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**THE INVESTIGATION OF VARIATION OF TL DOSE
RESPONSE CURVE OF NATURAL CALCITE AFTER
ANNEALING AT DIFFERENT TEMPERATURES**

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**The Investigation of Variation of TL Dose Response Curve
of Natural Calcite after Annealing at Different
Temperature**

**M.Sc. Thesis
in
Engineering Physics
University of Gaziantep**

**Supervisor
Prof.Dr. Ahmet Necmeddin YAZICI**

**by
Cengiz BOZADA
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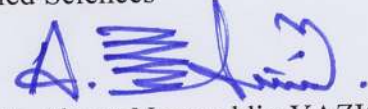
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Cengiz BOZADA

ABSTRACT

THE INVESTIGATION OF VARIATION OF TL DOSE RESPONSE CURVE OF NATURAL CALCITE AFTER ANNEALING AT DIFFERENT TEMPERATURES

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The thermoluminescence (TL) studies of calcite mineral have resulted in the development of a wider range of applications in ceramic industry field. The TL glow curve shapes of minerals changes as a result of crystal purity, radiation dose, and thermal history previous the irradiation. In this study, the TL dose response of natural calcite samples of unannealed and annealed at different temperatures has been studied. The calcite samples that were collected from Elazığ-Ağın city in Turkey exhibit two main TL peaks following β -irradiation. The samples were annealed at 600, 700, 800, 900, 1000 °C from 15 minutes to 240 minutes and then they were irradiated at room temperature with a point beta source for different time durations to study TL dose response curve. It was observed that the annealings at 900 and 1000°C have high pronounced effects on the dose response curve of natural calcite.

Keywords: thermoluminescence, annealing, calcite, dose response curve.

ÖZET

FARKLI SICAKLIKLARDA TAVLAMA SONRASINDA DOĞAL KALSİTLERİN TL DOZ TEPKİME EĞRİLERİNDEKİ DEĞİŞİMLERİN ARAŞTIRMASI

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Kalsit mineralinin termoluminesans (TL) çalışmaları seramik sanayii alanında geniş bir uygulama alanının gelişmesine yol açmıştır. Kristal saflığı, radyasyon dozu, ve ışınlama öncesi ısısal tavlama işlemleri bu mineralin TL ışıldama eğrisinin şeklini değiştirmektedir. Bu çalışmada, tavlammamış ve farklı sıcaklıklarda tavlammış doğal kalsit mineralinin TL doz tepkime eğrisi çalışılmıştır. Türkiye Elazığ-Ağın bölgesinden toplanan kalsit örneği beta ışınlaması sonucu iki ana ışıldama tepesine sahiptir. Numuneler 15 dakikadan 240 dakikaya kadar 600, 700, 800, 900, 1000 °C’lerde tavlammış ve daha sonra doz tepkime eğrilerini çalışmak için oda sıcaklığında ışınlanmıştır. 900 ve 1000 °C’lerde tavlamanın özellikle doğal kalsit numunelerinin TL doz-cevap eğrilerini etkilediği gözlemlenmiştir.

Anahtar kelimeler: termoluminesans, tavlama, kalsit, doz tepkime eğrisi.



I dedicate this work to the science of Physics

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CHAPTER 1

INTRODUCTION

The thermoluminescence (TL) phenomena could be observed at insulator and high band gap semiconductor materials. Because, the material should have necessary a band gap to observe TL phenomena. In the TL processes, the free electrons in the conduction band (CB) after ionizing radiations are trapped at fault sites in a metastable situation within the band gap of TL materials. The trapped charges can then be released by heat stimulation and they pass the potential barrier to the CB and then will move to lower energy states which is called as luminescent or recombination center with the diffusion of light. This process is called as thermoluminescence (TL) [1]. Simply, in the thermoluminescence phenomena, the TL material is firstly irradiated at room temperature (RT) by the ionizing radiation and then the material is heated at a temperature range in which all the electrical charges that were trapped in charge traps which is called as metastable states have been thermally excited out from these traps grades until a temperature level and the luminescence entirely vanish. When the emitted light intensity is plotted as a function of time or temperature; the resultant graph is called as the thermoluminescent glow-curve (GC) [2].

Since it includes a trap and a luminescence centre, the TL phenomena in solids is a comparatively complex process. If a wide band gap material such as an insulator or semiconductor is exposed ionizing radiations at low temperature, the electrons in the valance band are freed from the valance band (VB) to the conduction band (CB). That leaves a hole in the VB. Both types of charge carriers, electrons and holes, become mobile in their respective bands untill they recombine with each other or they are trapped in lattice glitches (defects) in the crystalline solids. These crystal defects play very considerable roles in the TL phenomenas. The trapped electrons could remain therein for a long period when the crystals are stored at the irradiation temperatures such as room temperature. When the crystal is heated the trapped charges, i.e. electrons; can be released from respective defects due to the

sufficient energy given to the charges (electrons or holes). Those charges may move in the respective band in crystal solid till they recombine with suitable recombination centres that contain opposite charge (i.e. hole) with the emission of TL light. The process of light emission from a crystalline solid by increasing the temperature of it with thermal stimulation after irradiation by ionizing radiations is called as thermally stimulated luminescence (TSL) or simply thermoluminescence (TL).

Three important constituents are necessary for the productions of the TL phenomena. Firstly, the material must have band gap. Therefore the material is a semiconductor or an insulator. The metals do not have band gap and therefore they do not exhibit luminescent properties. In general, the materials in thermoluminescent dosimetry (TLD) are insulators which trapped electrons in the traps are entirely due to absorbed radiation energy by the ionizing radiations. Secondly, in the course of exposure to radiation the material must have at some time adsorbed energy. Thirdly, the emission of light is induced from the material via heating. This ingredient is a specific characteristic of thermoluminescence phenomena. In this case, when the materials are heated in order to observe the light emission, the materials should not be re-emit the TL signal by simply cooling the material up to irradiation temperature, i.e. room temperature, and then reheating. So as to re-exhibit luminescence the material must be re-exposed to radiation, where upon increasing the temperature will once again produce light diffusion. The essential principles which administer the production of TL are actually the same as those that administer all luminescences continuum, and in this way, the TL is merely one of a large family of luminescence phenomena [3].

Adequate thermoluminescent materials, i.e. phosphors, should have high concentrations of electron and hole traps that were generated by doped impurities and crystal defects within the crystals [2]. For instance, rare earth elements either simultaneously or individually with more than one of those in impurities provide appropriate defects within the TL materials. When a valance electron has absorb enough energy form the ionizing radiation (alpha, beta and gamma or adsorption of light in the far ultraviolet), the electrons excite from valance band (leaving a hole in the valance band) to conduction band where move freely through the conduction band [4]. Therefore the determination of the kinetic parameters is a very active area

in the research of TL mechanisms and thereupon various techniques have been developed to obtain these parameters from the experimental TL glow curves.



CHAPTER 2

LITERATURE SURVEY

Calcite material is one of the widespread and most common minerals. It highly found in the limestone deposit which is a well known sedimentary rock within the earth [5]. The thermoluminescence properties of all types of calcites were highly studied. David and colleagues recorded the TL glow curves from natural calcites originated from different places. They have emphasized that it is difficult to compare the published TL results from different samples because of differences in heating rates, pre-irradiation treatment, impurity content, method of manufacture etc. [6]. Consequently; the scientific investigations on calcite materials have shown that they have different TL properties and characteristics depending on the impurity contents within them and on the origin of the samples.

Structure of calcite is hexagonal and its crystal structure is defined as a NaCl type arrangement of (Ca) an ionic groups [7]. The thermoluminescence features of crystal calcite (CaCO_3 cations) and (CO_3 crystal of trigonal symmetry) have been studied by various workers [8].

Many natural crystals display thermoluminescence (TL) features that are proper for TL dating. Therefore, the thermoluminescence dating method is an important tool for the investigation of age of archaeological and geological materials [3]. As a result; a literature survey on the TL properties of calcite materials has shown that they have different TL characteristics depending on the genesis of the sample and on the impurity content. It was watched on preternaturally grown CaCO_3 crystals that concentration of impurities within them modify type of both glow-curve shape and TL sensitivity [6]. Especially, the annealing processes are highly influences the shapes and sensitivity of TL materials. For example; in an air atmosphere, the calcite instances were annealed from 200 to 700°C with a temperature interval of 50 °C for 1 h duration and irradiated with a dose of 150 Gy handling ^{60}Co γ -source. As a function of annealing temperatures between 200 and

700°C, it is watched that the TL sensitivities of the glow peaks of calcites at 140 and 255 °C gradually increases with increasing annealing temperature up to 600 °C. On the other hand, the TL glow peak which is seen at 345 °C, even after annealing at 600°C, which were not showing any response to the radiation doses. For that reason, the glow peak at 345 °C was not taken into consideration for all instances, such as dating and etc. Moreover, the annealing process of each calcite instance in air at and above 700 °C caused a downfall in the TL sensitivity to ionizing radiations of all TL glow peaks [9]. The instances annealed at a temperature of 600°C for 1 hour causes a rise in the intensity of the TL glow peaks at 140 and 255 °C by a factor of 9 when compared to unannealed instances. In air, this type of behaviour of studied instances has been recorded by other authors [10].

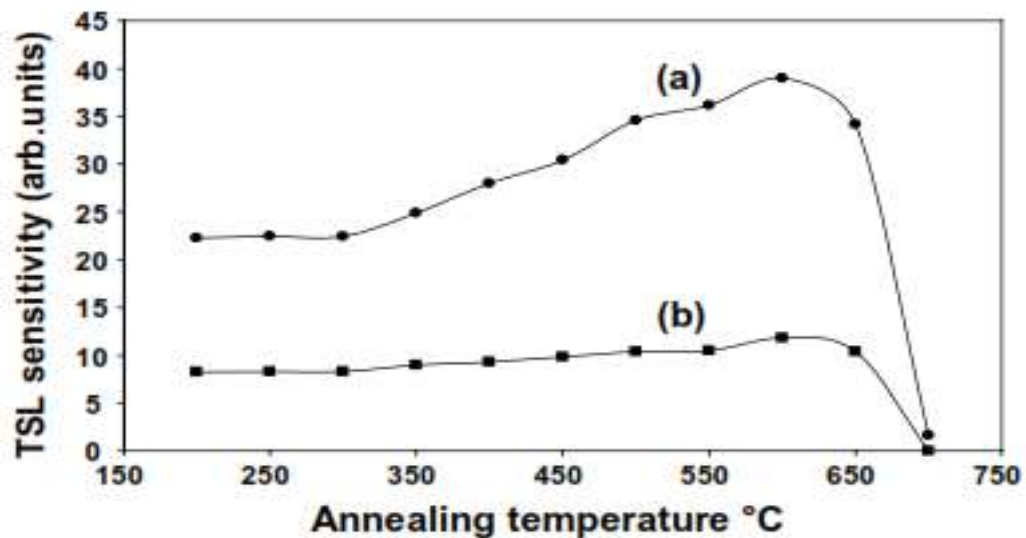


Figure 2.1. The effects of annealing temperature on the sensitivity of TL glow peaks of natural calcite crystals at (a) 140 °C and (b) 255 °C [11].

M.Urbina, A.Millan, P.Benitz and T.Calderon had examined dose rate effect in the calcite materials [5]. A study of the thermoluminescence intensity versus ionizing radiations such as γ and β -irradiations after different dose rates has been made for calcite materials. It was observed that the TL intensity of this material is initially supralinear and then becomes linear up to at least 7 kGy in both types of irradiations. On the other hand, if calcite samples previously γ -irradiated at a fixed dose rate, and then they are irradiated with beta rays, the relative populations of traps seems to be characteristic of the beta irradiation. The opposite effect is also been observed in these samples. An important conclusion of this dose rate effect may be

that the initially applied gamma doses to calcite minerals are optically bleached by sunlight exposure.

Ingotombi and S.Drendrajit Singh have investigated the TL glow curve characteristics of gamma irradiated brown and colourless calcites that were obtained in the sedimentary limestone deposits in Ukhrul, Manipur (India) [7]. It was observed that the natural TL intensity of these samples is very weak. Therefore, the TL glow curves of these materials have been handled for analysis after γ -irradiation. After the gamma irradiation, five TL glow peaks were seen in the glow curve of these samples. The brown and colourless calcite samples that were obtained from limestone deposits of sedimentary rocks do not show any prominent TL glow peak at and about 280 °C which is agree with the earlier findings. However, the presence of this peak could be discovered while fitting the whole glow curve in the brown calcite. Since the brown calcite showing a prominently strong TL peak at $\approx$ 330-340°C comparable with the 220-245 °C peak, the colourless calcite has an unique characteristic behaviour different. The trapping parameters, namely frequency factor s , the activation energy E , and the order of kinetics b of the TL glow peaks of these samples (brown and colourless varieties) are also determined by using the computurized glow curve deconvolution technique after irradiation with $\approx$ 4 kGy of gamm-rays. The order of kinetics of the TL glow peaks of calcite is found to be 2, except for the 180 °C peak. In addition, the electron lifetimes τ of the TL glow peaks of calcite are obtained to obtain the upper limits of their utility in the TL dating. The lifespans of the TL glow peaks at 230 °C and 330 °C glow peaks are found that they are approximately equal to 1330 years and 1.8×10^8 years, respectively.

The charge transport and local transition mechanisms in thermoluminescence of calcite were investigated by S.Shoval, P.D.Townsend and Y.Kirsh at university of Sussex in UK [8]. In this research; it was observed that the natural colourless calcite single crystals have several distinct TL peaks onlooking irradiation at room temperature. The second aim of that work was also to obtain the trapping parameters of TL glow peaks. To obtain these parameters, they were used standard analyzing methods; namely the initial rise method and a curve fitting computer programme which seeks the trapping parameters optimally describing the experimental TL glow curve. After the analysis, it was obtained that the main peak at about 80 °C discloses a continuous distribution of traps having the activation energy $\approx$ 0.73 eV and

distribution of frequency factors. For the other glow peaks at 152, 179, 254 and 296°C, the activation energies of them were obtained as 0.92, 1.01, 1.52 and 1.70 eV, respectively. The analysis of the emission spectra ascribes that the peak at 80 °C has local transitions such as tunnelling. The higher temperature glow peaks involve transport of ionic charge-carriers.

