On the thermoluminescence of LiF from 83 to 320 K

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Thermoluminescence was studied in LiF (TLD-100) single crystals from 83 to 320 K. In this temperature range, the glow curve presents six peaks at 138, 153, 193, 260, 283, and 300 K and a seventh peak at approximately 240 K. Based on annealing response, linearity, phototransference, and optical bleaching experiments, the glow peak at 138 K was related to V_K hole centers, while the remaining glow peaks were associated with electron traps, although a clear relation between the highest temperature glow peak, at 300 K, and electron centers could not be established with certainty. The seven glow peaks emit at three wavelengths, namely, 270, 300, and 420 nm. The emission band at 270 nm is more intense for the glow peaks at 138 and 153 K. For the remaining glow peaks, the emission bands at 300 and 420 nm are the most important ones. The emission band at 270 nm was related to the recombination of V_K holes at recombination centers other than the ones normally associated with the emission band at 420 nm. The emission band at 300 nm was related to the recombination of electrons and V_K centers. It was verified that the glow peaks at 138, 153, 193, and 260 K obey first order kinetics. © *1998 American Institute of Physics.* [S0021-8979(98)09623-6]

I. INTRODUCTION

Lithium fluoride, with about 100 ppm Mg and 10 ppm Ti as the essential impurities, LiF:Mg, Ti, is one of the most popular thermoluminescent (TL) materials used in personal and environmental monitoring. The characteristic which leads to this popularity is its approximate tissue equivalence, which makes it a good dosimetric material, together with the lack of the difficulties which are associated with the use of other TL phosphors. From a solid state point of view, however, LiF:Mg, Ti presents a rather complex TL mechanism.

The thermoluminescence induced in LiF:Mg, Ti by irradiation at room temperature is commonly explained in terms of a model proposed by Mayhugh[1] in which the mobile entities are electrons and holes.

More recently, Sagastibelza and Alvarez Rivas[2] proposed a different approach for the TL mechanism in LiF:Mg, Ti. As in other alkali halides, they suggested that the TL process in the material irradiated at room temperature is caused by the recombination with vacancy centers (F,Z_2) of interstitial halogen atoms thermally released from traps. According to Lakshmanan *et al.*,[3] Mayhugh's electron-hole model has some bearing only on the process of LiF:Mg, Ti TL glow peaks below 473 K. The TL process of peaks above this temperature is better explained by the model of Sagastibelza and Alvarez Rivas.

Though the thermoluminescence in LiF:Mg, Ti above room temperature has been extensively investigated, much less attention has been paid to the phenomenon at low temperatures. Townsend *et al.*[4] investigated the TL in LiF from 10 to 500 K using samples from different sources and having different impurities as dopants. Podgorsak *et al.*[5] and Cooke[6] studied LiF:Mg, Ti (TLD-100) in the range 77–500 K. Kuila[7] studied the thermoluminescence displayed by LiF:Mg single crystals, obtained from the Harshaw Chemical Company, USA, between 77 and 300 K. Jain[8,9] investigated the thermoluminescence in LiF (TLD-100) between 90 and 300 K. The results obtained by these authors are somehow conflicting. The glow curves obtained present differences among them and the explanations given to the phenomenon itself are not always in agreement.

In this article, investigations on the TL of this phosphor, in the 83–320 K range, were carried out to clarify some aspects of these mechanisms. The TL glow curve and TL emission spectra in different temperature ranges were determined for the material. Optical bleaching and phototransference experiments were executed. The thermal activation energy and the frequency factor associated with four TL glow peaks were also evaluated.

II. MATERIALS AND METHODS

LiF:Mg, Ti (TLD-100) single crystals, with dimensions of 10 mm×10 mm×2 mm, obtained from the Harshaw Chemical Company, were used. LiF:Mg, Ti samples, 1.2 mm thick and 6 mm in diameter, produced by the Instituto de Pesquisas Energéticas e Nucleares (IPEN), were also employed in some experiments. In order to investigate the samples thermoluminescent properties, in the 83–320 K range, three systems were developed around an HNDT-5

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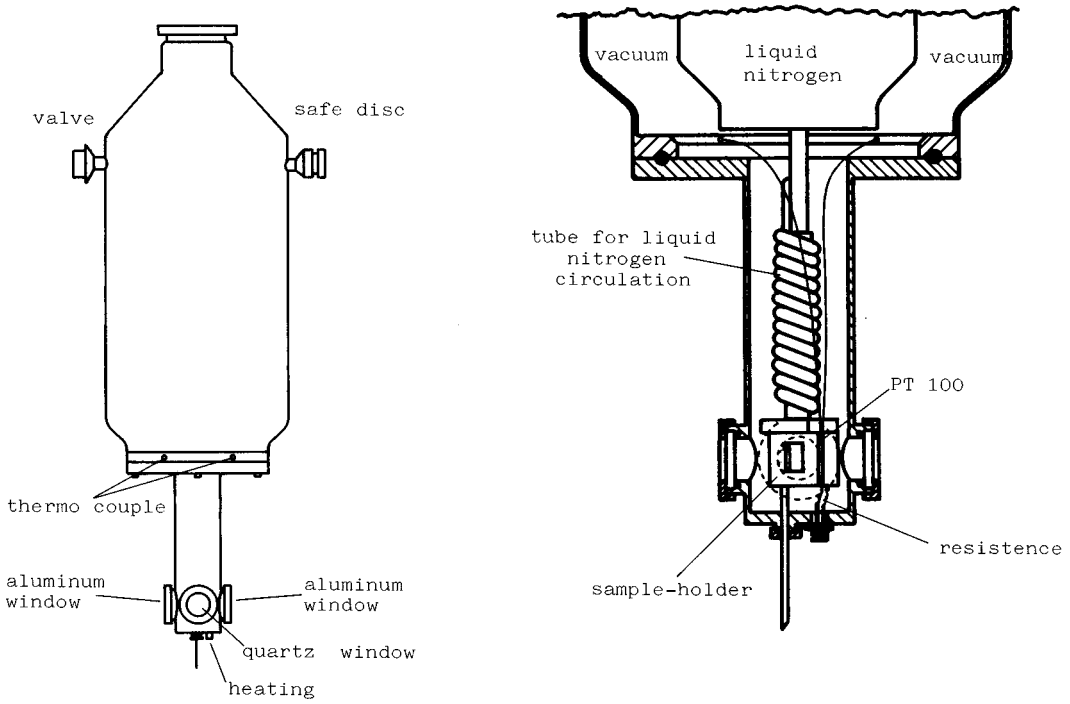

FIG. 1. Scheme of HNDT-5 model cryostat. The sample-holder chamber is detailed.

model cryostat, namely a system for glow curve determination, another one for optical bleaching and phototransference experiments, and a third one for emission spectra collection. The cryostat was manufactured by Minnesota Valley Engineering, USA. A HF rotary pump, Brazil, was used to evacuate the cryostat.

The HNDT-5 model cryostat has a sample chamber with three windows, specifically two aluminum windows and a quartz window. The sample holder is fixed inside the sample chamber maintaining an angle of 45° with one of the aluminum windows and the quartz window. Through the aluminum window that forms a 45° angle with the sample holder, the sample irradiation may be carried out. Figure 1 presents a scheme of the HNDT-5 model cryostat.

