minerals, and 3% water [1–3]. It is a complex biomaterial, a composite of elongated mineral crystallites in the form of biological apatite bonded by polymeric proteins and peptide chains saturated with water [4]. It has a hierarchical structure with crystals of hexagonal cross-section tightly packed into rods (prisms) (width ~5 μm) [5] and enclosed by polymeric sheaths (width 0.1 μm) [4]. In 1964 about twenty inorganic elements except oxygen, hydrogen and carbon were found in tooth enamel. Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] and fluorapatite [$Ca_5F(PO_4)_3$] are two major inorganic apatite minerals in tooth enamel. Apatites are a family of compounds characterized by a similar structure, albeit with different compositions. When fluor (F) ions substitute with OH in hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], fluorapatite minerals [$Ca_5F(PO_4)_3$] are formed [1–3,6]. Most of the current knowledge about the enamel apatite has been derived from studies of related synthetic or natural compounds. Biological apatites contain some ions such as CO_3^{2-}, PO_4^{3-}, OH^- and Ca^{2+} and different forms of apatite may form with substituting of present ions [7]. P, CO_3, Mg, Cl, and K are the major and Fe, Zn, Sr, F, Ca and Na are the minor constituents in tooth enamel [8]. For all that, Zn, Sr, Si, F, S, Al and Fe are the trace elements in tooth enamel. Minor constituents and trace elements get incorporated in tooth enamel during mineralization. Trace elements and minor constituents may play a role in the stability of apatite [9].

A few researchers [10–17] have investigated the thermoluminescence properties of synthetic and biological apatites. In the study of Secu et al. [11], they pointed out the tooth enamel shows a broad glow curve from 100 to 450 °C and TL signal in the 250–450 °C temperature range increases with irradiation dose. They supposed that the TL peaks below 300 °C are due to the impurities such as Mn^{+2} and trivalent rare earth impurities. For the TL peaks between 300 °C and 400 °C, the presence of several paramagnetic species such as CO_2^-, CO_3^- and CO^- revealed by EPR spectra of biological and synthetic apatite may cause higher TL peaks. Also they concluded the complex structure of the TL glow curve in tooth enamel had been attributed to the recombination of radiation induced CO_2^- radicals generated from surface CO_2 and or bulk CO_3 impurities. The radiation induced signal in tooth enamel may consist of several CO_2^- species located in different sites [16]. Fukuda [18] investigated some thermoluminescence properties of synthetic fluorapatite because the effective atomic number of synthetic fluorapatite is about 14 [19] and close to that

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of human bones and teeth. A TL glow curve with two main peaks centred at 100 °C and 235 °C was obtained.

Tooth enamel as a detector for in vivo dosimetry has been known for more than three decades [20]. The accumulated dose in tooth enamel was investigated by some researchers [10,21–26] using electro paramagnetic resonance (EPR) method based on the measurement of stable radiation induced radicals [10]. On the other hand, thermoluminescence (TL) retrospective dosimetry using tooth enamel is potentially an interesting alternative to EPR retrospective dosimetry since it requires considerably smaller amounts of sample (only few mg) that can be harmlessly obtained by dentists without tooth extraction [11]. A few researchers [10,12–16] have investigated the thermoluminescence properties of two major inorganic minerals which are hydroxyapatite and fluorapatite. Alvarez et al. [27] carried out the thermoluminescent characteristics of synthetic hydroxyapatite which is one of the most important ingredient in tooth enamel. Two main peaks centred around 200 °C and 300 °C are seen and good TL properties such as wide linearity range and good reproducibility is observed.

In the current study, the effects of pre-irradiation thermal treatments on thermoluminescence glow curve of fluorapatite mineral which is another important mineral in tooth enamel were investigated.

2. Experiment

2.1. Sample preparation

The tooth enamel samples were taken from a dentist who separated enamel from dentine. The samples were crushed in the agate mortar to get powder form. The powdered tooth enamel sample was etched for 5 min in a 20% acetic acid water solution followed by drying [11]. It is sieved using fine sieves which have different dimensions and the samples whose grain sizes are between 100 μm and 120 μm were used in all TL measurements. Each experiment was performed with 10 mg aliquot samples.