Vasilis Pagonish and Christodoulous Michaeli have investigated the effects of annealing process on the TL of synthetic calcite samples [12]. In their paper, they have studied the effects of annealing temperature on the trapping parameters of the TL trapping center of synthetic calcite samples. The activation energy values of the trapping centers associated with the TL glow peaks were obtained using the initial rise and least-square fit methods. The least-square fit method extracts the TL glow curves as the sum of at least five individual TL glow peaks which have general-order kinetics. It was obtained that all the measured TL glow curves after different various dose levels and annealing temperatures could be fitted to the same set of trapping parameters. The obtained results show that the annealing processes do not change the nature of the trapping centers. This investigation was shown that the change in the TL sensitivity of synthetic calcite powders annealed in air atmosphere can be ascribed to changes occurring within the luminescence center and that no apparent changes take place in trapping center themselves.

Vasilis Pagonish, Eric Allman and Albert Wooten have examined the TL intensity from a continuously distributed trapping levels in the ultraviolet irradiated calcite samples [13]. In this study; geological and synthetic calcite samples have been studied. Both of them exhibit a low temperature TL glow peak at around 80 °C. This glow peak has been the subject of many investigations. They have believed that the TL mechanism of this peak involves transitions between the trap levels in the crystal rather than the more usual electronic transitions through the energy bands. The results of this experimental are consistent with the presence of distribution of trapping centers and this peak has first-order TL kinetics. In this study, various methods were used by these authors to obtain the kinetic parameters. A good agreement has obtained between all methods, except the isothermal decay method. Based on Gaussian distribution of activation energies, a theoretical model provides a self reliable description of the TL glow curves and the dose dependence of the

observed TL intensity. The width of Gaussian distribution of activation energies becomes narrower when the samples are annealed at temperatures above 500 °C.

Birol Engin and Olgun Güven have made a research on “the effects of heat treatments on the the TL sensitivity of naturally-occurring calcite minerals and their use as a γ -ray dosimeter” [14]. The feasibility of using naturally occurring calcite samples for gamma ray dosimetry was investigated within the research. Ionizing radiation dosimeters, which rely on the TL properties of calcite materials, have assisted in the solutions of dosimetric problems due to their long time storing capacities, independence of dose with radiation intensities. The authors were used three types of calcites from different origins in this study. The first type of calcite sample is stalactite (speleothem) that was collected from the geologically significant cave of Gökgöl in Zonguldak in northern Turkey. The second type of geological calcite samples was a flowstone that is obtained from the Damlataş cave in southern Turkey. The third type of geological calcite samples was marble that were collected from Marmara islands (Balıkesir) of Turkey. The TL dosimetric characteristics of these calcite materials were studied after different thermal treatments in the air atmosphere after the applications of low and intermediate gamma doses. All the samples after irradiations were stored at room temperature in the dark conditions. For studying the effects of annealing heat treatments, the natural calcite samples were annealed at temperatures between 200 and 700 °C. After the annealing processes, the samples were irradiated with Co-60 γ -irradiation for different dose levels. The results of this investigation were shown that the annealing procedures change the sensitivity of all calcite samples. It was obtained that the intensity of all glow peaks increases after the annealing processes, expects the peaks above 300 °C. The dose response curves of all TL glow peaks were also studied and it was observed that the dosimetric peaks of annealed samples at high sides of temperatures are different from the unannealed calcite samples. The dose response curves of all glow peaks were also be fitted with the linear mathematical functions. According to their findings, the dose-response curve of the charge trapping centers of dosimetric peaks remains unaffected after annealing processes. They were concluded that the annealing process of the samples does not change the properties of the trapping centers.

The thermoluminescence mechanism of doped syhntetic calcite samples were investigated by ZS Macedo, MEG Valerio and JF De Lima [15]. The samples were doped with Mn^{+2} , Mg^{+2} or Sr^{+2} , either seperately or simultaneously with more than one of these impurities. The partial heating measurement, emission spectra, isometric curves and annealing treatment were performed to investigate the role played by the impurities in the TL glow peaks of these calcite samples. They conclude that the crystals doped with only Mn^{+2} impurities show five TL glow peaks with emission spectra due to the characteristics of Mn^{+2} . The relative intensities of these five glow peaks are closely related to the other divalent dopant impurities that are added in the solution as Sr^{+2} or Mg^{+2} . These results imply that although Sr^{+2} and Mg^{+2} act as TL activators stabilasing slightly different electron traps, these impurities are not directly connected to the Mn^{+2} luminescence centre.

J.F.de Lima, M.E.G. Valeriaio and E.Okuno have investigated the effect of γ and UV-radiations on the TL intesity of Brazilian calcite samples [16]. The irradiated samples presented three TL glow peaks at around 150, 245 and 320 °C. All of them have a main emission band centered at 615 nm due to the $^4G-^6S$ transitions due to Mn^{+2} . The ESR signals have also studied and it was shown that three lines related to carbonate groups. The annealing treatments and irradiations effects on the ESR signals lead to the conclusion that $(CO^3)^{-3}$ and the (CO) ions are the electron trapping centres stabilized in two different symmetries. In the irradiation process, it was found that the TL peaks of these samples follow t^{-1} decay as a function of UV illumination time. In that sudy an alternative model for the TL emission of calcite samples is also discussed. They have considered that the recombination of charges is processed via thermally assisted tunnelling mechanism. Their results clearly show that the $(CO^3)^{-3}$ and $(CO^2)^{-1}$ ions establish trapping centre roles and the Mn as the recombination and the luminescence centre roles in the TL process in their calcite samples. The recombination of charges between the electron and hole traps takes place via a tunnelling process. The tunnelling process takes place between them when both centers are close enough to each others. Therefore, they have suggested that during the irradiation of samples, the $(CO)^{-3}$ and $(CO)^{-2}$ centres are formed in the vicinity of Mn impurities substituting for a Ca^{+2} of the calcite matrix.

In another study, V.Ponnusamy, V. Ramasam, M. Dheenathayalu and J.Hemalatha have investigated the effects of annealing processes in the TSL

sensitivity on natural blue colour calcite samples [17]. In this study, the thermally stimulated luminescence (TSL) glow curve characteristics of ten blue coloured calcite crystal of Southern Tamilnadu were investigated in detail. The natural TL glow curve measurements were carried out for all the samples and annealed in air atmosphere at the temperatures ranges between 200 and 700 °C. In all cases, the TL glow curves of annealed or unannealed samples were measured after the irradiation with a γ -dose of 500 Gy. In these cases, the TL glow curves have three glow peaks at around 145, 225 and 345 °C. The emission spectras of all the glow peaks have an emission peak at around 610 nm but they have different intensities for each sample. These authors were cocluded that the enhancement in the TSL sensitivity is not only depending on the annealing temperature but also annealing time. The dose response curve of glow curve after the gamma irradiation is linear in the range from 1 to 10^4 Gy.

A.N.Yazıcı, H.Toktamış and D.Toktamış have investigated the TL features of the calcite take out from natural sand which is handled in doing roasted chickpeas [18]. Additionally, the effects of dissimilar thermal behaviours in TL glow curve were watched. For three annealing process, the prepared instances were weighted 20 mg: the cycle of measurement at different temperatures, the annealing of the samples at different temperatures and the annealing of the samples at different annealing time at a fixed temperature. At 130 °C and 230 °C two explicit TL peaks were watched. Especially at 900 °C, the annealing of roasted chickpeas induces a large enhancement of TL. In dose response, linearity is watched for the worths up to 0.6 kGy and above 0.6 kGy linearity is not protected and dose response becomes sublinear. When the samples are annealed between 400 °C and 600 °C, the best reproducibility is obtained. At room temperature, all roasted chickpeas were irradiated with beta source (^{90}Sr – ^{90}Y) which delivers 0.040 Gy/s. Except for heating rate experiment glow curve evaluations were done handling a Harshaw TLD System 3500 Manual TLD Reader at 1 °C/s heating rate. In order to avoid undesired signals, the irradiated instances were read out in N_2 atmosphere. In the reader a standard clear glass filter was forever installed between photomultiplier tube and the planchet. For dissimilar aliquots, every experiment was recured three times. The study was based on grain size influence, pre-irradiation thermal treatments (annealing), heating rate experiment and dose response. For example, 20 mg instances were prepared from sand instances

which were eliminated at different grain sizes. Every was irradiated with beta source of about 30 Gy and evaluated glow curve by the TLD reader. 13 samples, in the dose response work, weighted 20 mg, were irradiated for 13 different doses with beta source.



CHAPTER 3

THEORY OF THERMOLUMINESCENCE

3.1. Luminescence Phenomena

Light is a form of electromagnetic wave and it has energy. The other shape of energy such as thermal energy must be provided to the materials to create light from them. There are two general ways for emission of light from the materials, namely they are luminescence and incandescence. The luminescence is the emission of optical radiation from matter in the visible, ultraviolet and infrared regions. This phenomenon should be separated from incandescence phenomena. In the incandescence phenomena, the optical radiation diffused from the material by virtue of it being at high warmth (blackbody radiation). The luminescence phenomena can occur under many different circumstances and in a wide variety of matters. For example, organic or inorganic materials, many crystals, polymers and amorphous materials emit luminescence under suitable circumstances. There are many types of luminescence forms. The most of them are given their names, which to get the emission mechanism and reflect the type of radiation used to excite the material. However, the main characteristic of all luminescences is that the emission of light after the stimulation by some internal or external process and the emitted light is an attribution of the object itself.

As mentioned previously, the incandescence phenomenon is different from the luminescence phenomena. For example, the wire can then glow white hot as in an incandescent light bulb. In an ordinary light bulb filament seen this continuum is quite different to the incandescence. In this case, the electrical energy from a current of electricity is directly transferred to the metal atoms of the wire and this energy causes heat up and them to vibrate atoms. A great deal of heat accompanied with a characteristic of this type. The electrical energy is then transformed into optical radiation with an activity of about 80% in the UV-Visible-Infrared regions. On the

other hand, less than 10% of the total radiation is the visible region light being emitted. The remaining part of optical radiation is especially in the form of infrared spectrum. The spectrum of optical radiation emitted from any other object, or, a hot wire is not sensitive to the attributes of the object. Anyway, all hot objects emit heat and light with very like characteristics of them and that is well defined by models which based on a generic blackbody.

The term luminescence infers luminous emission which isn't thermal in root. Therefore, the light in the luminescence phenomena is called as 'cold light' which is light from energy sources, which lower temperature and takes place at normal. The luminescence occurrences can be observed in the nature like, fireflies, glowworms, and deep-sea animals and also in certain sea bacteria. This luminescence has been studied in several scientific areas by dissimilar scientists all over the world such as, chemist, physicists, bio medicine. In archaeology, geology, engineering and several industrial applications for quality control, developments and research areas, this technique is frequently applied. At the continuum of luminescence, if light is event on a substance, the energy of radiation is adsorbed and re-spreaded as a light of a longer wavelength (Stokes law). At the continuum of luminescence, the wavelength of light spreaded is not depend upon the event radiation. It is completely characteristics of a luminescent material. This diffusion of luminescence does not contain the diffusion of blackbody radiation. It includes two steps. The one step includes the the excitation of electronic system of a crystalline material to higher energy state. And the second step includes the subsequent emission of photons or simply light from the materials.

The emission of light from the materials takes place at luminescence phenomenon is classified under into parts; phosphorescence and fluorescence. If the characteristic time ' τ_c ' is greater than that of 10^{-8} sec, it is known as phosphorescence. If it is less than 10^{-8} sec, it is known as fluorescence. If the fluorescence diffusion is seen to be spontaneous as ' $\tau_c < 10^{-8}$ sec, so fluorescence diffusion is seen to be taking place immediately with stopping radiation ceases and adsorption of radiation. On the other hand; the phosphorescence is characterized by delay between the radiation absorption and the time ' t_{max} ' to reach full intensity. After the excitation, the phosphorescence is also seen to continue for some time has been removed. On the other hand, if the delay time between adsorption and emission is much shorter, it is very difficult to distinguish between phosphorescence and

fluorescence. The phosphorescence is also subdivided into two main types. They are long-period ($\tau_c > 10^{-4}$ sec) and short period ($\tau_c < 10^{-4}$ sec) phosphorescence. The fluorescence is actually independent of temperature, whereas phosphorescence displays powerful temperature dependence. An enormous number of materials indicate the feature of both luminescence types. But, especially inorganic solid and insulating materials such as alkaline earth halides and alkali, phosphates sulphate, borates, and quartz (SiO_2) are handled in various applications of luminescence applications. This type of luminescent solid materials is commonly referred to as phosphors.

The TSL is the phenomenon of diffusion of light from a solid which under circumstances of increasing temperature has been before hand exposed to ionizing radiation such as X-rays, UV rays, α -rays, β -rays, and γ -rays. The TSL is different from another luminescence continuum such as chemiluminescence, electroluminescence. In this luminescence, heat is not a stimulating agent but it moves merely as a stimulant. However, heat is a stimulating agent in TSL. Therefore, it is better familiar as thermally stimulated luminescence. But, the stimulation is firstly succeeded by any traditional radiation sources such as UV rays, X-rays, α -rays, β -rays and γ -rays. Many organic and inorganic solids such as plastics, ceramics and a host of materials glasses exhibit TSL. By far isolating solids contributed with proper chemical impurities that are termed as activator are the most susceptible TL materials.

The energy band theory of crystalline solids is normally used to clearly explain the TSL phenomenon. If a solid is irradiated with ionizing radiations at room temperature, the holes and electrons are produced from the valance band (VB). The crystal defects in the solid cause the entity of localized energy levels inside the forbidden gap of the material. After irradiation, the holes and electrons can be trapped at those defect sites within the band gap. If the solid is heated above room temperature, those trapped electrons/holes get adequate thermal energy to evade from the trap to the respective bands such as electrons to the conduction band and holes to the valance band. Then here they may recombine with trapped holes or electrons at the recombination centers and emit light or they may get re-trapped again in the traps.