For TL glow curve determinations, a photomultiplier tube (PMT), model EMI 6256, USA, is connected to the quartz window and is used to detect the light displayed by the heated irradiated sample. This PMT is fed by a Tectrol THC 3000 high voltage (HV) power supply, Brazil, and is connected to a Keithley 610 C electrometer, USA, which amplifies the PMT signal to be sent to an ECB RB 202 model graphic recorder (Brazil) where the sample TL glow curve is recorded.

The sample holder is heated by means of an electric resistance, Fig. 1. A specially designed temperature programmer provides linear heating of the sample. It was manufactured by S&E Instrumentos e Testes de Medição Ltda, Brazil, and uses as the temperature monitor a platinum resistance temperature detector (RTD). A heating rate of $(13.72 \pm 0.19)\ \mathrm{K\ min^{-1}}$ was used. The instrument is provided with a digital display where the sample temperature can be read in degrees Celsius. As a result, well-resolved TL peak temperatures may be determined with reasonable accuracy.

For optical bleaching and phototransference experiments, a GM 200 double grating monochromator, manufactured by Kratos Schoefel Instruments, USA, and a UV radiation high-pressure mercury lamp SR-200, manufactured by Bausch & Lomb, USA, were utilized. The monochromator exit slit was connected to the cryostat quartz window and the instrument was used for light wavelength selection. The UV lamp was connected to the monochromator entrance slit.

The system for emission spectra measurement is similar to the system for glow curve evaluation, with the added presence of the GM 200 monochromator between the quartz window and the photomultiplier tube. The monochromator is equipped with a small motor that enables the selection of wavelengths at constant rates between 0.2 and $200\ \mathrm{nm\ min^{-1}}$. In this work the spectra were obtained at scanning rates of 100 and $200\ \mathrm{nm\ min^{-1}}$, depending on the experiment carried out.

The TL emission spectra are recorded while the samples are heated. Therefore, these spectra have to be corrected for the different intensities of the light emitted by the samples, depending on their temperatures. Knowing the sample heating rate, in $\mathrm{K\ min^{-1}}$, and the monochromator scanning speed, in $\mathrm{nm\ min^{-1}}$, it is possible to correlate the intensities of the light emitted by the sample to each wavelength value. Additionally, it is necessary to correct the spectra for the PMT response, which is dependent on the wavelength of the light detected. This dependence is given by the PMT manufacturer. Finally, it is still necessary to correct the spectra for the monochromator sensitivity, which is also dependent on the light wavelength. This dependence is given by Kratos Schoefel Instruments.

In order to investigate TLD-100 single crystal optical absorption, a system was developed using a HNDT-3 model

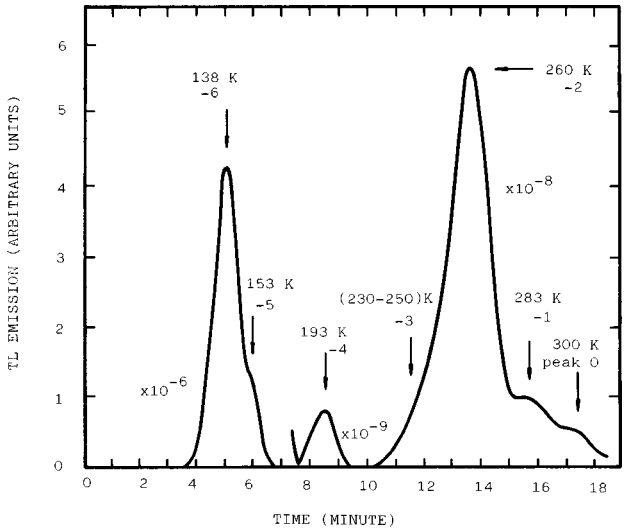

FIG. 2. TL glow curve displayed by a TLD-100 single crystal between 83 and 320 K. Sample thermally treated at 400 °C for 1 h, irradiated at 83 K, 2.88 C kg^{-1}.

TABLE I. Comparison, in terms of the number of TL glow peaks and their temperatures, among TL glow curves obtained by different authors for LiF:Mg, Ti.

Present work (K)	Podgorsak *et al.*[a] (K)	Cooke[b] (K)	Kuila[c] (K)	Jain[d,e] (K)
138	145	142	138	137
153	164	156	153	149
⋯	⋯	⋯	163	166
193	185	189	⋯	187
⋯	⋯	⋯	⋯	202
230–250	⋯	235	228	228
260	267	250	268	254
283	287	270	288	275
300	⋯	287	⋯	287

[a]Reference 5.
[b]Reference 6.
[c]Reference 7.
[d]Reference 8.
[e]Reference 9.

cryostat. This cryostat was also manufactured by Minnesota Valley Engineering. Its sample chamber has four windows, namely two parallel aluminum windows used for sample irradiations, and two parallel quartz windows at 90° through which the sample is illuminated. The sample holder may be placed parallel to the quartz windows or to the aluminum windows by means of an external mechanism that enables the sample chamber to be rotated. A special brass device was developed and used to couple the HNDT-3 model cryostat to a double beam spectrophotometer (Carl Zeiss model DMR 21, Germany) that was used to measure optical absorption spectra.

Before each experiment, the samples were thermally treated. The annealing procedure normally utilized was 400 °C for 1 h. Additional annealing procedures of 100 °C for 3 h and 80 °C for 24 h were also used when the influence of the sample thermal treatment on the material glow curve structure was tested. The sample cooling down was always slow. After each thermal treatment, the samples were left on a thick brick until they reached room temperature.

The samples were submitted to x rays generated by a Rigaku Denki system (60 kV), Japan, with a Philips tube, which belongs to the Calibration Laboratory of IPEN, Brazil.

III. RESULTS AND COMMENTS

A. Glow curve structure

Figure 2 presents the TL glow curve displayed by a TLD-100 single crystal, thermally treated at 400 °C for 1 h, irradiated at 83 K, 2.88 C kg^{-1}, between 83 and 320 K. In this curve, six peaks can be identified at 138, 153, 193, 260, 283, and 300 K. Between 230 and 250 K the presence of a seventh TL peak is also observed. The 193 K TL glow peak presents the lowest sensitivity. The TL glow peak temperatures were directly observed from the display of the temperature programmer at the exact moment of the TL peak appearance during the glow curve determination. Therefore, except for the case of the TL glow peak between 230 and 250 K, it was possible to evaluate the peak temperatures with a reasonable accuracy. Naturally, uncertainties due to thermal lag and the overlap of some peaks may occur. In order to make the identification of these peaks easier, they are labeled as peak −6 (138 K), peak −5 (153 K), peak −4 (193 K), peak −3 (between 230 and 250 K), peak −2 (260 K), peak −1 (283 K), and peak 0 (300 K).

Table I compares, considering the number of TL glow peaks and the temperature of their maxima, the curve obtained in this work with those reported by Podgorsak and co-workers,[5] Cooke,[6] Kuila,[7] and Jain.[8,9] Small differences in the temperature of the maxima for some TL glow peaks may be explained in terms of different heating rates, different annealing procedures, different thermal lag, or even in terms of more precise temperature evaluation systems. However, there are some differences in temperature that are not easily understood and, more seriously, there are peaks found by some authors which could not be detected by others. In addition, the relative sensitivities among TL peaks and the TL glow curve shapes are not all the same. This may be explained by differences in the materials studied or the efficiencies of the detection systems.