2.2. Procedure

A point beta source (^{90}Sr–^{90}Y) which delivers 0.040 Gy/s was used to irradiate samples at room temperature. The activity of beta source was about 100 mCi. The beta source was installed in a 9010 optical dating system which is interfaced to a PC using a serial RS-232 port to control irradiation time. It is calibrated by manufacturer on March, 10, 1994. The glow curve measurements were made using a Harshaw TLD System 3500 Manual TLD Reader at 1 °C/s. The irradiated samples were read out in an N_2 atmosphere in order to avoid any undesired signals. A standard clear glass filter was always installed in the reader between the planchet and photomultiplier tube. A microprocessor controlled furnace was used to perform thermal treatments.

Seven aliquots weighted 10 mg were used to see the effects of different annealing temperature at fixed annealing time. Aliquots were annealed at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C about 30 min before irradiation process and quickly cooled on a metal plate. After annealing process, annealed aliquots were irradiated about 35 Gy by the beta source and read out by the TLD reader at 1 °C/s.

Five aliquots were annealed at 1000 °C for different annealing times (15, 30, 60, 90 and 120 min) to see the effects of different annealing time at fixed annealing temperature before irradiation process. The aliquots were irradiated 35 Gy before reading process.

Another part of the current study is the effects of different annealing temperatures on the reproducibilities of samples at fixed annealing time. For each annealing temperature, the experiment was repeated six times. Also each sample was irradiated 35 Gy before reading process.

In the dose response experiment, the samples were irradiated at different higher doses (154 Gy, 308 Gy, 616 Gy, 1.23 kGy and 2.4 kGy) at different annealing temperatures (400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C) and read out.

In the fading experiment, the irradiated samples at 154 Gy were waited in a dark room for different storage times (30 min, 4 h, 32 h, 64 h, 128 h, 256 h) and read out.

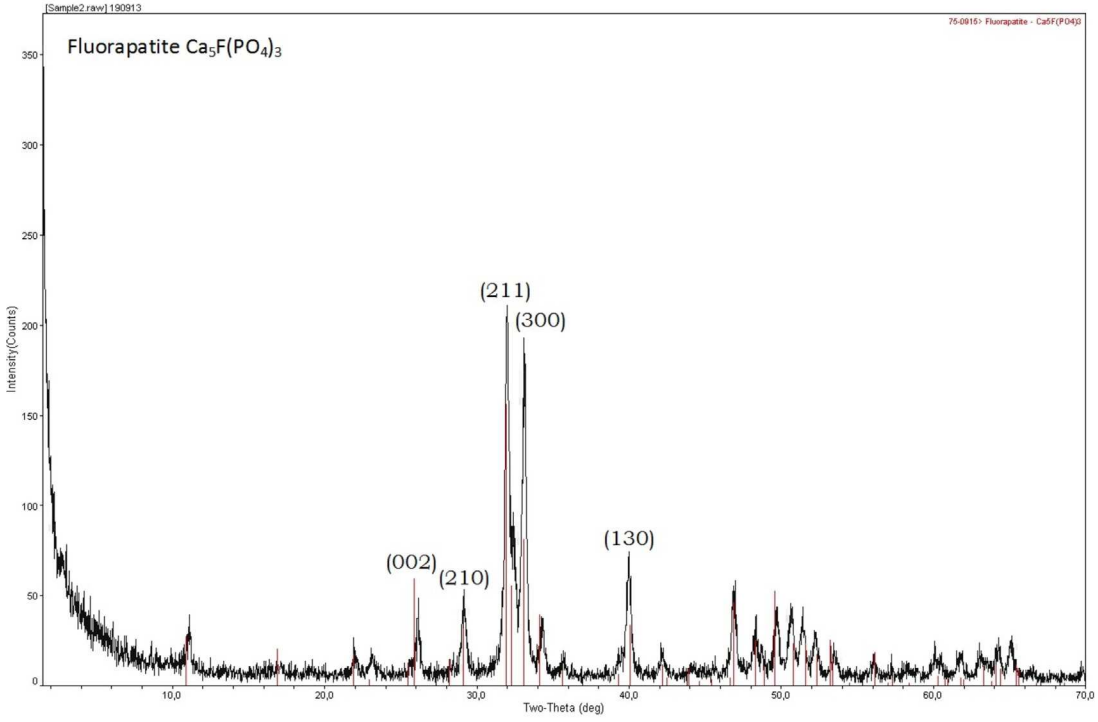


Fig. 1. X-ray diffraction (XRD) pattern of tooth enamel.

Table 1
The peak ID extended report of tooth enamel.