Recombination center or sometimes called as luminescent center is the site of recombination of electrons and holes. When the recombination is radiative between electrons and holes in the recombination center, that center is named as luminescence center. The plot of density of spreaded light versus the temperature or sometimes time, it is known as TL glow curve. The glow curve can display one or more glow peaks depending upon the number of hole/electron traps with dissimilar trap depths, present in the lattice. Those peaks can or can not be well sapartted from each other. The peak temperature, intensity of the glow peaks and shape of these glow peak are characteristic of the particular substance and defects presents and impurities within the lattice. The nature of the TL glow peaks and glow curve give information about the luminescent and trapping centers present in the material. This is could be mentioned that the TL is largely susceptible to constructural defects in crystals. Whereas the other techniques such as Electron Paramagnetic Resonance and Optical Absorption Spectroscopy techniques are sensitive only for comparitevely higher defect concentrations within the crystals such as 10^{12} cm^{-3} , the defects concentrations as low as 10^7 cm^{-3} also can give measurable TL signal if radiative recombinations are dominant in the recombination centers. Simply, we can understand that the thermoluminescence glow peak is the identification of the trapping center and the reunification centers for the watched light diffusion. Aside from being a tool for the investigation of crystal defects in solids, the TL has also found prevalant handle in archeological dating of pottery, ceramics, meteorite research and etc.

As mentioned previously, when some semiconductor or insulator materials are heated, the TL signal is the emitted from these materials. Barely, it should have adsorbed high energy radiation prior to its excitement by heat. In general, three fundemantal ingredients are required to see the TL signal from materials. They are: 1-) The luminescence emission is should be triggered by heating the materials. 2-) The material must have band gap such as insulators or semiconductors. It is well known that metals do not exhibit luminescent properties, because they don't have band gap. 3-) The materials must absorbed radiation energy during exposure to ionizing radiation before heating process. Another important characteristic of TL materials is that, once they have heated to stimulate the light emission, they could not be re emitted TL signal by simply cooling the sample room temperature and again reheating. So as to display the TL signal from the substance, it has to be re-exposed

to ionizing radiation and then increased its temperature to again see light diffusion from it.

Many investigators have extensively studied the mechanism of TL in many different crystals. The understanding of TSL emission mechanism in the materials is the considerable field of fundamental research in physics area. To understand the roles of impurities in the TL phenomena, some researchers have studied the TL mechanism from impurity doped materials and compared them their results with pure (undoped) materials. Therefore, it is a topic of investigation to give latest reasonable mechanism of TL with enlarging knowledge of solid state physics. Barely, the understanding mechanism of TL had discovered very high application potentials of it in several fields. For example, the development and modernization in the equipments; and better understanding of thermoluminescence mechanism have helped the professional to solve their problems in many fields [3, 19].

Thermoluminescence (TL) dating by means of evaluating the assembled radiation dose, it is the specification of the time elapsed due to substance including crystalline minerals that were either warmed (ceramics, lava) or exposed to sunlight (sediments). The process of thermoluminescence starts when a crystalline material is warmed in the course of evaluations. A feeble light signal by thermoluminescence spreads that is related to the radiation dose adsorbed by the substance. It is a sort of luminescence dating. Settlements are more expensive in the dating process. A relatively significant amount of sample material has been destroyed, which can be a limitation in artworks. The heating have taken the object above 500 °C, which covers many ceramics, although very high-fired porcelain creates another difficulties. It usually works well with stones heated with fire [20].

3.2. Crystal Structures and Crystal Defects

3.2.1. Alkali Halides

The alkali halides are typical ionic compounds, and their physical properties are in general well known. The majority of the alkali halides crystallize in the rock salt structure, as shown in figure 3.1. In this structure each cation (alkali metal ion M^+) is surrounded by six nearest-neighbour anions (halogen ions X^-) and each by six nearest neighbour cations. The cations and anions are each situated on the points of

separate face-centered cubic lattices, and these two lattices are inter-leaved with each other. These materials, of the type M^+X^- , where M=Group I alkali metal and X=Group VII halogen, are possibly the best known of all ionic compounds.

Research into alkali halides was initiated in the early 1920s in the hope that it would aid our understanding of the behaviour of solids as a whole. At normal temperatures the alkali halides are highly insulating solids. The difference in energy between the valance band and the conduction band in pure alkali halides varies from 5.38 eV (229 nm) for sodium iodide (NaI) to 13.6 eV (105 nm) for lithium fluoride (LiF) [21].

The alkali halides are transparent to light in the visible, far infrared and near ultraviolet. The ultraviolet absorption is related to the electronic transitions, while the infrared absorption is correlated with the vibrations of the ions composing the solids. Many chemical impurities, when incorporated in the alkali halides even in parts-per-million (ppm), affect the physical and chemical properties of alkali halides. When the temperature is raised, the electrical conductivity increases very rapidly. The carriers of electric charge are ionic in nature, not electronic [21].

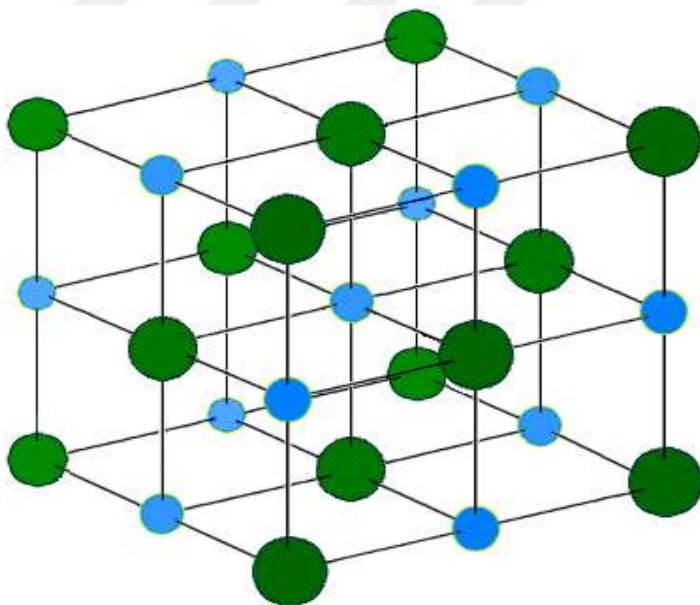


Figure 3.1. The structure of the rock salt (NaCl) type alkali halides. [22]

3.2.2. Imperfections in the Alkali Halides Crystals

The crystal lattice is formed by a repeated arrangement of atoms. The positions of molecules or atoms happen on iterating fixed distances, defined by the unit cell parameters. The detail of this arrangement can be determined by analyzing the diffraction effects which are produced when a beam of some appropriate radiation (x-rays, electrons, or neutrons) is incident on the crystal.

In reality, crystals are never perfect and contain various types of imperfections and defects. The crystallographic defects interrupted the regular patterns. There are two types of geometrical defect in a crystal. These are; point defects and dislocations. In general; point defects are easy formed in the alkali halide crystals by irradiations or impurities. The point defects are one of the types of crystals defects and they happen only at or around a single lattice point. They aren't offered in space of any size. The elemental impurities are incorporated into alkali halide crystals and can be splitted into the following 7-groups which give point defects in these crystals. They are (1) monovalent metals; (2) hydrogen and alkali metals; (3) metals of group IIA of the periodic table; (4) metals of group IIB of the periodic table; (5) rare earths; (6) halogens; (7) transition metal impurities [21].

In ionic crystals, many point defects are named as luminescence center, F-center, or a color center. Vacancy defects are occupying a perfect crystal lattice sites, but they are empty. When a neighboring atom acts to occupy a vacant site, the vacancy acts in the contrary to the site which is used to be occupying by the acting atom. The steadiness of the encircling crystal structure ensures that the adjacent atoms would not easily downfall around the vacancy. The neighboring atoms essentially act away from a vacancy in some materials, because they experience pull from atoms in the environments. A couple of vacancies in an ionic solid (or a vacancy) is occasional named a Schottky defect [23].

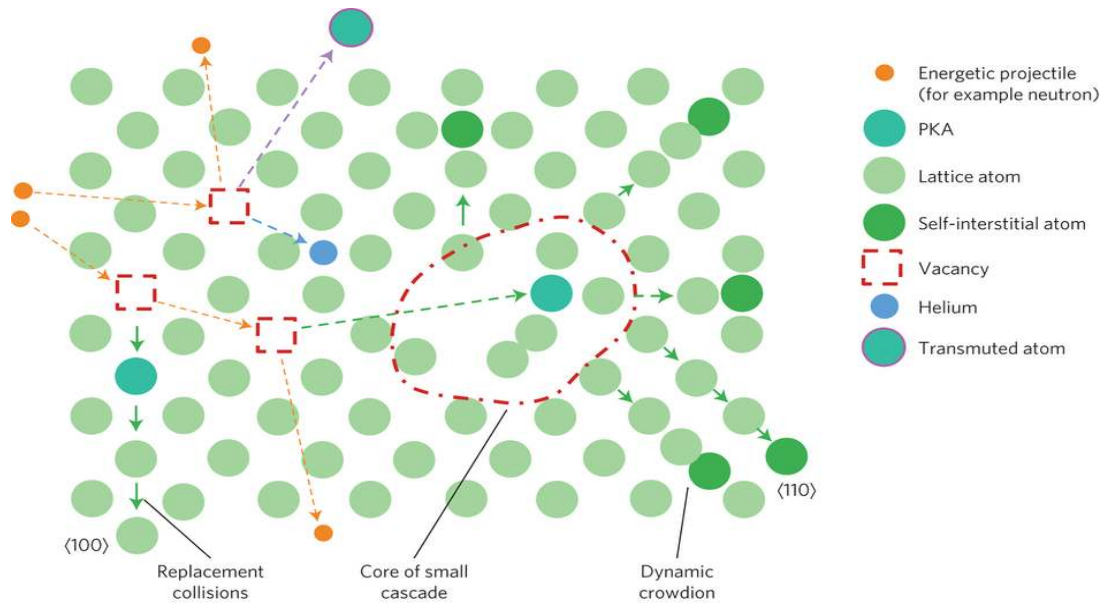


Figure 3.2. The schematic representation of some types of point defect in a solid [23].

The interstitial crystal defect is an atom that occupies a site in the crystal structure at which it is generally not an atom. An interstitial and an adjoining pair of a vacancy is frequently called as Frenkel pair or Frenkel defect. It is caused when an ion enters the interstitial sites, it creates a position. Because of the fundamental limitations materials treatment methods, the materials can never be completely pure, which many factors cause defects in the crystal structure. In the event that an impurity; the atom is frequently penetrated at a regular atomic site in the crystal structure. That is neither the atom on an interstitial site nor is a vacant site and it is named a substitutional defect. This atom was not supposed to be crystalline atom and therefore it is not an impurity. In some instances where the radius of the ion (substitutional atom) is highly smaller than that of the ion (atom) it is replacing. So its balance position could be moved away from the lattice site. Those kinds of substitutional defects are frequently called as off-center ions. There are two different sorts of substitutional defects: Aliovalent substitution and isovalent substitution. The aliovalent substitution is where the ion that is substituting the original ion is of a different oxidation substituting that original ion is of a different oxidation state than the ion it is replacing. The isovalent substitution is the ion that is substituting the original ion in the same oxidation state as the ion it is replacing [21-23].

When atoms of different types exchange positions, anti site defects occur in compounds or in an ordered alloys. For instance, many alloys have a regular crystal structure in which every another atom is a different kind; for suppose that sort A atoms sit on the corners of a cubic lattice, and sort B atoms sit in the center of the cubes. If one A atom is at the center of a cube, the atoms usually occupied by an atom B, and is therefore an antisite defect. That is neither an impurity nor an interstitial, nor a vacancy [21-23].

The complexes can be formed between different types of point defects. For instances, if a space come across an impurity, both of them connected together, if the pollution is excessively large for this lattice. The interstitials could form 'dumbbell' structures or 'split interstitial' where two atoms actively share an atomic site, resulting in neither atom essentially occupying the site. The displacements are linear defects around which many of the atoms of the crystal lattice are misaligned. There are two simple sorts of dislocations, the screw dislocation and the edge dislocation. The "mixed" dislocations, connecting aspects of both sorts, are also general. The edge substitutions (dislocations) are caused by the finality (termination) of a plane of atoms in the middle of a crystal. On such an occasion, adjacent planes are not straight, but instead bend around the edge of the terminating plane crystal structure, arranged on both sides excellent. The screw dislocation is many difficult to envision, but simply comprises a structure in which a helical path is traced around the dislocation line (linear defect) by the atomic planes of atoms in the crystal lattice. The entity of substitution (dislocation) results in lattice strain (distortion). The substitution (dislocation) are line defects corresponding to "subtracting" an angle around a line or "adding". Basically, if you follow the directions around the line of crystal defect, which means you get a rotation [21-23].

3.2.3. Defect Production Techniques in the Alkali Halides Crystals

Defect centers can be generated in a crystal by a variety of techniques. These are simply (1) additive coloration, (2) electrolytic coloration and (3) exposure to ionizing radiation. The first two techniques are extremely difficult and require a high technology to produce defect centers in the alkali halide crystals. The third type of defect production techniques is to utilize the ionizing radiation. The term ionizing radiation includes all sources that can generate free electrons and holes in the

materials. The energies range from ultraviolet photons of about 10 eV, through soft x-rays of 10-60 keV and ^{60}Co gamma rays of 1.25 MeV, $^{90}\text{Sr}/^{90}\text{Yb}$ β -rays of 2.25 MeV, up to high energy protons or neutrons of 100 MeV. Many specifically; the thermally stimulated luminescence (TSL) is a phenomenon of light emission of ionizing radiation exposure in the remaining solid under increasing temperature conditions [21].

3.3. Theoretical Background of Thermoluminescence

As mentioned previously, the TSL is the phenomenon of light diffusion from a previously irradiated material with linear heating rate in the course of heating. If a material is applied to ionizing radiation it undergoes mechanical stress or certain chemical reactions and an apparent proportion of the released charge carriers (holes and electrons) could be trapped at apparent defects in the lattice. They are named as the charge traps. The TL from the material is very susceptible to;

- i-) Defect pattern present in the material,
- ii-) Crystallization history,
- iii-) Thermal history,
- iv-) Size of particle,
- v-) Pre-thermal, mechanical and radiation effect, and
- vi-) The amount and nature of impurity.