The curve of Fig. 2 is similar to the glow curve obtained by Jain[8] for TLD-100 exposed to x rays, 0.41 C kg^{-1}, at 90 K, and heated between 90 and 300 K. However, Jain[8] was able to resolve nine TL glow peaks, while Fig. 2 displays only seven peaks. Observing the curve obtained by Jain[8], it is possible to note the presence of a TL peak around 200 K, however the TL peak that the author affirms to exist at 166 K is indeed difficult to see. Podgorsak and co-workers,[5] Cooke,[6] and Kuila[7] do not report a TL glow peak around 200 K either, and the peak, which Jain[8] identified around 166 K, was only reported by Kuila[7] around 163 K. It is interesting that the TL glow peak at 163 K appears very clearly in the curve determined by Kuila,[7] but this curve presents a different structure when compared to those reported by others including Podgorsak *et al.*,[5] Cooke,[6] Jain,[8,9] and Fig. 2. While it is possible to say that these latter reports present a similar shape, they differ in the number of maxima.

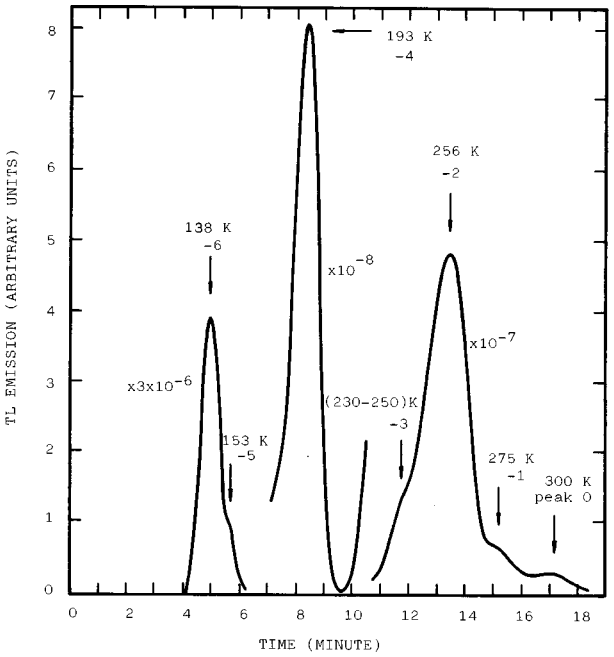

FIG. 3. TL glow curve displayed by IPEN LiF:Mg, Ti between 83 and 320 K. Sample thermally treated at 400 °C/1 h and irradiated at 83 K, 16.95 C kg^{-1}.

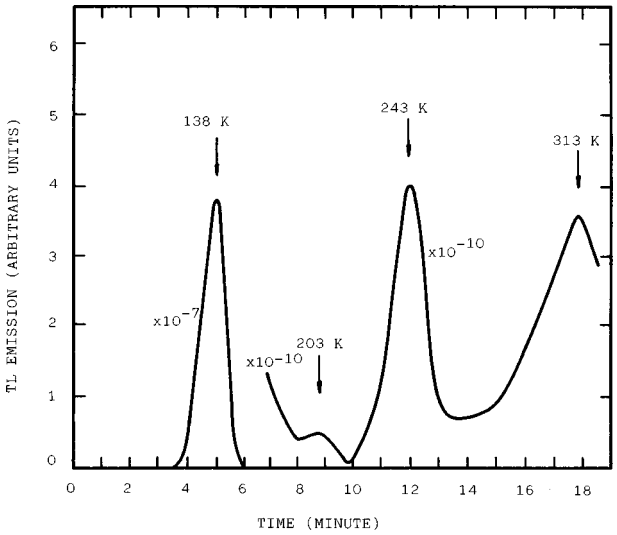

FIG. 4. TL glow curve displayed by an undoped LiF sample between 83 and 320 K. Sample thermally treated at 400 °C/1 h and irradiated at 83 K, 16.95 C kg^{-1}.

In order to evaluate the influence of the origin of the LiF:Mg,Ti samples on their TL glow curves, glow curves obtained with TLD-100 and LiF:Mg,Ti produced by IPEN were compared. Figure 3 presents the TL glow curve displayed by LiF:Mg,Ti sample produced by IPEN. Before being evaluated between 83 and 320 K, the sample was annealed at 400 °C for 1 h and exposed to x rays, 16.95 C kg^{-1}, at 83 K. The structure of this curve is similar to that of TLD-100, presenting seven peaks at 139, 153, 193, 233–243, 256, 275, and 300 K. However, peaks -2 and -1 present considerable differences in the temperatures of their maxima and peak -4 in the glow curve is larger than peak -4 in TLD-100. Note that TL peaks at 160 and 200 K were not detected once again. These results show that the composition and origin of the sample is important to the TL glow curve shape.

Figure 4 presents the TL glow curve of an undoped LiF sample. This material presents an amount of Mg 10 and 15 times less than that present in TLD-100 and IPEN LiF:Mg,Ti, respectively, but it is similar in Ti content. It is possible to observe the presence of a TL peak at 138 K. One concludes that this peak is not related to defects created by the doping of the material. Except for the 138 K peak, the remaining peaks in LiF:Mg,Ti between 83 and 320 K appear to be related to Mg as evidenced by the low emission in this undoped sample. TL glow peaks at 313, 243, and 203 K are also present in the TL glow curve of Fig. 5. The sensitivities of these peaks are very low. TL glow peaks at 313 and 203 K are not observed in the TL glow curve of LiF:Mg,Ti, Figs. 2 and 3. The TL glow peak at 243 K may be TL glow peak -3 of LiF:Mg,Ti, Figs. 2 and 3, but it is difficult to affirm this. In summary, a phosphor poor in Mg presents a low TL sensitivity and a TL glow curve structure very different from that presented by TLD-100. The amount of Ti seems to have no influence on the TL glow curve structure.

Figures 5 and 6 present TL glow curves obtained with the same TLD-100 sample which produced the curve shown in Fig. 2, but with different annealing before irradiation. In order to obtain those curves, the sample was exposed, at 83 K, to the same exposure value, namely 2.88 C kg^{-1}, of x radiation. The sample evaluation conditions were the same, identical to those used to obtain the curve presented in Fig. 2. The annealing procedures applied to the sample, in each case, however, were different. Recall that for Fig. 2 a heating treatment of 400 °C for 1 h was used. In order to obtain the curve presented in Fig. 5, the sample was annealed at 100 °C for 3 h, in addition to the usual annealing of 400 °C for 1 h. Finally, the curve of Fig. 6 was obtained when the sample was annealed at 80 °C for 24 h after an annealing at 400 °C

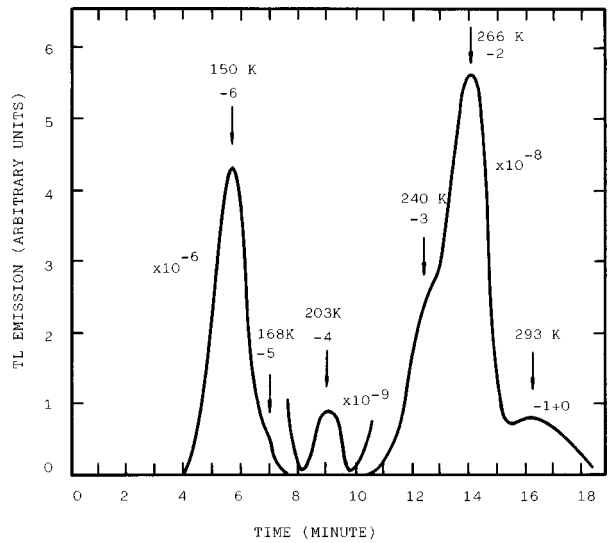

FIG. 5. TL glow curve displayed by the same sample of Fig. 2, between 83 and 320 K. Sample thermally treated at 400 °C/1 h+100 °C/3 h, irradiated at 83 K, 2.88 C kg^{-1}.