2θ	d(Å)	Height (%)	Phase ID	hkl
26.175	3.4018	21.5	Fluorapatite	(0 0 2)
29.177	3.0582	23.5	Fluorapatite	(2 1 0)
32.019	2.7929	100.0	Fluorapatite	(2 1 1)
33.122	2.7024	92.0	Fluorapatite	(3 0 0)
40.035	2.2503	34.5	Fluorapatite	(1 3 0)

3. Experimental results and discussions

The X-ray diffraction (XRD) pattern and Peak ID Extended Report of tooth enamel were performed by a Rigaku D/MAX-Ultima +/PC X-ray diffraction equipment from XRD Facility of Bogaziçi University Advanced Technologies R&D Center, are shown in Fig. 1 and Table 1. The Rigaku D/MAX-Ultima+/PC X-ray diffraction equipment is engineered to create a multiple purpose configuration. The X-ray generator is a part of Rigaku D/MAX-Ultima+/PC X-ray diffraction equipment and operates at 20–60 kV rated voltage, 2–80 mA rated current and 3 kW maximum rated output with SCR phase control. The focal spot size in the X-ray generator is $1 \times 10\,mm^2$.

3.1. Effects of different annealing temperatures at fixed annealing time

The aim of this part is to see the effects of different annealing temperatures on TL glow curves. Fig. 2 shows the variation of TL glow curve as a function of annealing temperature at (a) 500–800 °C and (b) 900–1100 °C. For each annealing temperature, the samples were annealed about 30 min. It is seen that the different glow curves were obtained for each annealing temperature. This is probably explained by thermal alkali self-diffusion through the lattice interfaces [28]. Annealing of the sample at higher temperatures causes an increase in TL peak intensities and a decrease in the number of peak in the glow curve to single peak which is located around 200–230 °C. Also a huge increase about 150 times was observed in maximum TL intensity when annealed sample at 1100 °C is compared with the un-annealed sample.

The effect of annealing of the sample is seen clearly in Fig. 3. In Fig. 3, the variation of area under the glow curve as a function of

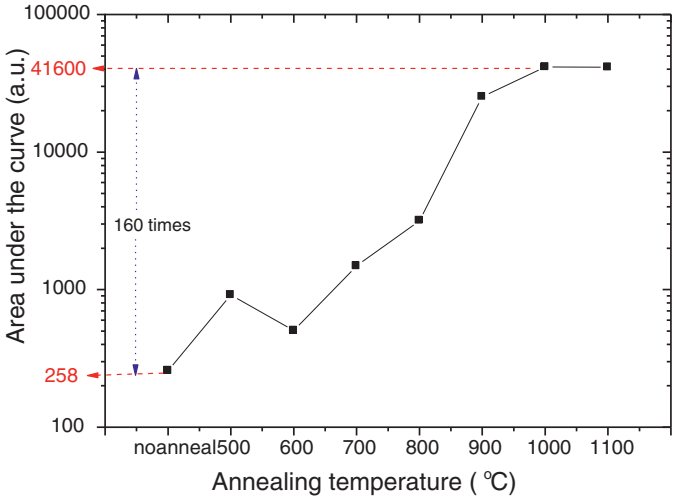
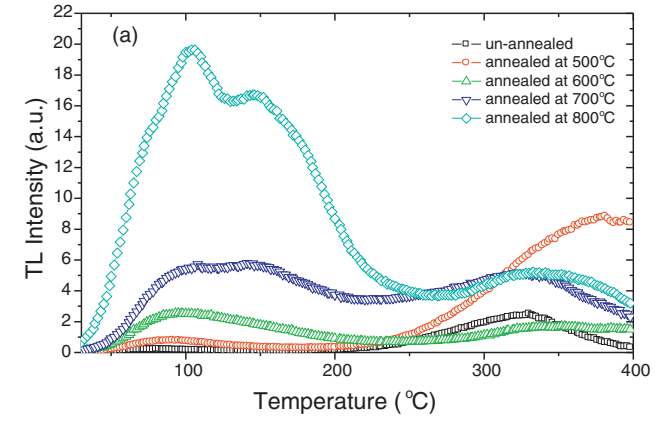


Fig. 3. The variation of area under the glow curve as a function of annealing temperatures at 500–1100 °C about 30 min.