Firstly, the theory reports that no electron could exist in the substance with energy states between valance and conduction bands. If the substance is stimulated by any ionizing radiations many electrons in the VB are stimulated and they obtain energy states corresponding to the CB. Generally, those electrons couldn't remain stimulated forever. The life span of an electron in the CB is very short and the electron remains in its ground state instantly giving away the energy to heat up the crystal lattice or in the form of light. Barely, present in the material (for example, suitable ionic size and charge) an impurity atom could have energy situation in the prohibit band. Those are the metastable energy states having significant life span. An excited electron, instead of getting back to normal valance band situation, it is

'trapped' by an electron trap. Likewise, also a 'hole' is trapped at an energy state very close to the VB. The trap depth is called as the energy level of hole trap with respect to the VB or the electron trap with respect to the CB. These traps correspond to energy storage after the first excitation of a material with ionizing radiations. When now the material is heated above irradiation temperature, the heat supplied to the material is able to excite the electron out of the traps (detrapping) and the electrons get back to the ground state. When the conditions are suitable for the emission of light in this 'get back process' then thermoluminescence occurs. Alternatingly, a hole can be stimulate in the valence band where it wanders till it re-joins with an electron at the trapped counter- part emitting the TSL [19].

When the traps are not very profound, recombination and de-trapping can already happens at an important rate around the irradiation temperature and this is resulting in a short half-life of the stored energy. If the half-lives of trapped electrons are a few months, they are generally corresponding to glow peak temperatures bigger than about 150 °C (the traps are the profound enough to result in adequate storage stability at room temperature), the influence becomes of dosimetric interest. The glow curve, generally corresponds to a trap has different energy depth, exhibits several peaks. It is possible that the holes and electrons are de-trapped more or less simultaneously in many phosphors and they re-join at a completely new site which is named recombination center or luminescence center. The TL glow curve will in that case represent an influential thermal activation energy needed by the trapped hole/electron to overcome a potential barrier between recombination center and the trap. If that retrapping possibility is substantial, the shape of glow curve is different from the case when the retrapping is absent. Furthermore, the recombination possibility for the detrapped charge carrier depending upon on the number of existing unused recombination centers with time (i.e. as the heating proceeds). Suchlike process is named bimolecular process or a second order. Whereas the simplest case where the recombination has a constant possibility with time is named monomolecular process or a first order. There are practical circumstances where the de-trapped charge carriers re-join directly without having to be stimulated in the valence/conduction bands. That is a case of TL including isolated luminescence center and process follows first order kinetics [19].

In dosimetric investigations, the precise amount of radiation energy should be absorbed from the material. It is an important factor to achieve the desired result. In addition, the better use of dosimeters could be succeeding usually by accurate measurement of absorbed energy from the material. The measurements of quantities form the radiation dosimetry are referred as dose measurements by TL dosimeters. Therefore, the professionals have highly studied the TL dosimeters to standardize and investigate some analytical methods to guess (estimate) the doses of radiations. The principal basis in the thermoluminescence dosimetry (TLD) is that TL output is directly commensurate to the radiation dose received by the phosphor before the measurement and therefore ensures the means of guessing occult irradiations. Additionally, the TL is an excellent passive measurement even during long years of order, so we can provide integrated irradiation level. Therefore, this technique finds a high application in the monitoring of radiation doses received by workers on a routine basis; weakly/monthly/yearly depending on whatever a circumstance some warrant. Some of the TL phosphors aren't similar to tissue (in terms of energy adsorption by irradiation) and therefore the related dose which is medically substantial to a radiation worker from conservation point of view is not readily obtained [19].

3.3.1. Band Model and Electronic Transitions in the Alkali Halides

If an insulator likes an alkali halide, it can be described quantum mechanically by the band model. The CB is separated from the VB by the forbidden region. Figure 3.3 shows schematically the energy band models of an alkali halide, the electronic energy levels within the forbidden band gap, and the common electronic transitions in these levels [21].

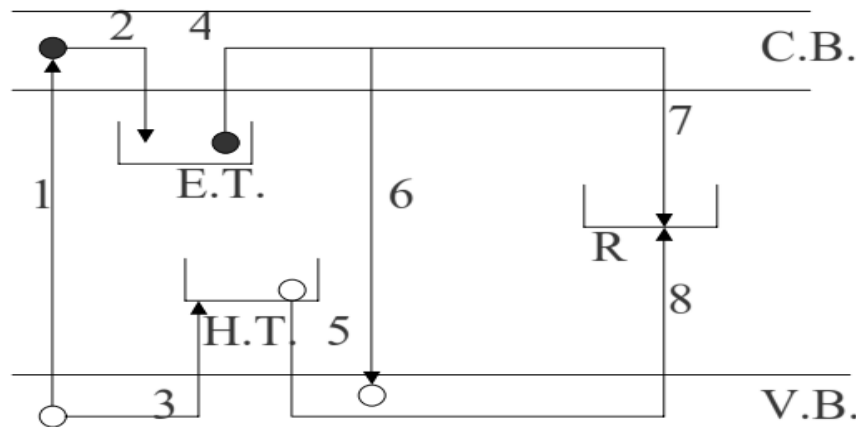


Figure 3.3. Common electronic transitions in crystalline solids: (1) ionization; (2) and (3) electron and hole trapping respectively; (4) and (5) electron and hole release; (6) direct recombination; (7), (8), (9), (10) indirect recombination. (ET: Electron Trap; HT=Hole Trap; R_1 , R_2 , and R_3 Recombination Centers) [21].

For a crystal without any lattice defects within it, the energy levels are not generated between the valance and conduction bands. The localized energy levels within the band gap introduced may be discrete or may be distributed. It depends upon the exact nature of the defect and host lattice. The true energy dispersion is defined by the Fermi level and the temperature of the electrons. When the temperature is greater than zero kelvin ($T > 0$ K), the energy levels within the band gap are filled following a Boltzmann distribution. But; all of the electrons have energy below the Fermi level at absolute zero temperature. The Fermi level in semiconductors lies in the middle of forbidden band gap.

The valence band (VB) just below forbidden band gap has been occupied almost entirely normally. The conduction band (CB) is above the Fermi level, normally almost completely empty. The VB is so nearly full in materials. Thereupon, electrons are not mobile inside this band and not flow as an electric current. If VB electrons acquire sufficient energy to pass CB, it could flow freely among the nearly empty CB energy states. After passing CB, the electrons left behind an electron hole. It could flow as electrical current absolutely like a physical charged particle. While the *recombination* defines processes by which a CB electron misses energy and in the VB re-occupies the energy state of an electron hole; the carrier generation defines continuums by which electrons earn energy and act from the VB to the CB. [22].

The net charge carrier density to remain constant, the thermal balance of generation and recombination in a material are balanced. The balance (equilibrium) carrier intensity (density) that results from the equilibrium of those interactions is guessed (predicted) by thermodynamics. Each energy state resulting in the occupation of the energy bands probability given by the Fermi-Dirac statistics [23].

3.4. Models for Thermoluminescence

3.4.1 Mathematical treatment

The purpose of the thermoluminescent light emission related mathematical analysis of the phenomenon in this connection is to obtain satisfactory information. From a theoretical perspective, the TL is connected directly with the band structure of crystalline solids and lattice irregularities and especially to the effects of impurities within the crystals. When ions of either signs act away from their original sites, those can be described as centers that may happened. Therefore, these vacancy states can interact with free charge carriers during the irradiation process and trap them. Alternatively, ions can locally disturb and break the ideal lattice geometry and diffuse in interstitial positions. Ultimately, impurity ions could disturb the lattice order, because of their valences and sizes, usually different from their neighbour ones. In addition, these external defects could interact with internal ones, and at the end you could combine them both into more complex configurations. From an atomic point of view a defect could be defined by means of the sign. For such explanation, each center corresponds to a characteristic energy. When supplied heat energy to the trapped charges to liberate them from traps, this energy may be called as the amount of minimum energy. Therefore; the center and traps are demolished after this process and restoring a situation of local order.

3.4.2 First-Order (b=1) Kinetics

In 1945, Randall and Wilkins starting the work on phosphorescence, they developed a widely used mathematical representation for each TL glow peak in a thermoluminescence glow curve. They produced the well-known first order statement and their mathematical derivation was based on the energy band model that includes one trap and one recombination (OTOR) center. Figure 3.4 displays the basic model for the theoretical treatment of this model. As seen, the metastable states (two localized levels electron and hole traps) are considered between delocalized bands; valence band (VB) and conduction band (CB). Anyone, one of the localized band acts as a trap T , and the other acts as a recombination center R . The energy level differences between the bottom of the CB and the trap T is named trap depth. It is

generally known as activation energy E . This energy is the necessary energy in order to liberate a trapped charge; i.e. an electron, from its trap which is called as T . The probability rate (p) has get away of a trapped charged particle per second from the trap. It is given by the Arrhenius equation and having take into account that the trapped charges such as electrons in the trap T have a Maxwellian dispersion of thermal energies [2, 4, 19].

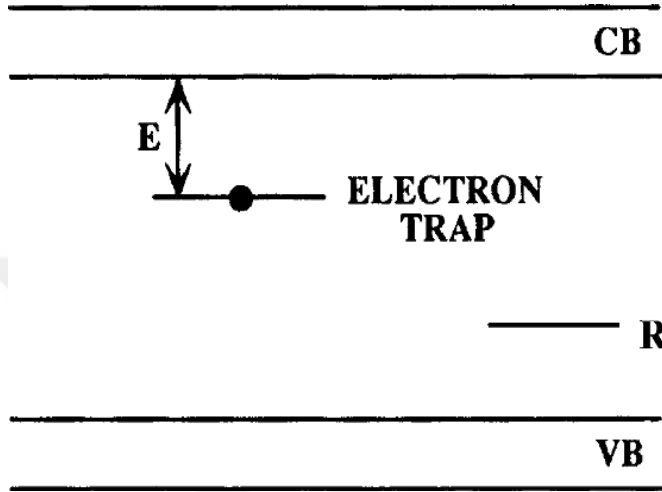


Figure 3.4. Randal-Wilkins model [2].

Wilkins and Randall was supposed insignificant retrapping by the traps during the heating process. They have supposed that $m\sigma_{mn} \gg (N - n) \sigma_n$. Note that this is a circumstance among missions $m(t)$ and $n(t)$. It can be true at the starting of the glow peak. The retrapping probability beings to start with increasing temperature and then it may become advancingly false at a later stage. Under those "slow-retrapping" situations, the equation becomes

$$I_{TL} = n s \exp \{-E / kT\} \quad (3.1)$$

Also we noticed that $-dn/dt \propto n$, so we have a first-regulation reaction. When integrating this equation from $t=0$ up to a desired time t , using a stable heating rate, $\beta = dT/dt$, it gives the well known Randall–Wilkins first-order ($b=1$) statement for the mission $I_{TL}(T)$; namely

$$I_{TL} = n_0 s \exp\{-E/kT\} \exp\{-(s/\beta) \int_{T_0}^T \exp\left\{-\frac{E}{kT}\right\} dT\} \quad (3.2)$$

where E (eV) is the activation energy, I is the glow-peak Intensity, n_0 is the initial concentration of the trapped carriers in the traps, s (s^{-1}) is the frequency factor, T_0 is

the initial temperature, $T(K)$ is the precise temperature, β is the heating rate and k (eV K⁻¹) is the Boltzmann's constant [2, 4, 19].

3.4.3 Second-Order (b=2) Kinetic

Gibson and Garlick (1948) take into account the alternative probability that retrapping dominates, i.e. $(N-n)\sigma_n \gg m\sigma_{mn}$. Applying that inequality to the GOT statement, together with $N \gg n$ and $n = m$, gives

$$I_{TL} = -dn/dt = s (\sigma_n / N \sigma_{mn}) n^2 \exp\{-E_1/kT\} \quad (3.3)$$

Contrary to the first-order ($b = 1$) case, if it is real at the beginning, the inequality $m\sigma_{mn} \ll (N - n)\sigma_n$ will remain real all over the TL peak. Integration of this gives

$$I_{TL} = (n_0^2 \sigma_n / N \sigma_{mn}) s \exp\{-E_1/kT\} [1 + (n_0 s \sigma_n / \beta N \sigma_{mn}) \int_{T_0}^T \exp\{-E_1/kT\} dT]^{-2} \quad (3.4)$$

This equation is known as the Garlick and Gibson TL equation and it is satisfied for second-order ($b=2$) TL kinetics. Moreover note without the presumption of dominating retrapping that one can reach at an alike equation directly, handling only the presumption $\sigma_n = \sigma_{mn}$, as long as $n = m$. The ratio here, $\sigma_n = \sigma_{mn}$ is union. Equation could be recast in both cases as [2, 4, 19]

$$I_{TL} = n_0^2 s \exp\{-E_1/kT\} [1 + (n_0 s / \beta \int_{T_0}^T \exp\{-E_1/kT\} dT)]^{-2} \quad (3.5)$$

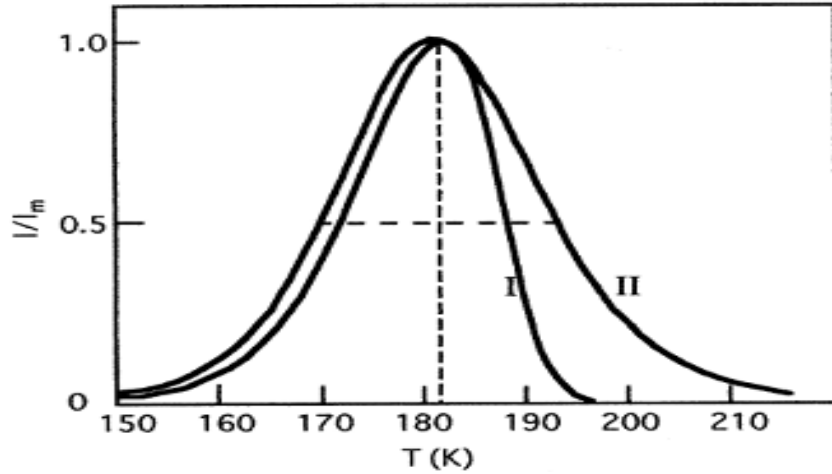


Figure 3.5. The comparison of first-order ($b=1$), second-order ($b=2$) TL glow peaks [19].