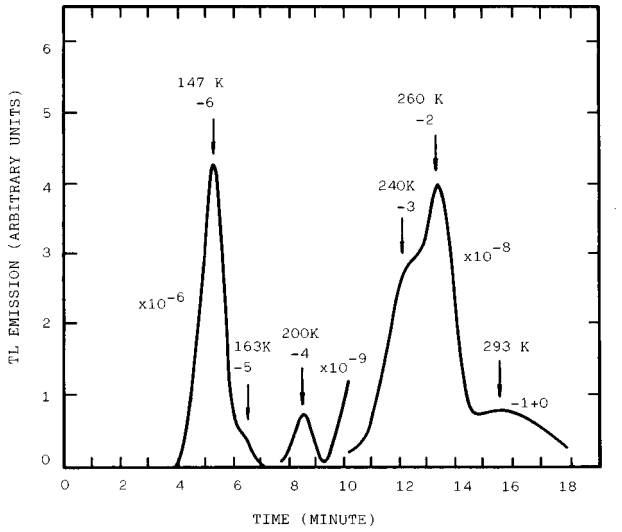

FIG. 6. TL glow curve displayed by the same sample of Fig. 2, between 83 and 320 K. Sample thermally treated at 400 °C/1 h+80 °C/24 h, irradiated at 83 K, 2.88 C kg^{-1}.

for 1 h. These same pre-irradiation anneals influence the glow curve and optical absorption above room temperature and are thought to result from changes in Mg related trap centers.

The first observation from Figs. 5 and 6 is the strong influence of the annealing procedure on the shape of the low temperature TL glow curve of TLD-100. This may explain why it is difficult to compare TLD-100 TL glow curves obtained by different authors, when the annealing procedures used are unknown.

It is also possible to observe the presence of peak −3, more clearly, around 240 K, in the curves of Figs. 5 and 6, and particularly in Fig. 6, when the material is annealed at 400 °C for 1 h plus 80 °C for 24 h, perhaps because of a relative decrease in the overlapping peak-2. At the same time peak −5 decreases in intensity. Peaks −6 and −4 present little change due to the different annealing procedures. Peaks 0 and −1 become one peak at 293 K. Additionally, the maxima of the curves presented in Figs. 5 and 6 are localized at slightly higher temperatures when compared with the maxima presented by the curve of Fig. 2. These results indicate that the traps responsible for peaks −5, −3, −2, −1, and 0 are present in the material before its irradiation and their concentrations are altered by pre-irradiation anneals. The observation is consistent with the association of these traps with Mg related traps.

B. X-ray exposure dependence of TL glow peaks

Figure 7 presents the x-ray exposure dependence of TL glow peaks −6, −5, −2, −1, and 0. The study was carried out between 2.41 and 67.80 C kg^{-1}. Before irradiation, the sample was annealed at 400 °C for 1 h. The response of the TL glow peaks is unambiguously linear, presenting no supralinearity. The sensitivity of all peaks presents a linear behavior up to a certain exposure value, when it starts to show a tendency to saturation. The responses of peaks −6 and −5 show a linear behavior up to approximately 34 C kg^{-1}. Peaks −4, −2, −1, and 0 present linearity up to 20 C kg^{-1}. These results are similar to these obtained by Jain[8].

The linearity of peaks −6, −5, −4, −2, and −1 heights indicates that they obey the kinetics of first order. TL glow peaks which obey a kinetics of order greater than one do not present linear responses to exposure, if peak heights are considered.[10] To confirm this fact, the order of the kinetics of TL glow peaks −6, −5, −4, and −2 were determined. The order of the kinetics of a TL glow peak may be evaluated through its symmetry factor, μ_g, which is defined as

$$\mu_g = \frac{\delta}{\omega}, \tag{1}$$

where $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$. T_m is the temperature of the maximum of the TL glow peak. T_1 and T_2 are, respectively, the temperatures inferior and superior to T_m where the intensity of the peak is equal to half of its maximum value. See for reference Halperin and Braner[11] and Chen.[12] The TL glow peaks that obey the first order kinetics present $\mu_g \approx 0.42$, according to Chen,[12] while those which follow a

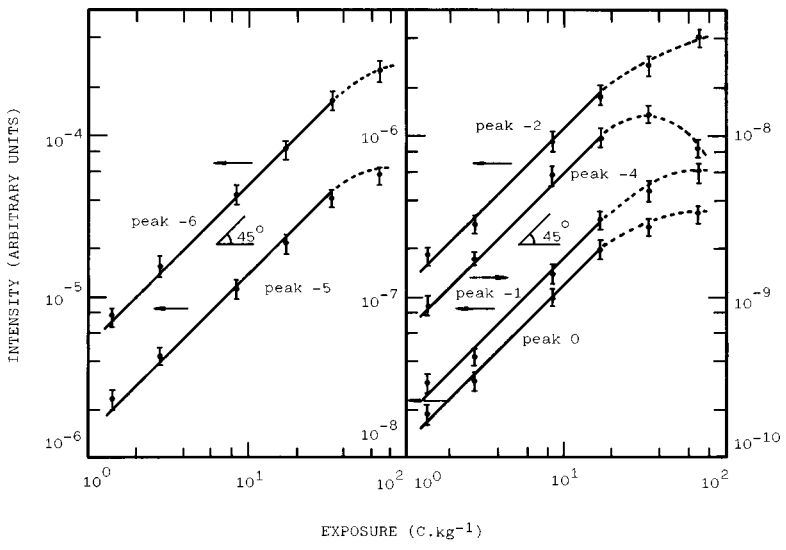

FIG. 7. X-ray exposure dependence of TL glow peaks −6, −5, −4, −2, −1, and 0.