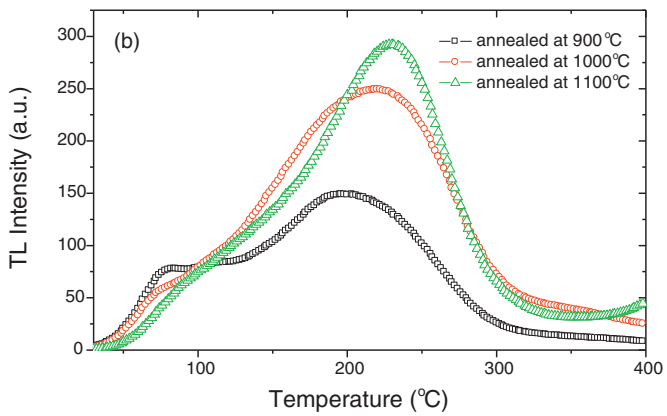
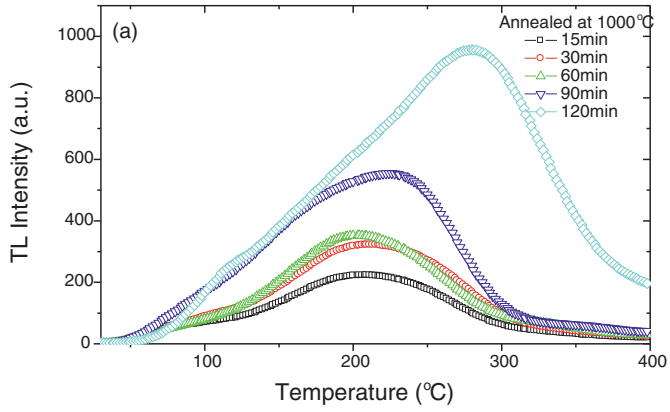


Fig. 2. The variation of TL glow curve as a function of annealed temperatures at (a) 500–800 °C and (b) 900–1100 °C about 30 min.



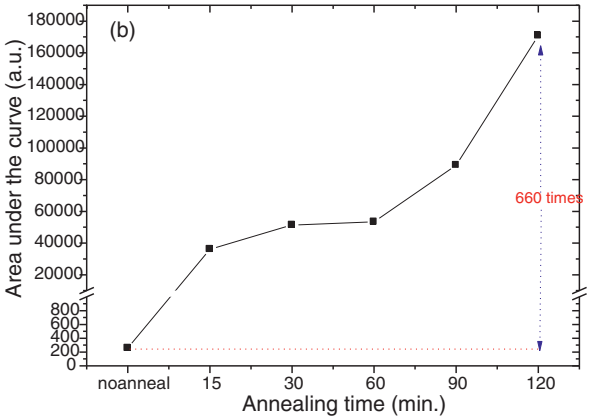


Fig. 4. The effects of different annealing times at fixed annealing temperature (1000 °C) on (a) the glow curve and (b) the area under the curve.