3.4.4. General-Order ($b \neq 1$) Kinetics.

The Garlick-Gibson and Randall-Wilkins types of the TL equations have been provided with the use of specific presumptions relating the relative sizes of the recombination possibilities and retrapping. Taking into account the form of the statements produced from those presumptions, May and Partridge (1964) wrote an empirical statement for general-order ($b \neq 1$) thermoluminescence TL kinetics:

$$I_{TL} = n^b s^1 \exp\{-E_1/kT\} \quad (3.6)$$

Integration of this gives

$$I_{TL} = s^{11} n_o \exp\{-E_1/kT\} [1 + ((b-1) s^{11}/\beta) \int_{T_0}^T \exp\{-E_1/kT\} dT]^{-b/b-1} \quad (3.7)$$

where $n_o s^{11} = s^1 n_o^{(b-1)}$. May and Partridge (1964) improved that statement so as to perform it to these situations where the disparity handled above do not perform. Actually, one can easily visualise some combinations of worths for N , n , m , σ_{mn} and σ_n for which the first-order or second-order possibility could be inoperative. When it is remembered that especially every of those parameters is also depend on the temperature. For the Garlick-Gibson or Randall-Wilkins expression to be acceptable one need restricts concerning the notional dimensions of these periods to perform across the all temperature range of interest [2,4,19].

CHAPTER 4

THERMOLUMINESCENCE ANALYSIS

4.1 CGCD Method

The Computer Glow Curve Deconvolution (CGCD) is an important technique to obtain kinetic parameters from TL glow curves. This technique has been used by researches who are working in thermoluminescent dosimetry area for at least two decades. The CGCD applications began to appear in the scientific literature in the early 1980s. This method is one of the most important ways to derive values of parameters E , s , and b these methods of computerized curve fitting it is more accurate in values with apparent success in use. The procedure is began, by find out the approximate positions of the most prominent peaks in the glow-curve and estimate each values of E , s , and b by using one of the analytical method and a theoretical curve is computed by using the general-order equation for $b \neq 1$, or the first-order equation for $b=1$ [21, 25].

The numerically calculated and computed glow curve was compared with the measured actual experimental glow curve and a root mean square (RMS) deviation was estimated between them. The next actions are changing E , s , and b values up to a minimum value of the RMS deviation were obtained. This method can be used in largely overlapping glow peaks without acting to heat treatment. Therefore it is useful and better than experimental methods to analyze the glow curves. In this method, two different models was used in the computer programs. In the first model, the TL glow curve is approached to the first-order thermoluminescence (TL) kinetic by using the below expression [21, 25],

$$I(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left[\left(-\frac{skT^2}{\beta E}\right) \exp\left(-\frac{E}{kT}\right) \right]^{(0.9920-1.620\frac{kT}{E\alpha})} \dots\dots\dots(4.1)$$

In the second TL model; the TL glow curve is approached with general order thermoluminescence (TL) kinetics by using below the following equation.

$$I(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \left[1 + \left(-\frac{(b-1)skT^2}{\beta E} \exp\left(-\frac{E}{kT}\right)\right)^{(0.9920-1.620\frac{kT}{E\alpha})} \right]^{b/b-1} \dots (4.2)$$

where all of them are previously annotated. The summation of overall glow peaks and contribution of background can lead to complex glow curve formula as described below:

$$I(T) = \sum_{i=1}^n I_i(T) + a + b \exp(T) \dots\dots\dots(4.3)$$

where $I(T)$ is the intensity of fitted total glow curve, a and b allows for the electronic noise contribution from the planchet and TL dosimeters infrared to the background. Starting from the equation (4.3), the procedure of the least square minimization and also the figure of Merit (FOM) was used for judging the fitting results on whether they are good or not. Like,

$$FOM = \sum_{i=1}^n \frac{[N_i(T) - I(T)]}{A} = \sum_{i=1}^n \frac{[\Delta N_i]}{A} \dots\dots\dots(4.4)$$

where $(N_i(T))$ is i -th experimental data points (total number of data points is $n=200$), $I(T)$ is i -th fitted points, and (A) is the integrated area of the deconvoluted TL glow curve. From many experiences, it can be said that if the (FOM) values are between (0.0%) and (2.5%) the fit is good, and for (2.5 %) and (3.5%) the fit is fair, and if greater than (3.5%) the fit is bad. To obtain the graphic representations of the agreements between the experimental and fitted TL glow curves, the fitting computer program also plots the function,

$$X(T) = \frac{N_i(T) - I_i(T)}{\sqrt{I_i(T)}}$$

which is a normal variable with an expected value (0) and $(\sigma=1)$ where $(\sigma^2(T)=I_i(T))$ [21, 25].

CHAPTER 5

Experimental Prodecures

The materials, equipments and experimental procedures utilized in this work are described in below sections.

5.1. Materials

The samples used in this study were natural calcite crystals obtained from the environmental regions of Gaziantep city.

5.2. Equipments

5.2.1. Radiation Source and Irradiation Prodecure

After thermal annealing processes, the samples were abruptly cooled to room temeperature and then the collected calcite samples were immeadiately irradiated at room temperature. They were irradiated with ^{90}Sr - ^{90}Y β -source. The activity of this source is approximately 100 mCi. It was calibrated by manufacturer in 1994. The recommended working life-time of this radiation source is about 30 years. Sr-90 emits high energy beta particles from its daughter products (^{90}Sr -0.546 MeV together with ^{90}Y β -2.27 MeV). It is well known that the β -radiation is absorbed in the medium, i.e in air. Therefore, its intensity is quickly decreases with distance much more rapidly than inverse square law calculations. Therefore, the maximum range of Y-90 beta particles in air is approximately 9 meter [21]. The irradiation apparatus is a supplementary part of the 9010 Optical Dating System. This system was purchased from Little More Scientific Engineering in England [26] and it is interfaced to a personal computer (PC) using a serial RS-232 port. This source approximately gives 0.015 Gy at per second. In this study, the calcite samples were irradiated to different dose levels in the region ≈ 0.9 Gy and ≈ 864 Gy.

5.2.2. TL Analyzer and TL Measurement

The glow curve measurements of all studied samples in this study were performed using a Harshaw TLD System 3500 Manual TL Reader [27]. This reader economically provides high reliability to the researchers in the TLD area. This system includes both a TLD Reader and a personal computer that is connected through a standard RS-232 serial communication port to control the TLD Reader. The block diagram of this reader is shown in figure 5.1.

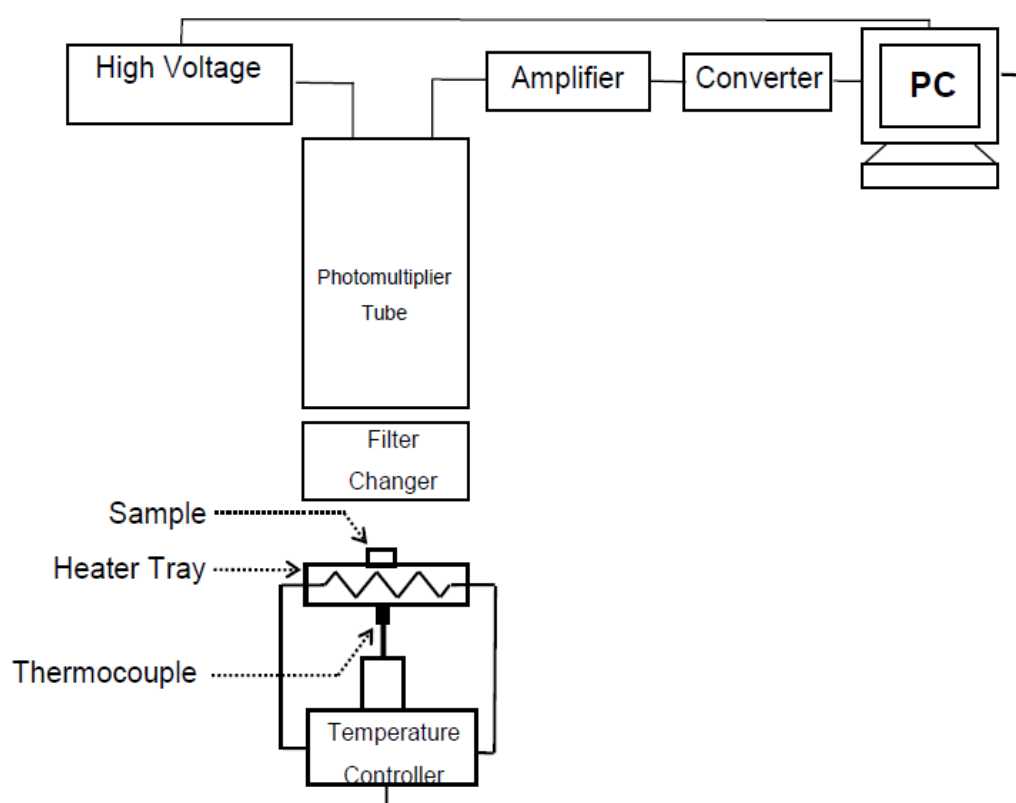


Figure 5.1. Basic Block diagram of TL reader [21]

All operating requirements of this system are shared between TLD reader and PC that controls this reader. TLD Shell software runs on the PC. The TL intensity acquisition and conditioning are performed in the TLD reader. All data storage and operator inputs are performed on the PC. In this way, each TL glow curve is analyzed using a computerized glow curve deconvolution (CGCD) program which is based on a Marquardt algorithm minimization procedure, associated to first- and general-order kinetic expressions. The CGCD program resolves the individual TL glow peaks present in the glow curve. This program provides the best values for the

different TL peak parameters. The TLD reader uses a contact heating regime between the samples with a closed loop feedback system. This system produces an adjustable linearly ramped temperatures from 1 °C to 50 °C per second that accurate to within ± 1 °C to 400 °C in the standart reader. The Time Profile Profile (TTP) is user defined in three parts. They are: Preheat, Acquire, and Anneal, each of them with independent times (Pre-read anneal: adjustable 0 to 1000 sec, Linear ramp: adjustable from 1 °C to 50 °C per second, Post-read anneal: 0 to 1000 sec) and temperature (Pre-read anneal: room temperature to 200 °C, Post-read anneal: up to 400 °C). A TTP is shown in figure 5.2. To recover the accuracy of low-exposure measurements due to low signals and to extend planchet lifetime of the TLD reader, it delivers for nitrogen to flow around the platinum planchet. The nitrogen flow destroys the unwanted oxygen molecules induced TL signal by eliminating oxygen in the planchet area. Nitrogen is especially routed around the photo-multiplier tube (PMT) chamber to eliminate moisture caused by condensation. In this study, the TL glow curves were measured using a metal planchet such as platinum at a linear heating rate of 1 °C/s. The passing time after irradiation up to reading processes are always kept constant at about 1 min. On the other hand, for the variable heating rates were varied from 2 to 5 °C/s. In this thesis, each sample was read out two times. The first one is normal redour. On the other hand, the second reading is considered to be background of reader plus sample. This reading was subtracted from the first one. All of the recorded glow curves were analyses after subtraction operations.

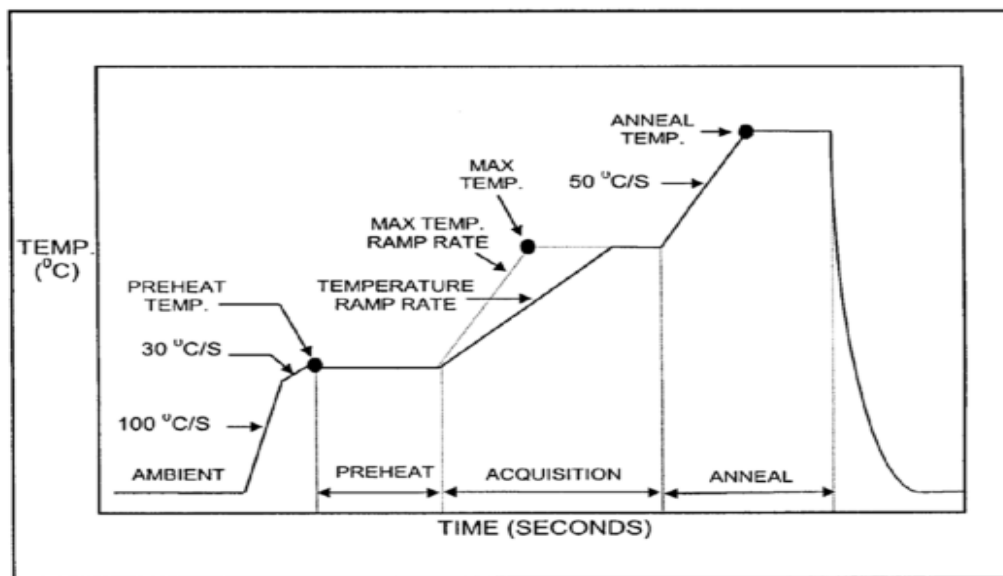


Figure 5.2. Typical time temperature profile (TTP) [21].

5.3. Annealing Procedure for Calcite

As mentioned previously, the calcite samples were collected in environmental regions of Gaziantep city. They were heated up to different annealing temperature for a fixed time of 30 min. In this study, the samples were annealed at 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C from 5 minutes up to 240 minutes. The TL studies with all heating processes are specifically designed at microprocessor controlled an FN 501 electric oven. During the heating process, the temperature of the furnace continuously can be read digitally. The The sensitivity of this furnace is in the range of 1 °C. This oven is used in high-temperature heat treatment between 400 °C and 1100 °C.



Figure 5.3. FN 501 Electric stove.

CHAPTER 6

EXPERIMENTAL RESULTS

The main purpose of this study is to observe the effects of annealing process at different temperatures on the TL glow curve shapes, peak temperatures, peak intensity, and peak area under the TL curve of natural calcites which were collected from the environmental regions of Gaziantep. Because, it is well known that the glow curve shapes of many natural and synthetic materials change after annealing temperatures. Therefore, the thermoluminescence (TL) measurements of calcite materials were carried out after annealing in air at different annealing temperatures ranging from 600 to 1000 °C. The glow curve measurements after each annealing temperature were repeated a few times. It was observed that the bad reproducibility was obtained after higher annealing temperature between 800 and 1000 °C. On the other side, the good reproducibility is seen if the instances were annealed between 600 and 700 °C.