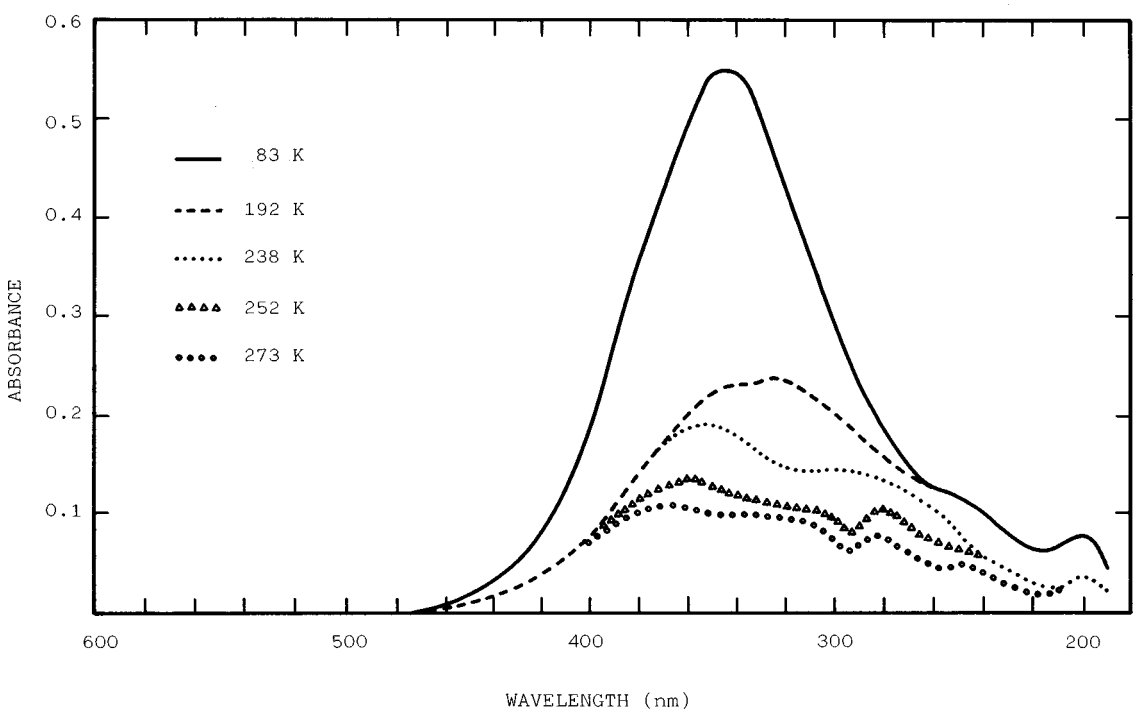

FIG. 8. TLD-100 single crystal (10 mm thick) optical absorption spectrum obtained at 83, 192, 238, 252, and 273 K with a sample irradiated at 83 K.

kinetics of order 2 present $\mu_g \approx 0.52$. Obviously, TL glow peaks may present intermediary kinetics values and in these cases the values of μ_g are between 0.42 and 0.52 (see Chen[13]).

The μ_g values for TL glow peaks -6, -5, -4, and -2 were determined from ten TL glow curves obtained from a sample always annealed at 400 °C for 1 h and exposed to x rays, 2.88 C kg^{-1}, at 83 K. The results are mean values taken from the ten curves and the corresponding uncertainties have a confidence level equal to one standard deviation. In order to determine μ_g for peaks -6 and -5, they were separated graphically. Peaks -6, -5, -4, and -2 presented μ_g values, respectively, equal to 0.42 ± 0.01, 0.41 ± 0.01, 0.43 ± 0.01, and 0.43 ± 0.01. These results show that these peaks present a kinetics of first order which agrees with the linear behavior observed for the peak sensitivity.

C. Optical absorption spectra of TLD-100 at low temperatures

Figure 8 presents TLD-100 single crystal (10 mm thick) optical absorption spectra obtained at 83, 192, 238, 252, and 273 K with a sample irradiated at 83 K. At this temperature, three bands are clearly evident around 348 nm (V_K band), 250 nm (F band), and 200 nm. In the spectra obtained at temperatures above 192 K, the 348 nm band seems to be absent. This fact is explained by the thermal instability of V_K centers above 130 K. See, for example, Seidel and Wolf.[14] However, absorption bands at 380, 310, and 280 nm become visible, mainly above 252 K, in addition to the bands at 250 and 200 nm. It is interesting to note that the F band which appears in the optical absorption spectra obtained at 252 and 273 K presents a lower relative intensity, when these spectra are compared with that determined with a room temperature irradiated TLD-100 single crystal, see Lakshmanan *et al.*,[3] Da Rosa and Caldas.[15] For room temperature irradiated samples, the F band is the most prominent one. Based upon results from Nepomnyashchikh and Radzhabov,[16] F centers are not easily formed when LiF samples are irradiated at temperatures near 77 K. It should be mentioned that the band at 280 nm does not appear clearly in the optical spectrum determined with a room temperature irradiated TLD-100 single crystal.[3,15]

D. X-ray exposure dependence of V_K band

The x-ray exposure dependence of the V_K band of the LiF:Mg,Ti optical absorption spectrum is presented in Fig. 9, which also presents the x-ray exposure dependence of the 138 K TL peak displayed by the material. As can be observed, both show linearity between 1.4 and 34 C kg^{-1}. These behaviors further confirm the relation between the V_K band and the 138 K TL glow peak of LiF:Mg,Ti.

E. 348 nm optical bleaching on LiF:Mg,Ti

Figure 10 shows the effect of a 348 nm optical bleaching, radiant exposure of 1029 J m^{-2}, on the LiF:Mg,Ti TL glow curve, when the material is irradiated and bleached at 83 K. The 138 K TL peak is reduced by 75%. This is the same reduction that occurs in the 348 nm optical absorption band (V_K band) after submitting the sample to exactly the same treatments, as shown in Fig. 11. The 348 nm optical bleach also causes significant reductions in the intensity of the 193 K peak and the remaining peaks, except the 300 K TL peak, are also somewhat reduced. Except for the 138 K

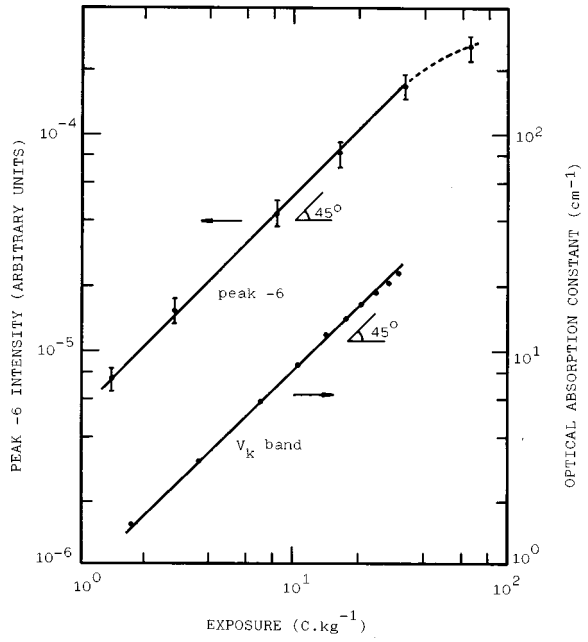

FIG. 9. X-ray exposure dependence of V_K band of LiF:Mg, Ti optical absorption spectrum and 138 K LiF:Mg, Ti TL glow peak. Samples 10 mm thick were used.

peak, the other peaks cannot be due to hole centers, because they can be produced by phototransferred electrons coming from *F* centers, as will be shown later.

The holes produced by V_K center destruction may recombine with the trapped electrons causing the observed reduction. Additionally, the losses of sensitivity displayed by those peaks, due to 348 nm optical bleaching, are different

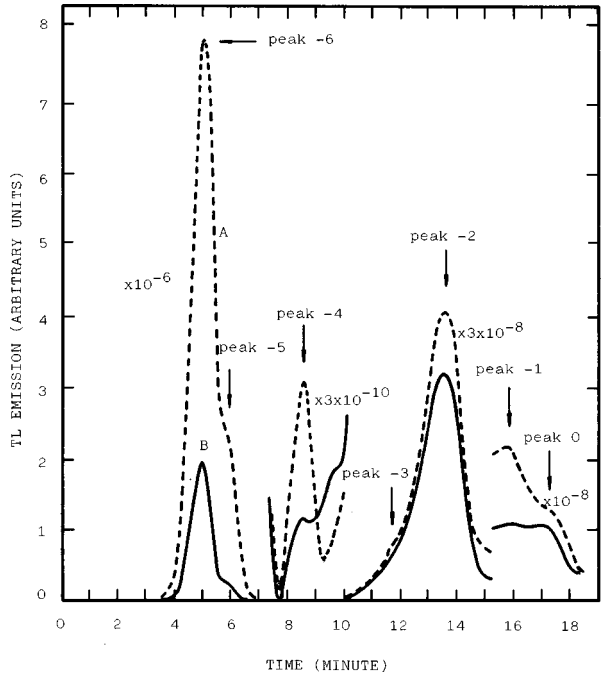

FIG. 10. Effect of 348 nm optical bleaching, radiant exposure 1029 J m^{-2}, on the LiF:Mg, Ti TL glow curve, when the material is irradiated and bleached at 83 K. Curve A-obtained immediately after the sample irradiation. Curve B-obtained after 348 nm optical bleaching.