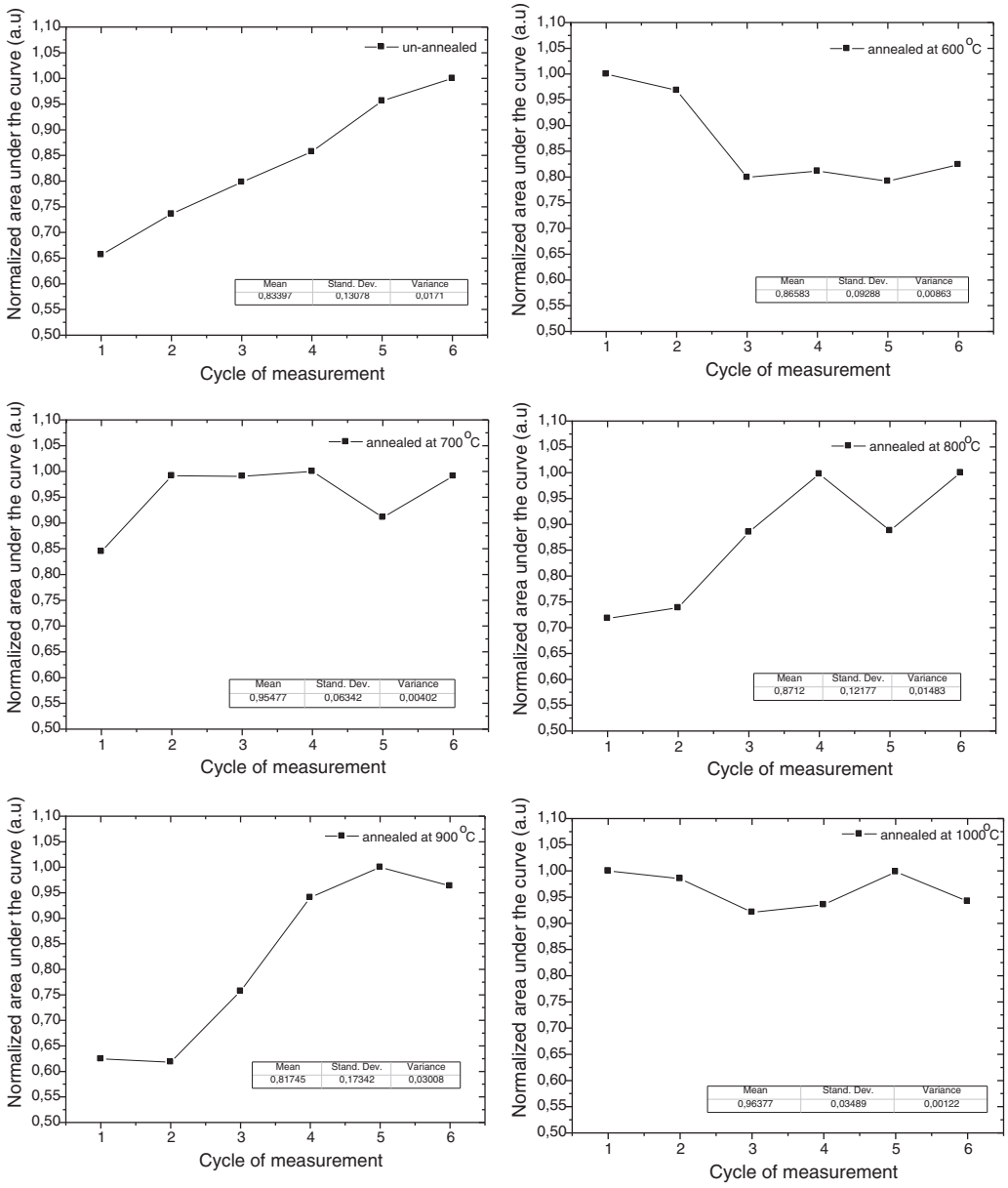


Fig. 5. The reproducibility of the sample for different annealing temperatures at fixed annealing time (30 min) and standard deviation of each experiment.

annealing temperatures at 500–1100 °C is seen. The area under the curve increases with increasing annealing temperature up to 1000 °C then reaches to its saturation value. In short, the area under the curve of the sample annealed at 1000 °C is bigger than un-annealed sample about 160 times. This similar effect and enhancement are seen in the study of Toktamiş et al. [29]. They analyzed TL glow curves of calcite ($CaCO_3$) extracted from natural sand used in making roasted chickpea at different annealing temperatures and the area and maximum TL peak intensity increase tremendously beyond 600 °C annealing temperature and the biggest area and maximum TL peak intensity are seen at 900 °C annealing temperature. According to their study, annealing at 900 °C causes an enhancement in the area under the curve and maximum TL peak intensity of about 70 times when it is compared with no-annealed sample. This effect is explained with an enhanced probability of radiative recombination at the luminescence site due to transfer of holes from so-called reservoir centres to luminescence centre [30].

3.2. Effects of different annealing times at fixed annealing temperature

In the second part of the current study, the effects of different annealing times at fixed annealing temperature (1000 °C) were carried out and shown in Fig. 4. In Fig. 4a, it is seen that there is no important change in shape of glow curve and TL peak temperature with the variation of annealing time except for 120 min. When the sample is annealed about 120 min, the peak temperature shifts to higher temperature region about 60 °C and glow curve becomes wider. Furthermore, maximum TL peak intensity increases with increasing annealing time. An increase is observed in the area under the curve with increasing annealing time, shown in Fig. 4b. Especially, an incredible increase (about 660 times) is seen in the area under the curve when the result of un-annealed sample is compared with the sample annealed at 1000 °C about 120 min. In the study of Toktamiş et al. [29], they observed the largest area under the curve and maximum TL intensities are seen at 15 min annealing time at 900 °C annealing temperature. In