6.1. Dose Response of The Calcite annealed at 600 °C

Firstly, in order to observe the effect of annealing temperature on the dose response curve of calcite samples studied in this study, the calcite samples were firstly annealed at 600 °C. Then, the calcite samples were irradiated at different doses between ≈ 12 Gy and ≈ 576 Gy to check annealing effects on the dose dependence effect and peak position. After different dose levels; some of the selected glow curves are shown in figure 6.1. It is seen that there is no important change observed in the peak temperatures of 110 °C and 300 °C peaks with increasing applied dose levels (see figure 6.2). The dose response curve of this sample is shown in figure 6.3. It is seen that the peak intensity and peak area under the glow curve are not increased with increasing dose level at low dose levels up to ≈ 40 Gy. Thereafter, the peak intensity and at the same the peak area under the glow curves are linearly

increased up to ≈ 200 Gy. And then, the area reaches the saturation value. And then they are not affected significantly by increasing the applied dose levels.

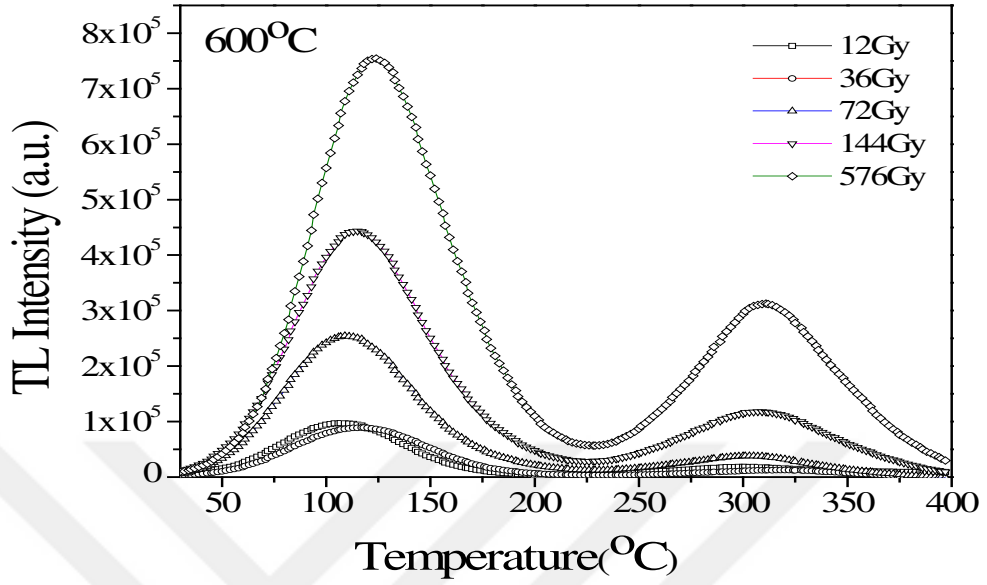


Figure 6.1. The glow curves of calcite samples measured after various dose levels. The samples were firstly annealed at 600 °C and then irradiated with β -ray at room temperature from ≈ 10 Gy to ≈ 600 Gy.

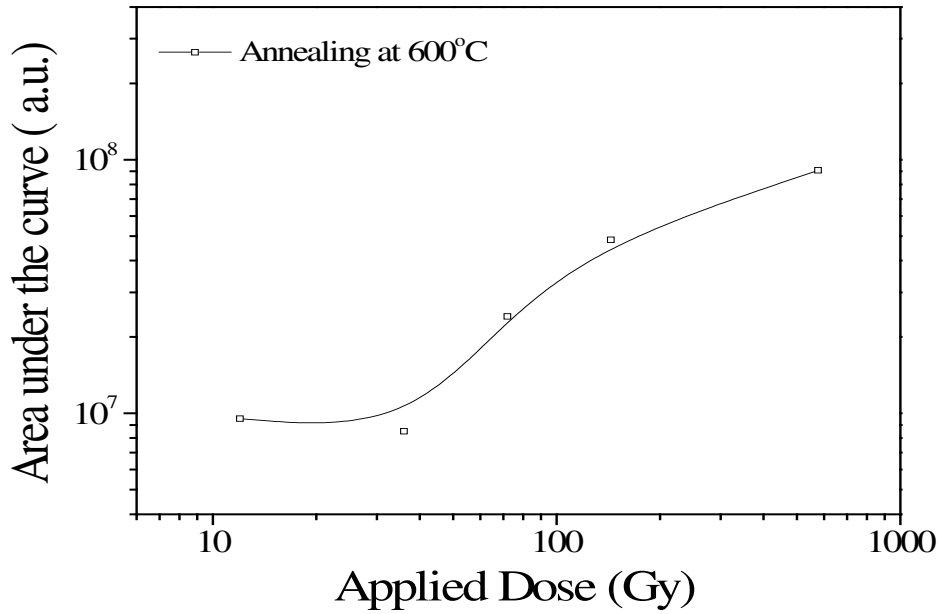


Figure 6.2. The effect of dose variation on TL peak temperatures of calcite samples after annealing temperature at 600 °C.

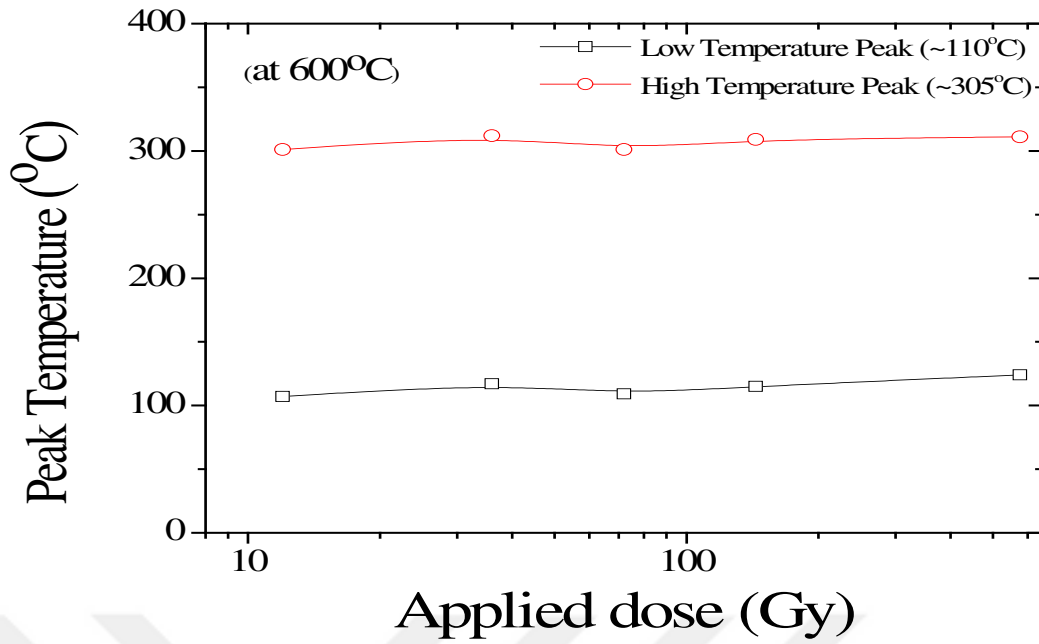


Figure 6.3. The dose response curve of calcite samples after annealing temperatures at 600 °C.

6.2. Dose Response of The Calcite annealed at 700 °C

The calcite samples were then annealed at 700 °C to observe the effect of annealing temperature on the dose response curve and peak temperatures of calcite samples at this temperature. The calcite samples were again irradiated at different doses between 12 Gy and 576 Gy to check annealing effects at 700 °C on the dose dependence effect and peak position. After different dose levels; some of the selected glow curves are shown in figure 6.4. It is seen that there is no important change in observed peak temperatures on glow peak at 115 °C and 305 °C with increasing applied dose levels (see figure 6.5). The dose response curve of this sample after annealing at 700 °C is shown in figure 6.6. It is seen that the peak intensity and peak area under the glow curve are not increased with increasing dose level at low dose levels up to ≈ 40 Gy. Therefore, the peak intensity and at the same time the peak area under the glow curves are linearly increased up to ≈ 200 Gy. And then, the area reaches the saturation value. And they are not affected significantly by increasing the applied dose levels.

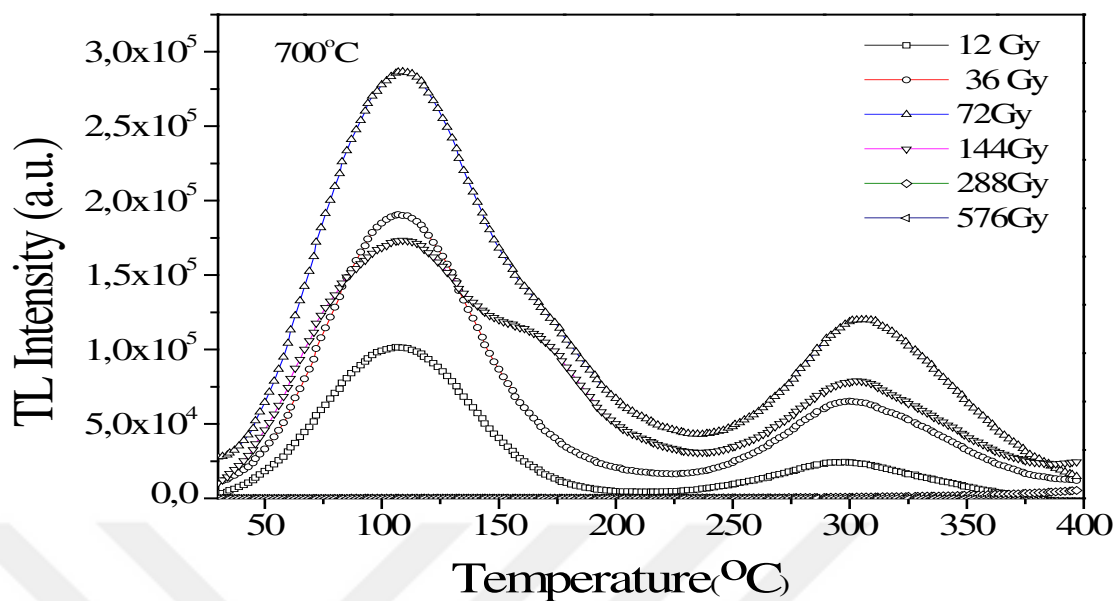


Figure 6.4. The glow curves of calcite samples measured after various dose levels. The samples were first annealed at 700 °C and then irradiated with β -ray at room temperature from ~ 10 Gy to ~ 600 Gy.

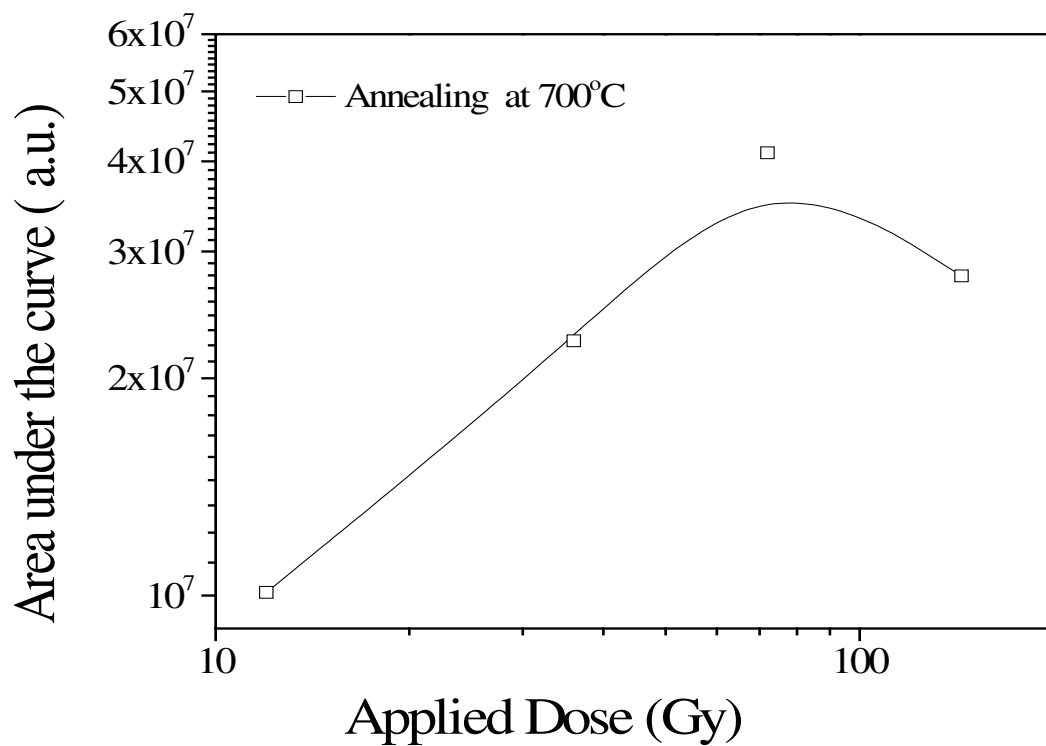


Figure 6.5. The dose response curve of calcite samples after annealing temperatures at 700 °C.