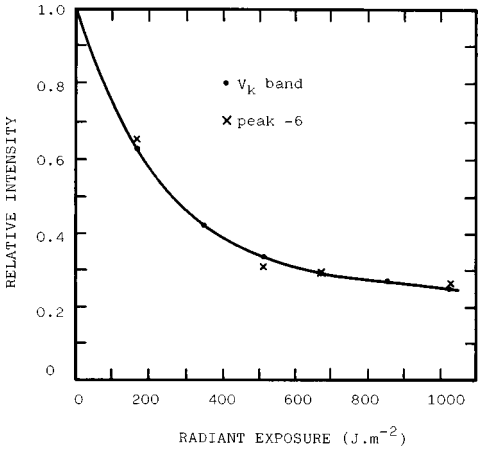

FIG. 11. Optical decay of TLD-100 V_k optical absorption band (dots) and 138 K TL peak (crosses) due to 348 nm optical bleaching.

from the V_K band sensitivity loss. Kuila[7] reported that optical bleaching with ⟨110⟩ polarized V_K light on the 77 K x-irradiated LiF sample reduced the intensity of 138 K glow peak, whereas the 163, 268, and 288 K glow peaks underwent a relative increase. Kuila[7] related the TL peaks at 138 and 163 K to V_K hole centers and those at 268 and 288 K to V_F hole centers. Following Kuila[7], the 163 K peak sensitivity increase leads to the inference that this peak is also related to V_K centers, but in a different crystal environment compared to the 138 K peak. However, the author did not explain the difference. Considering that V_F centers are thermally unstable above 230 K, it is difficult to associate TL peaks at 268 and 288 K with these hole centers.[14] Townsend *et al.*[4] refused to associate LiF TL glow peaks at 225 and 255 K with V_F centers, preferring to relate them to electron traps. Additionally, it is important to mention that Kuila[7] did not carry out phototransference experiments to confirm his conclusions.

Figure 11 presents the V_K band and the 138 K TL peak relative intensities for different 348 nm optical bleachings. It can be observed that both the V_K band and the 138 K TL peak present the same loss of sensitivity due to 348 nm optical bleaching. Again a clear indication of a relation between the V_K band and 138 K TL glow peak is presented.

F. Phototransferred thermoluminescence

In order to determine the TL glow peaks related to electron traps, phototransference experiments with light of 250, 310, and 380 nm were carried out. The destruction of *F* centers with 250 nm light liberates electrons. The destruction of the defects related to the optical absorption band at 310 nm also liberates electrons, because it enhances the *F* band,[17] and the defects related to the optical absorption band at 380 nm are also electron traps[18] and liberate electrons after their optical destruction as well. Therefore, through phototransference experiments, with these three wavelengths, it is possible to repopulate only the empty electron traps, if they exist, and, thus, the phototransferred TL glow curve will display only peaks related to electron centers.

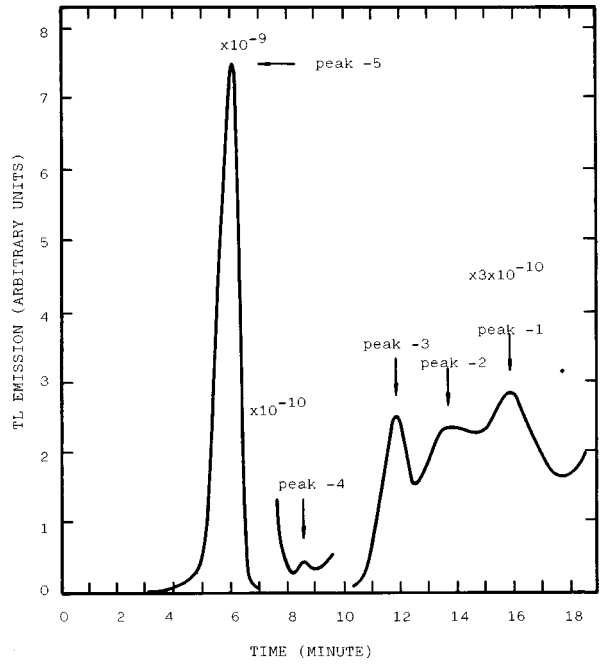

FIG. 12. Phototransferred TL glow curve obtained after irradiated TLD-100 sample exposure to UV light of 250 nm.

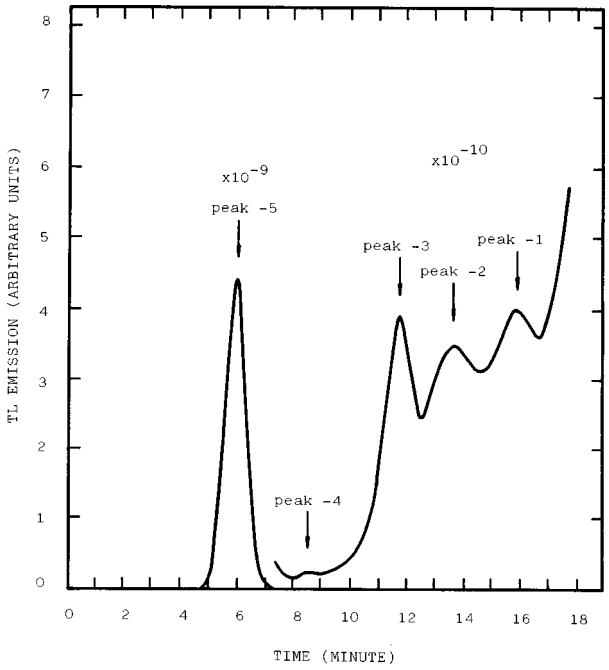

FIG. 14. Phototransferred TL glow curve obtained after irradiated TLD-100 sample exposure to UV light of 380 nm.

The sample annealing procedure used in the three experiments was 400 °C for 1 h. The sample was always exposed to x rays, 192.8 C kg^{-1}, at 288 K. After the x-ray exposure, it was cooled to 83 K and, at this temperature, exposed either to UV light of 250 nm, with a radiant exposure of 1043 J m^{-2}, or to 310 nm, with a radiant exposure of 14 870 J m^{-2}, or to 380 nm, with a radiant exposure of 9000 J m^{-2}. For each different UV light wavelength a complete separate experiment was performed.

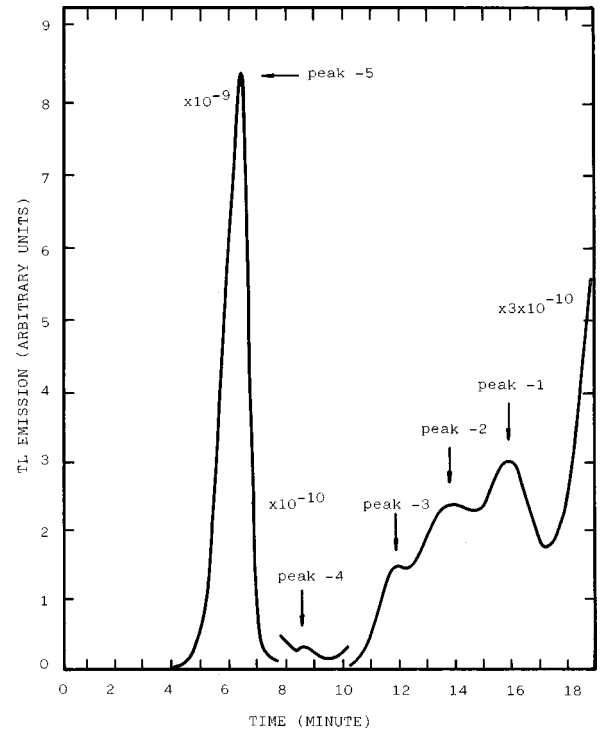

FIG. 13. Phototransferred TL glow curve obtained after irradiated TLD-100 sample exposure to UV light of 310 nm.