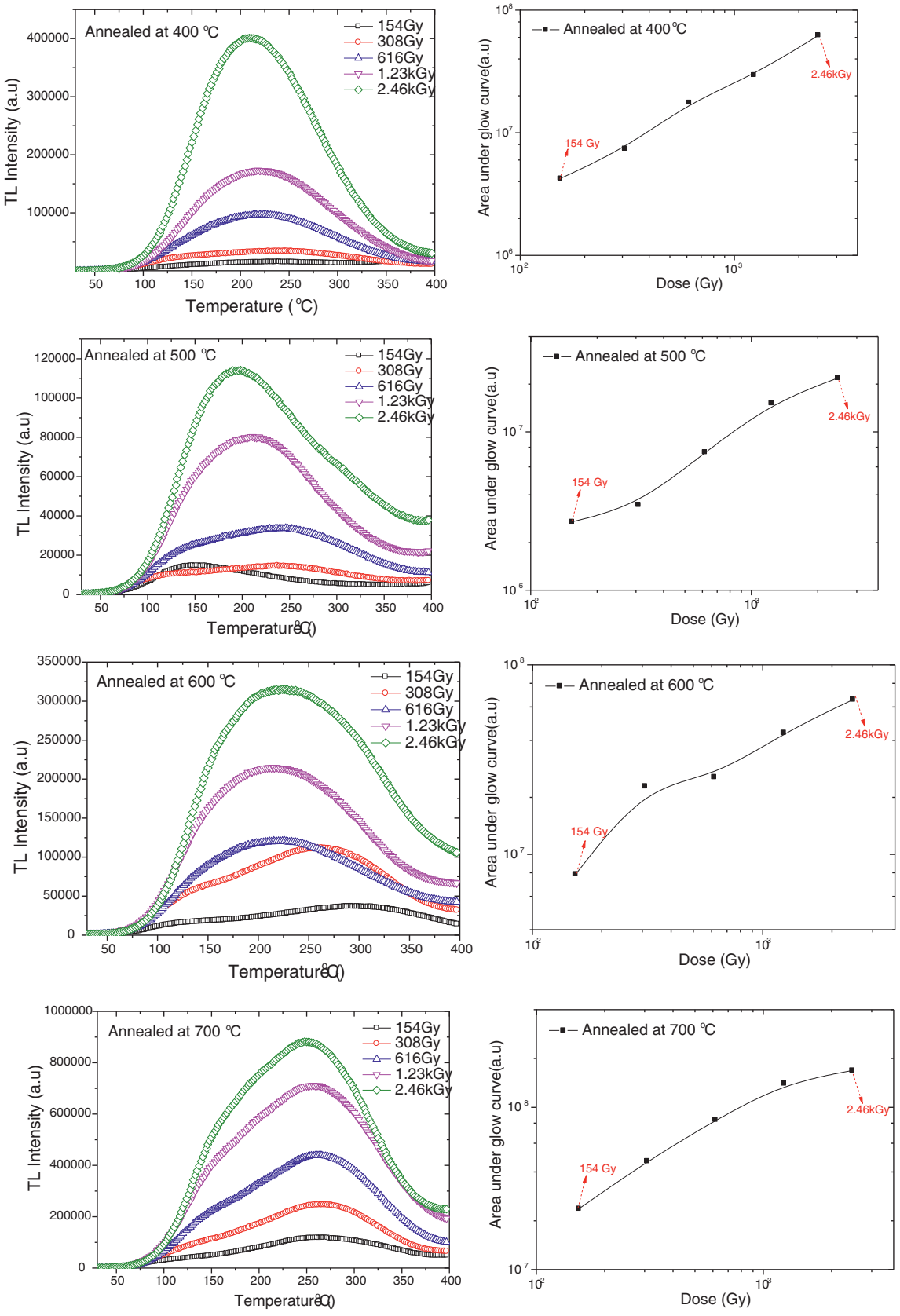


Fig. 6. The dose responses of the samples annealed at different annealing temperatures (400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C) at fixed annealing time (30 min) for different higher doses (154 Gy, 308 Gy, 616 Gy, 1.23 kGy and 2.46 kGy).