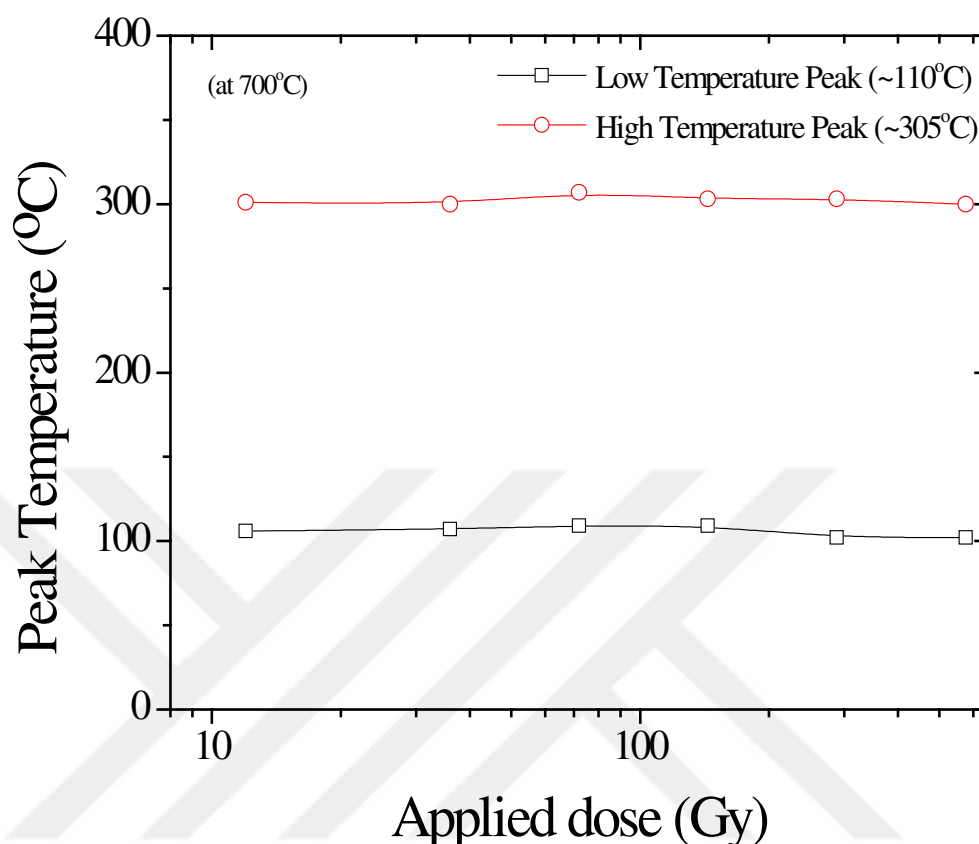


Figure 6.6. The effect of dose variation on TL peak temperatures of calcite samples after annealing temperature at 700 °C.

6.3. Dose Response of The Calcite annealed at 800 °C

In order to observe the effect of annealing temperature on the dose response curve and peak temperatures of calcite samples, the calcite samples were thirdly annealed at 800 °C. Also in this case, the calcite samples were irradiated at the different dose levels between 12 Gy and 576 Gy to check the annealing effects at 800 °C on the dose dependence effect and peak position. Some of the selected glow curves after different dose levels are shown in figure 6.7. As seen in the earlier annealing experiments at 600 and 700 °C, it was observed that there is no important change in peak temperature and glow curve shape with increasing applied dose levels. The dose response curve after annealing at 800 °C is shown in figure 6.9. It is seen that the peak intensity and peak area under the glow curve are linearly increased

with increasing dose level at low dose levels up to ~ 200 Gy. And then, the area reaches the saturation value. And they are not affected significantly by increasing the applied dose levels.

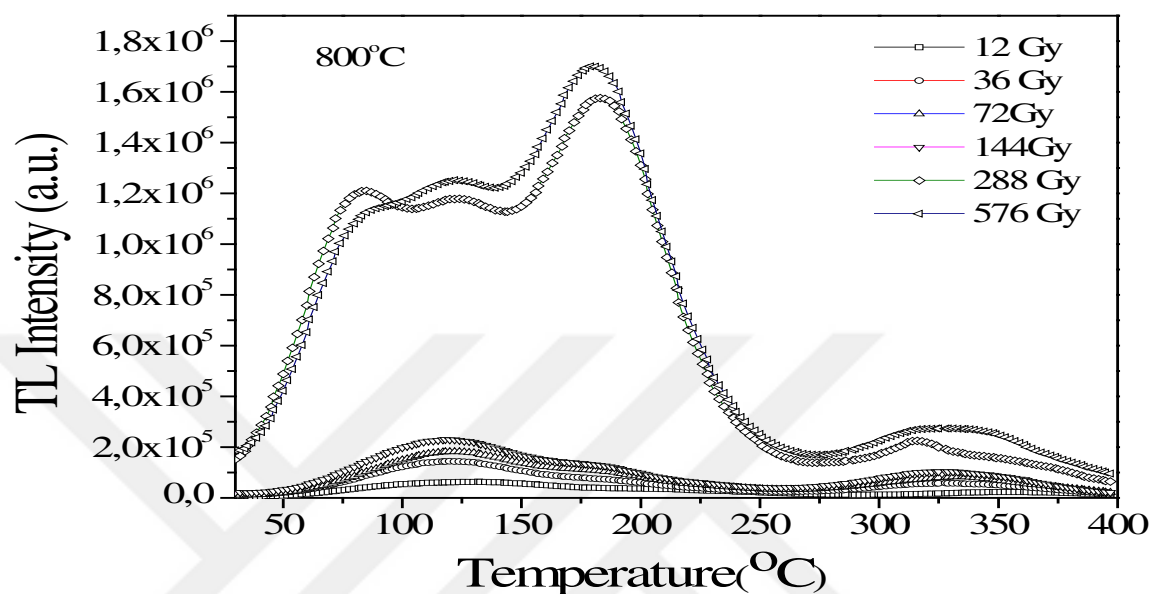


Figure 6.7. The glow curves of calcite samples measured after various dose levels. The samples were annealed at 800 °C and then irradiated with β -ray at room temperature from ~ 10 Gy to ~ 600 Gy.

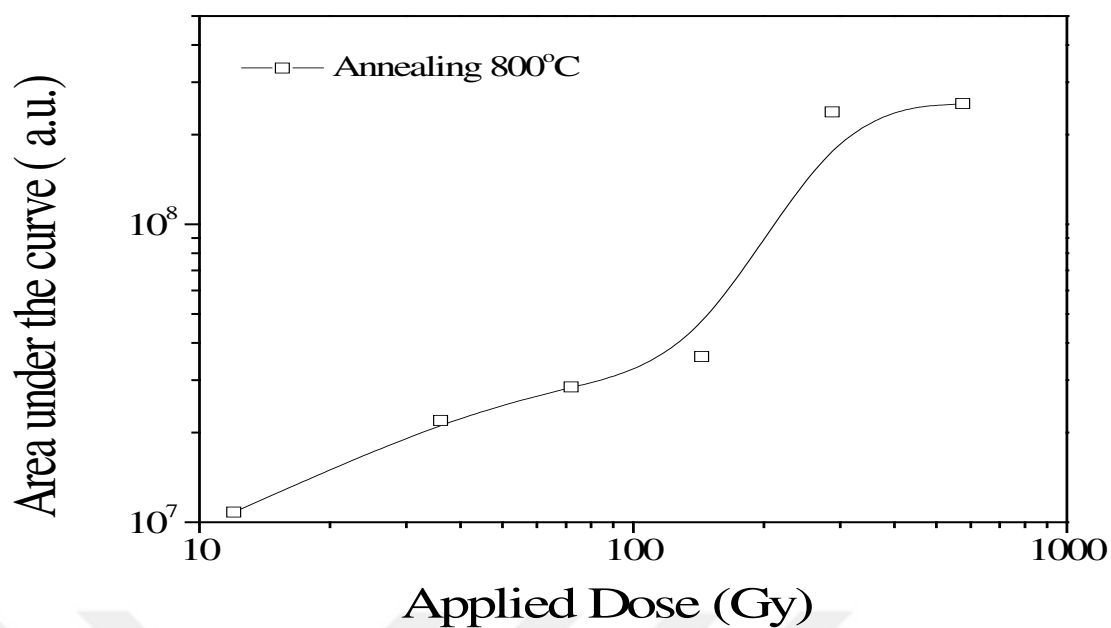


Figure 6.8. The effect of dose variation on TL peak temperatures of calcite samples after annealing temperature at 800 °C

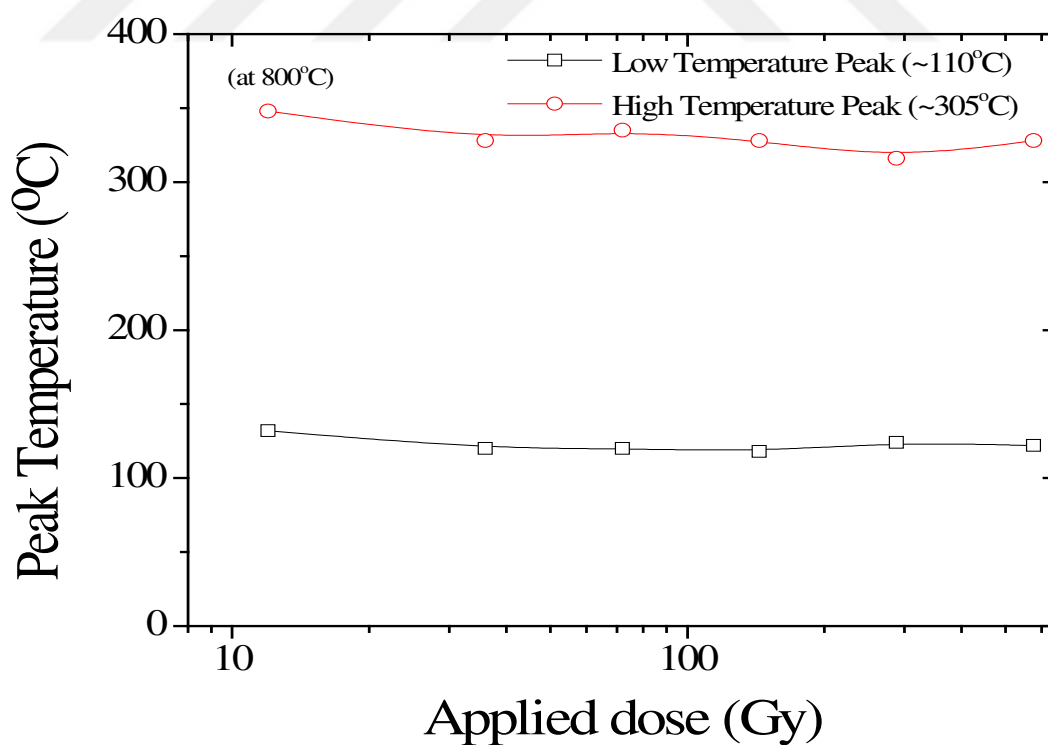


Figure 6.9. The dose response curve of calcite samples after annealing temperatures at 800 °C.

6.4. Dose Response of The Calcite annealed at 900 °C

In the next step, in order to observe the effect of annealing temperature on the dose response curve and peak temperatures of calcite samples, the calcite samples were then annealed at 900 °C. As applied doses in the previous example, the calcite samples were again irradiated at the different dose levels between 12 Gy and 576 Gy to check annealing effects at 900 °C on the dose dependence effect and peak position of glow curves. After different dose levels; some of the selected glow curves are shown in figure 6.10. After annealing at 900 °C, the glow curves of this sample were completely changed and as seen in Fig.6.10, two distinct TL peaks were observed at 120 °C and 190 °C. On the other hand, it is seen that there is no important change in glow curve shape with increasing applied dose levels (see figure 6.11). The dose response curve of this sample after annealing at 900 °C is shown in figure 6.12. It is seen that the peak intensity and at the same the peak area under the glow curves are linearly increased up to ~ 200 Gy. And then, the area reaches the saturation value. Then, they are not affected significantly by increasing the applied dose levels.

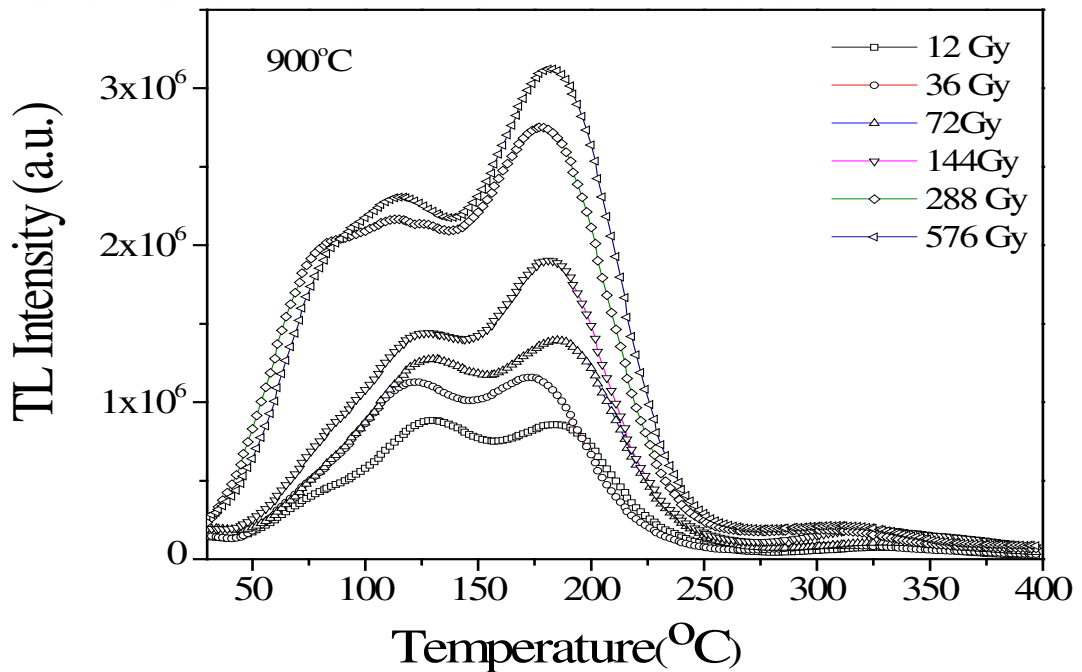


Figure 6.10. The glow curves of calcite samples measured after various dose levels. The samples were annealed at 900 °C and then irradiated with β -ray at room temperature from ~ 10 Gy to ~ 600 Gy.