Figures 12, 13, and 14 show the phototransferred TL glow curves obtained, respectively, after the sample exposure to UV light of 250, 310, and 380 nm. It is possible to observe, in the three curves, the presence of all TL glow peaks found when the material is irradiated at 83 K, except the one at 138 K, whose experiments of optical destruction with UV light of 348 nm and intensity versus x-ray exposure showed that it is related to V_K hole centers. Thus, it is possible to conclude that, except for the TL glow peak at 138 K, all remaining peaks are related to electron traps. It should also be noted that the relative intensities of peaks -3, -2, and -1, in the phototransferred TL glow curve, are different when compared to those of the same peaks in the TL glow curve displayed by LiF:Mg, Ti irradiated at 83 K.

The possibility that illumination (photorepopulation) experiments would be a source of holes, according to the Mayhugh model,[1] could be considered. During room temperature irradiation, F and V_3 centers are produced. In the subsequent low temperature illumination, electrons captured at V_3 centers should leave V_k centers. This single hole center could then produce a glow peak upon warming. The prominent peak -5, located very close to the demonstrated V_k peak -6, could be this peak. However, if this is true, why isn't peak -6 sensitized? Therefore, an important presence of holes during photoillumination was not considered.

It is necessary to single out the behavior of peak -3 obtained by phototransference with 310 nm UV light. In this case, peak -3 presents, when compared with peak -2, a lower sensitivity, not similar to those obtained by phototransference with light of 250 and 380 nm, suggesting some kind of relation between peak -3 and the defects responsible for the 310 nm optical band. It is possible to imagine that the

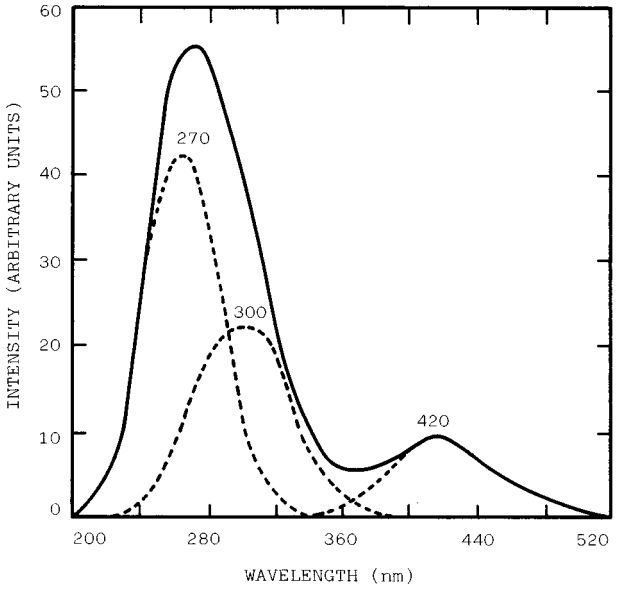

FIG. 15. TL emission spectrum determined for the 133–160 K region of TLD-100 TL glow curve.

exposure to UV light of 310 nm simultaneously liberates electrons from the deep traps to the shallow ones and liberates phototransferred electrons from the traps related to peak −3, considering that these traps are effectively related to defects which absorb at 310 nm. A competitive process of phototransferred electron trapping and detrapping may occur in the traps related to peak −3.

G. Thermoluminescence emission spectra

X-ray-induced TL emission spectra were recorded at two regions of the TLD-100 TL glow curve. The first region, from 133 to 160 K, comprises TL glow peaks −6 and −5 and the second one, from 243 to 300 K, includes TL glow peaks −3, −2, −1, and 0. Individual emission spectra, for each TL glow peak, were not possible to be obtained, because these peaks appear rather overlapped and the spectra were determined simultaneously with the controlled heating of the material, since it was impossible to maintain its temperature constant below 273 K.

Figures 15 and 16 present the two TL emission spectra determined, respectively, for the 133–160 K and 243–300 K regions of the TLD-100 TL glow curve. These spectra are corrected for the efficiencies of the photomultiplier tube and the monochromator used as a function of the light wavelength and for the intensity of light emitted by the material as a function of the temperature. The TL emission spectrum for peak −4 was not recorded because the sensitivity of this peak is very low.

The TL emission spectrum relative to TL glow peaks −6 and −5, Fig. 15, presents, clearly, two emission bands at 270 and 420 nm. Cooke[6] found similar emission bands at this temperature region. The existence of an emission band at 300 nm is also possible.

The TL emission spectrum relative to TL glow peaks −3, −2, −1, and 0, Fig. 16, displays two emission bands at 300 and 420 nm, but the possible presence of a third emission band at 270 nm should not be neglected. In this temperature range, different authors[5–9] agree with the existence of the emission band at about 420 nm; however, with respect to the emission band at 300 nm, only Kuila[7] and Podgorsak *et al.*[5] described, respectively, emission bands at 305 and 310 nm. Kuila[7] also determined, around 268 K, an emission band at 255 nm.

The emission band at 420 nm is associated with the recombination of a mobile hole with an electron tunneling from an F center at a titanium-F center complex, according to the model of Mayhugh.[1] The emission band at 270 nm is related to the recombination of V_k holes at recombination centers other than those associated with the emission band at 420 nm. The remaining emission band at 300 nm was related to the recombination of electrons and V_k centers.

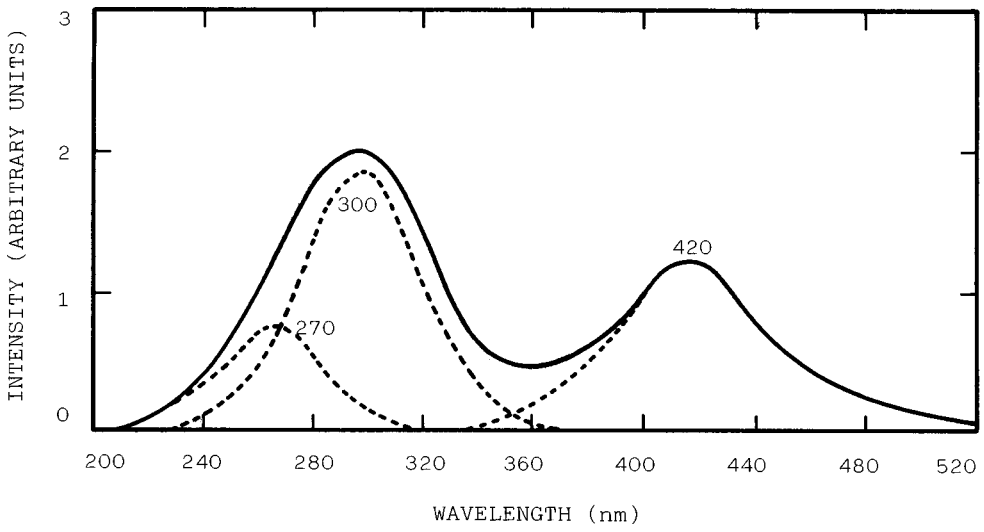

FIG. 16. TL emission spectrum determined for the 243–300 K region of TLD-100 TL glow curve.