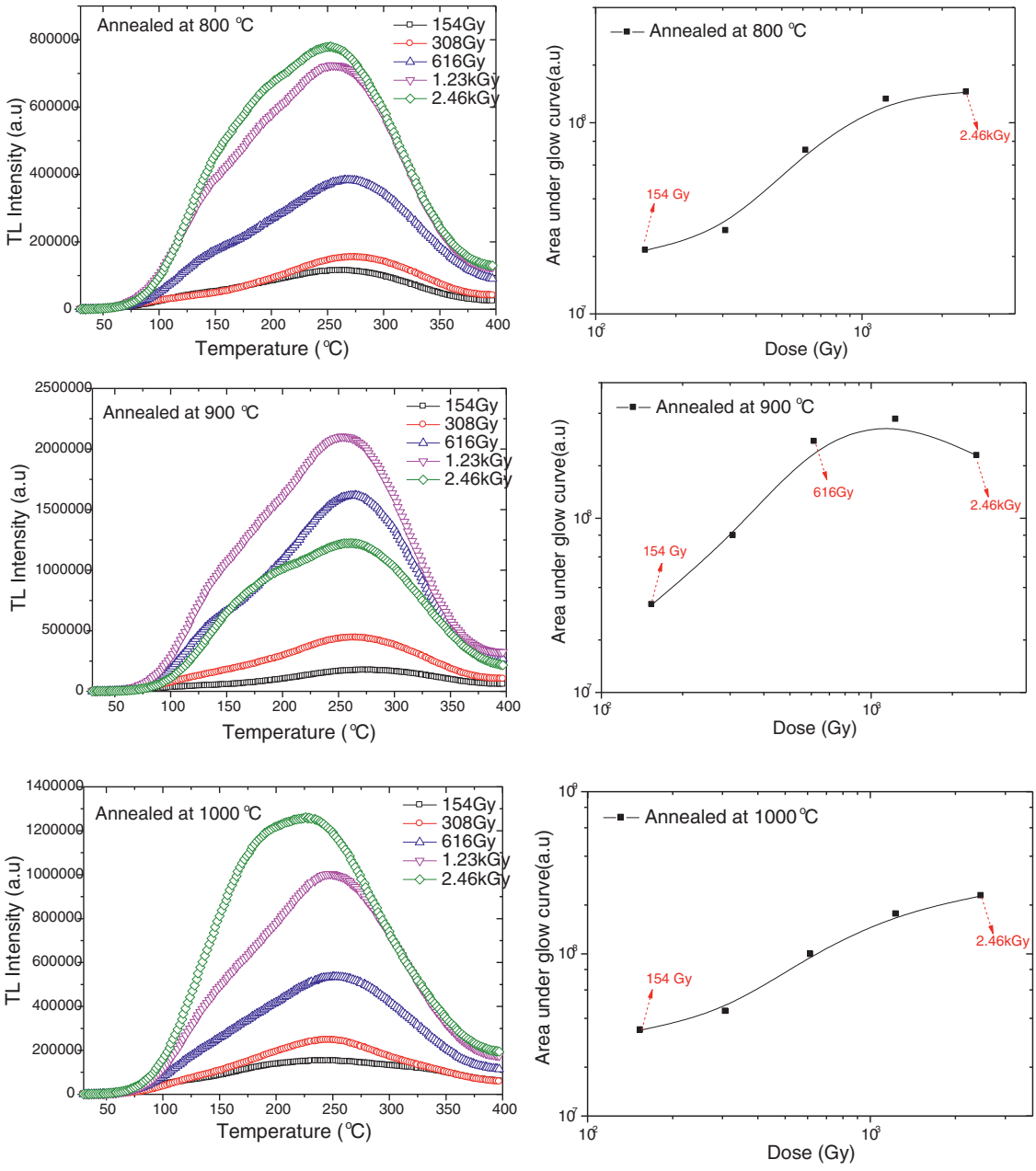


Fig. 6. (Continued)

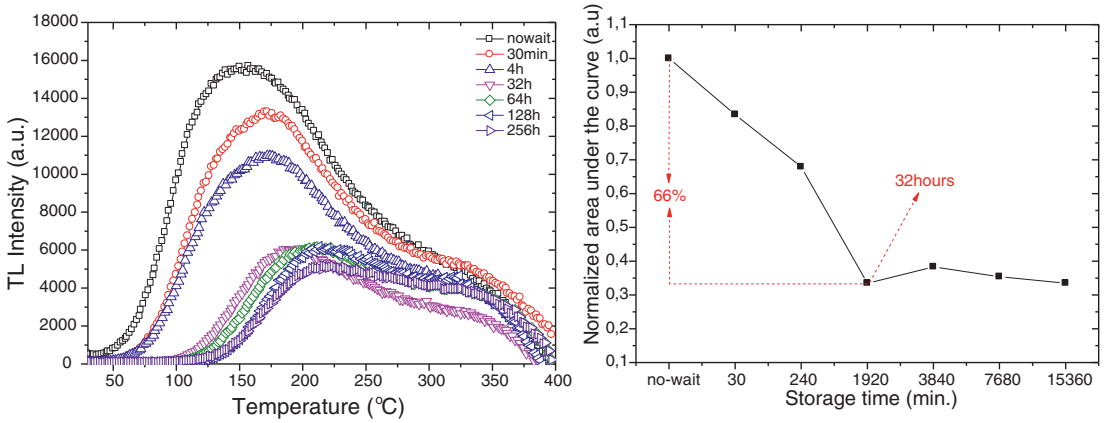


Fig. 7. The variations of glow curve and normalized area under the glow curve as a function of storage time in a dark room.

addition enhanced probability of radiative recombination at the luminescence site, Zimmerman [30] proposed also competing traps where the deeper traps were partially removed during the thermal treatment. The enhancement in the area under the curve may be caused by the competing traps.