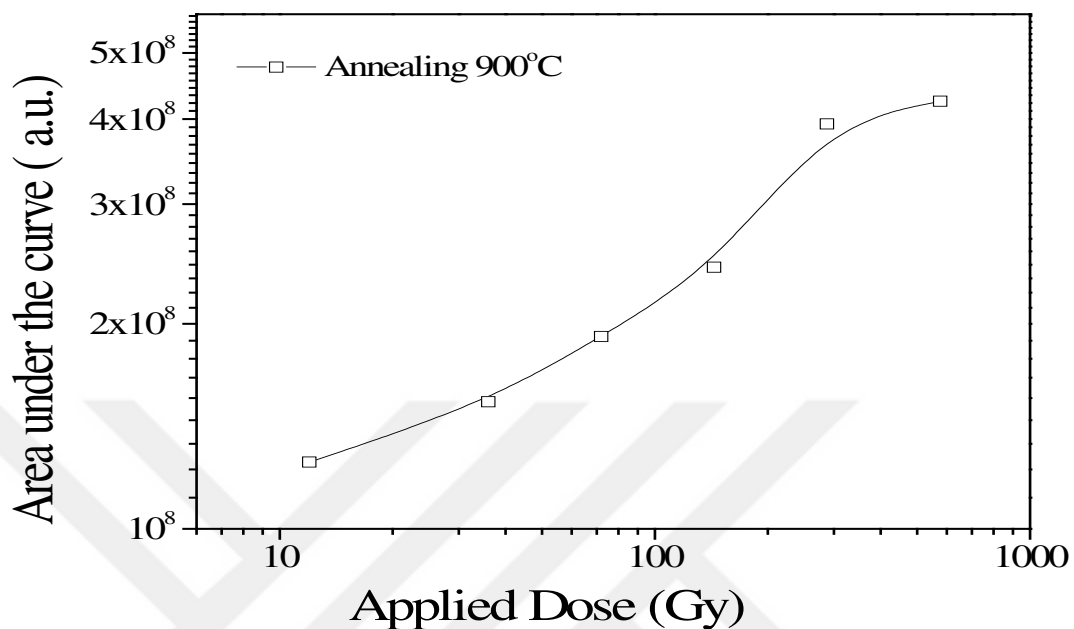


Figure 6.11. The effect of dose variation on TL peak temperatures of calcite samples after annealing temperature at 900 °C.

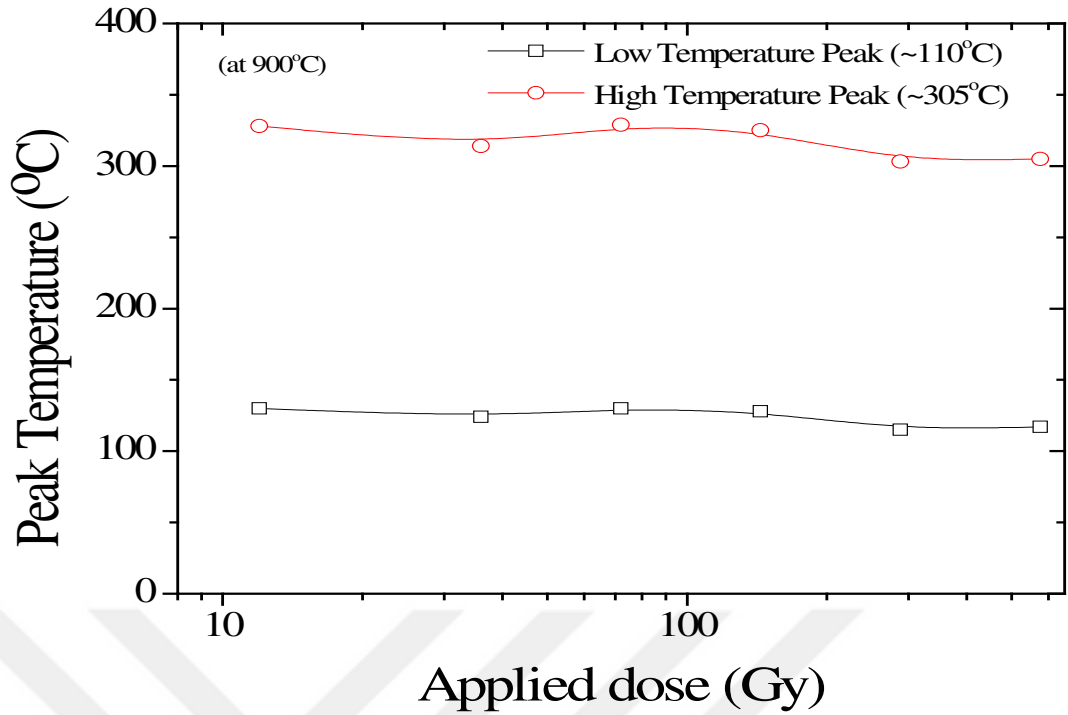


Figure 6.12. The dose response curve of calcite samples after annealing temperatures at 900 °C.

6.5. Dose Response of The Calcite annealed at 1000 °C

Finally, in order to observe the effects of annealing temperatures on the dose response curve and peak temperatures of calcite samples, the calcite samples were then annealed at 1000 °C. Similarly, the calcite samples were irradiated at the different dose levels between ~ 10 Gy and ~ 600 Gy to check annealing effects on the dose dependence effect and peak position. After annealing at 1000 °C, the selected some glow curves after different dose levels are shown in Fig.6.13. As the result obtained in the previous result, two distinct TL peaks were again observed at 120 °C and 190 °C. After annealing at 1000 °C, it is seen that there is no important change in glow curve shape with increasing applied dose levels (see Fig.6.14). The dose response curve of this sample is shown in figure 6.15 after annealing 1000 °C. As seen from this figure, the area under the glow curve is not increased linearly with increasing doses.

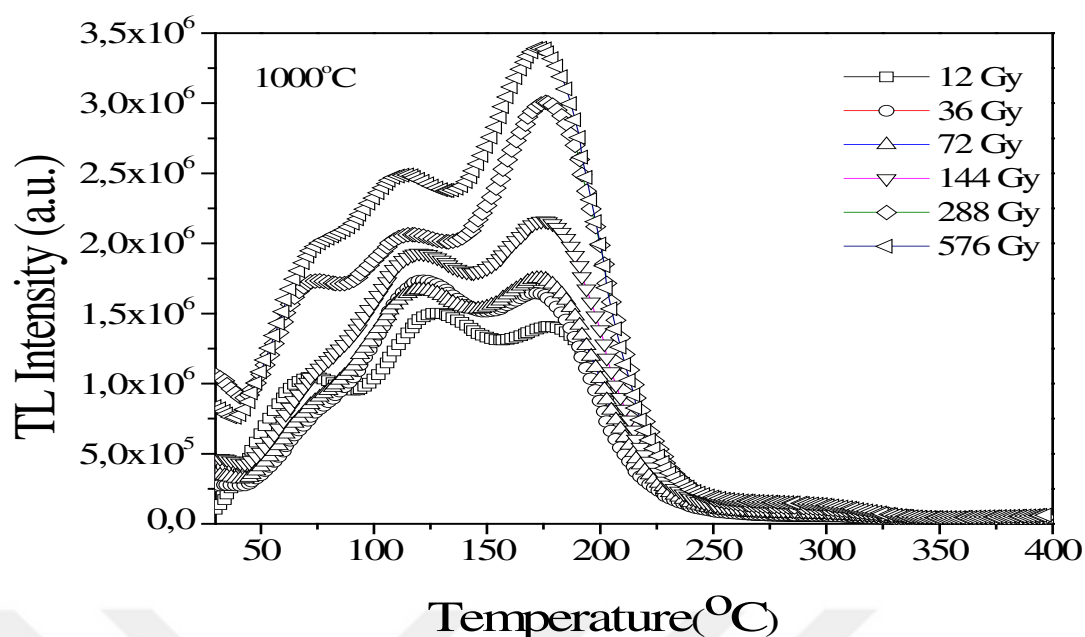


Figure 6.13. The glow curves of calcite samples measured after various dose levels. The samples were annealed at 1000 °C and then irradiated with β -ray at room temperature from ≈ 10 Gy to ≈ 600 Gy.

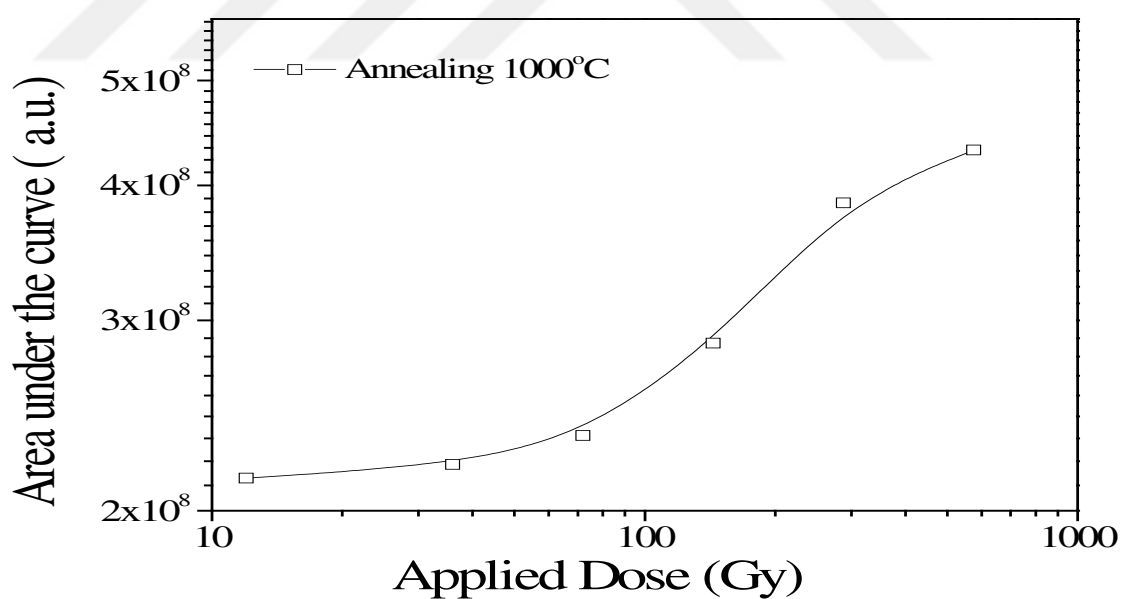


Figure 6.14. The effect of dose variation on TL peak temperatures of calcite samples after annealing temperature at 1000 °C.

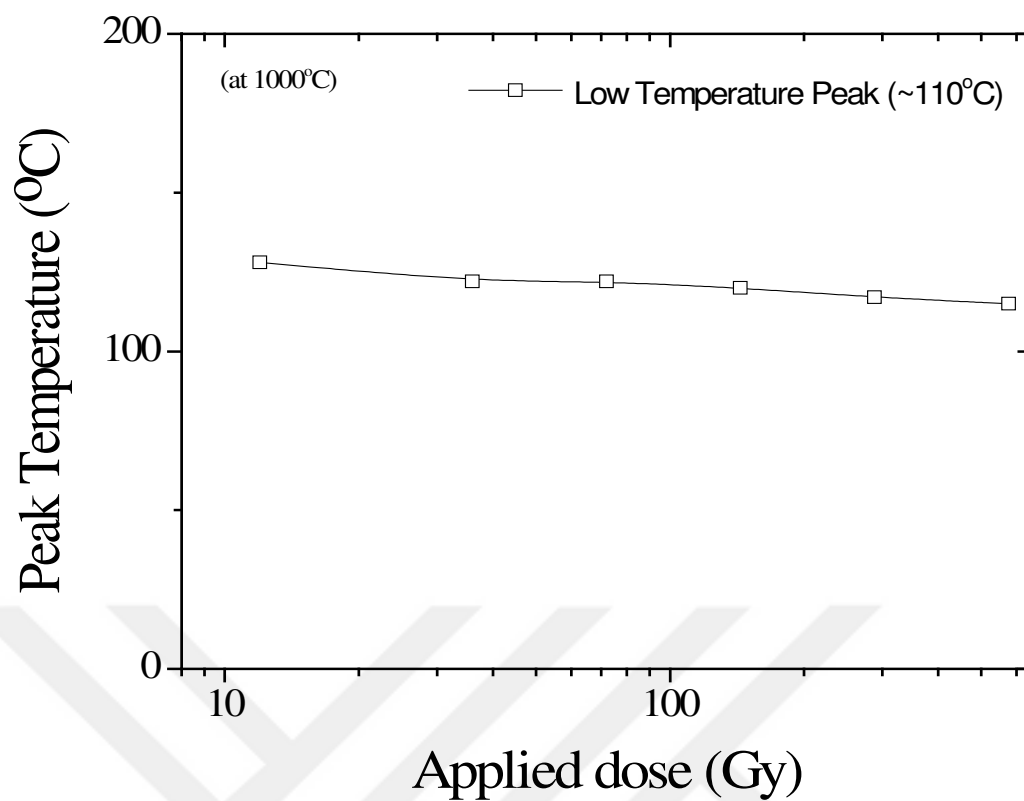


Figure 6.15. The dose response curve of calcite samples after annealing temperatures at 1000 °C.

CHAPTER 7

CONCLUSION

It is well known that the TL susceptibility, peak intensity, peak area and shape of the glow curves of some TL materials based on the annealing temperature and time. Therefore, the calcite instances which were handled in that work were annealed at the different temperatures between 600 °C and 1000 °C. It was observed that the TL susceptibility of that substance is highly based on the annealing temperature. The agreeable annealing temperature was found between 600 and 700 °C. On the other hand the shapes of glow curves were changed after annealing at 800 °C and above temperatures. At low annealing temperatures such as 600 °C and 700 °C, two glow peaks at ≈ 110 °C and ≈ 300 °C in the glow curves of this sample are well separated from each other. The shape of glow curves are very similar to each other after annealing at these two temperatures. In addition, it is seen that there is no important changes in the peak temperatures of these peaks with increasing applied dose levels after annealing 600 and 700 °C. Also, there isn't change in the shapes and positions of these glow curves. On the other hand, the shapes of the glow curves of samples are completely changed after annealing at and above 800 °C. In these cases, the glow curves of this sample are immediately started at room temperature and generally end above the 250 °C. It is seen as superposition of at least three glow peaks near 80 °C, 120 °C and 200 °C. However, there is great change in the shapes and positions of glow curves, peak temperatures of glow peaks after annealing at 800 °C, 900 °C and 1000 °C. In addition, it is seen that peak area under the glow curves and the peak intensities are linearly increased with increasing dose level at low dose levels up to 200 Gy after annealing at temperatures between 600 and 900 °C. On the other hand, the area under the glow curve is not increased linearly with increasing doses after annealing at 1000 °C.

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