TABLE II. E and s values determined for TL glow peaks -6, -5, -4, and -2 of TLD-100, obtained by different authors.

	Activation energy (eV)				Frequency factor (s^{-1})		
	Present work						
TL glow peak	Peak shape method	Initial rise method	Kuila[a]	Bhasin *et al.*[b]	Present work	Kuila[a]	Bhasin *et al.*[b]
-6	0.26 ± 0.02	0.27 ± 0.01	0.15 ± 0.02	0.36	1.8×10^{8}	1.37×10^{4}	4.4×10^{12}
-5	0.29 ± 0.02	⋯	⋯	0.32	16.5×10^{7}	⋯	7.0×10^{9}
-4	0.49 ± 0.02	⋯	⋯	⋯	3.4×10^{15}	⋯	⋯
-2	0.82 ± 0.02	⋯	0.60 ± 0.03	0.71	2.9×10^{14}	9.2×10^{9}	1.0×10^{13}

[a]Reference 7.
[b]Reference 20.

H. Determination of activation energy and frequency factor

In the determination of the activation energy, E, and the frequency factor, s, two methods were used, namely the peak shape method and the initial rise method. The initial rise method, proposed by Garlick and Gibson,[19] is the simplest one and is independent of the order of kinetics involved in the TL process responsible for the TL glow peak considered. The method assumes that three conditions are satisfied:

(a) In the temperature range of the beginning of the TL glow peak's initial rise, i.e., $T \ll T_m$, where T_m is the temperature of the peak maximum, the trapped charge carrier population variation rate is very small, and, thus, the intensity of the glow peak considered is proportional to $\exp(-E/kT)$;
(b) The frequency factor remains essentially the same for all temperatures;
(c) There is no superposition of TL glow peaks due to different traps.

The method requires the solution of the following equation:

$$\ln I(T) = C - \frac{E}{kT}, \tag{2}$$

where $I(T)$ is the intensity of the TL glow peak for the absolute temperature T, E is the activation energy, k is the Boltzmann constant, and C is a constant. Plotting of $\ln I(T)$ versus $1/T$, over the temperatures of the TL glow peak's initial rise, gives a straight line with slope $-E/k$. Once E/k is known, the determination of E is trivial. The value of s can be assessed, in the case of the TL glow peaks obeying first order kinetics, using Eq. (3)

$$\frac{\beta E}{kT_m^2} = s\ \exp\left(-\frac{E}{kT_m}\right), \tag{3}$$

where β is the heating rate used to obtain the TL glow peak.

Chen[13] presented the following equation to calculate E considering the TL glow peak shape:

$$E_\alpha = C_\alpha\left(\frac{kT_m^2}{\alpha}\right) - b_\alpha(2kT_m), \tag{4}$$

where α may be δ, τ, or ω, depending on the part of the TL glow peak considered, and the coefficients C_α and b_α depend not only on the part of the TL glow peak analyzed, but also on the order of its kinetics constant. The term ω is related to the whole TL glow peak and is equal to $T_2 - T_1$, τ is related to the region of the glow peak for $T < T_m$ and is equal to $T_m - T_1$, and δ is related to the region of the TL glow peak for $T > T_m$ and is equal to $T_2 - T_m$. T_m, T_2, and T_1 are defined as in Eq. (1). In the case of first order kinetics, the following equations are obtained:

$$E_\tau = 1.51\left(\frac{kT_m^2}{\tau}\right) - 1.58(2kT_m), \tag{5}$$

$$E_\delta = 0.976\left(\frac{kT_m^2}{\delta}\right), \tag{6}$$

$$E_\omega = 2.52\left(\frac{kT_m^2}{\omega}\right) - (2kT_m). \tag{7}$$

Once the value of E is determined, the determination of s is easy through Eq. (3).

Table II presents the values of E and s determined for TL glow peaks -6, -5, -4, and -2 of TLD-100. In the case of peak -6, two methods for E assessment were used, namely the peak shape method and the initial rising method. For peaks -5, -4, and -2, only the peak shape method could be employed. The E determination for the remaining peaks was not possible due to the superposition of different peaks that impedes the definition of their geometrical forms. These values are also compared to those obtained by Kuila[7] and Bhasin *et al.*[20]

In the determination of E for TL glow peaks -6, -5, -4, and -2, ten TL glow curves of a TLD-100 sample, annealed at 400 °C for 1 h, exposed to x radiation at 83 K, 2.88 C kg^{-1}, were used. In the case of peaks -6 and -5, in order to use the peak shape method, they were graphically separated. The results presented are mean values with an associated uncertainty equal to one standard deviation.

IV. CONCLUSIONS

The TL glow curve displayed by TLD-100 single crystals, thermally treated at 400 °C for 1 h, presents seven peaks between 83 and 320 K, namely at 138, 153, 193, 260, 283,

300, and approximately 240 K. These peaks are, respectively, labeled as -6, -5, -4, -2, -1, 0, and -3. Their relative sensitivities are dependent on the annealing procedure to which the phosphor is submitted and, except for the TL glow peak at 138 K, on the amount of Mg dopant present in it. Different annealing procedures also change the temperature of TL peak maxima.

The responses of peaks -6 and -5 show a linear behavior up to approximately 34 C kg^{-1}. Peaks -4, -2, -1, and 0 present linearity up to 20 C kg^{-1}. Peaks -6, -5, -4, and -2 present symmetry factor values, respectively, equal to 0.42 ± 0.01, 0.41 ± 0.01, 0.43 ± 0.01, and 0.43 ± 0.01. These results show that these peaks obey a kinetics of first order and are in agreement with the linear behavior of the peaks' sensitivities with exposure.

Activation energy and frequency factor values for TL glow peaks -6, -5, -4, and -2 of TLD-100 are, respectively, (0.26 ± 0.02)eV, (0.27 ± 0.01)eV, and 1.8×10^{8} s^{-1}, (0.29 ± 0.02)eV and 16.5×10^{7} s^{-1}, (0.49 ± 0.02)eV and 3.4×10^{15} s^{-1}, and (0.82 ± 0.02)eV and 2.9×10^{14} s^{-1}. In the case of peak -6, two methods for activation energy assessment were used. The agreement of both methods is very good.

The 348 nm UV light bleaching experiment and the x-ray exposure dependence results permit the establishment of a clear relationship between the 138 K TL peak and V_k hole centers. Additionally, phototransference experiments with 250, 310, and 380 nm UV light demonstrate that, except for the TL peak at 138 K, five TL peaks displayed by TLD-100, between 83 and 283 K, are due to electron traps. The 300 K TL glow peak seems not to be related to V_k centers. However, the present results do not clearly indicate that it is related to electron centers.

The seven TL glow peaks displayed by TLD-100 between 83 and 320 K emit at three wavelengths, namely, 270, 300, and 420 nm. The emission band at 270 nm is the most intense in the case of glow peaks at 138 and 153 K. For the remaining glow peaks, the emission bands at 300 and 420 nm are the most important ones. The emission band at 270 nm is related to the recombination of V_k holes at recombination centers other than those ones normally associated with the emission band at 420 nm. The emission band at 300 nm is related to the recombination of electrons and V_k centers.

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