3.3. Reproducibility at different annealing temperatures at a fixed annealing time

Reproducibility of a sample is an important parameter in the dosimetric studies. For a good dosimeter, the same glow curve and same area under the glow curve are expected at the end of each repeat of the experiment. Fig. 5 shows the reproducibility of the sample at different annealing temperatures at fixed annealing time (30 min) before irradiated 35 Gy and standard deviation of each experiment. It is seen that the best reproducibility is obtained when the sample is annealed at 1000 °C whereas the worst reproducibility is obtained for the un-annealed sample. However, the reproducibility of the sample annealed at 700 °C is good but no satisfying results are obtained in the reproducibilities of sample annealed at 600 °C, 800 °C, 900 °C.

Roman-Lopez et al. [23] pointed out the higher annealed aliquots probably tend to the amorphisation and the crystalline index is homogeneous along the lattice structure giving rise to a less scattering in the reproducibility.

3.4. Dose response at different annealing temperatures at a fixed annealing time

Dose response is an important experiment in the dosimetric studies for getting knowledge about relationship between TL light output and applied dose. In Fig. 6, the dose responses of the samples annealed at different annealing temperatures (400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C) at fixed annealing time (30 min) for different higher doses (154 Gy, 308 Gy, 616 Gy, 1.23 kGy and 2.46 kGy) are seen. A good linearity in dose response is observed in the sample annealed at 400 °C and 700 °C. However a saturation point is observed at the dose level of 1.23 kGy in the graph of sample annealed at 700 °C. The saturation is observed at 616 Gy for the samples annealed 800 °C and 900 °C.

3.5. Fading experiments

Another important parameter of a dosimeter is fading to investigate that how an irradiated dosimetric sample fades with storage time. In Fig. 7 the variations of glow curve and normalized area under the glow curve are given. The maximum TL intensity and area under the curve fall to 34% of their initial values at 32 h (1920 min) of storage time. Beyond 32 h of storage time, no important change is seen in the maximum TL intensity and area under the curve.

4. Conclusions

In the current study, the effects of pre-irradiation thermal treatments on thermoluminescence properties of fluorapatite mineral which is an important apatite mineral in tooth enamel were investigated. The results can be summarized in several headlines:

1. The pre-irradiation annealing process at different temperatures cause to change in TL glow curve shape of fluorapatite in tooth enamel. At higher annealing temperatures, the number of distinct peak in the glow curve decreases to single peak which is located around 230 °C. The possible reason may be change of position of the defects due to the annealing of sample at different pre-irradiation temperatures.
2. A huge increase (about 160 times) was observed in maximum TL intensities and area under the glow curve when the un-annealed sample was compared with the sample annealed at 1100 °C. The carrier concentration (area under the glow curve) reaches to its saturation value. The annealing may cause an increase of the trap concentrations, especially at higher temperatures.
3. As a result of annealing time experiments, variation of annealing time at fixed annealing temperature does not affect the shape of TL glow curve but peak temperature shifts to higher temperature region about 60 °C when the sample is annealed about 120 min. Moreover, annealing about 120 min causes an enhancement (660 times) in maximum TL peak intensity and area under the curve (carrier concentration in traps) when it is compared with un-annealed sample.
4. When the reproducibility of the sample is carried out at different annealing temperatures, the best reproducibility is obtained at 1000 °C of annealing temperature whereas the worst reproducibility is obtained for un-annealed sample.
5. A good linearity in dose response is observed in the sample annealed at 400 °C and 700 °C.
6. In the fading experiment, the maximum TL intensity and area under the curve decrease with increasing storage time up to 32 h (1920 min). Beyond this value they do not fade anymore.

In brief, the fluorapatite mineral extracted from tooth enamel shows TL properties. Annealing of the sample affects extremely the TL glow curve and causes a huge enhancement in the sensitization of TL peak.

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