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ADVANCES IN RESEARCH OF DEFECTS IN QUARTZ BASED ON LUMINESCENCE

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Abstract

The first part of this paper reviews the observation of the unconventional thermoluminescence {TL(M), where $M = \text{Li}$ or Na } peaks observed in the glow curve of Li- and Na-containing quartz, and describes the full solution of the puzzling effect of the TL(M) peaks which needed a two irradiation procedure for their formation. Of interest is the intermediate warming (IW) method, which consisted of two irradiations and warming of the sample to 150-300 K between the two irradiations. This was explained as follows: the first low temperature irradiation produces $\{\text{AlO}_4/\text{M}/h\}^+$ centers, when the now loosely bound M ions will be released from the Al-sites by warming to, let us say, 250 K. This model differs from the one accepted in literature according to which irradiation at above 200 K releases the M ions from the $\{\text{AlO}_4/\text{M}\}^0$ centers.

The second part describes some characteristics of the $\{\text{SiO}_4/\text{M}\}^0$ centers which were found to be related to the TL(M) peaks. These include the dose dependence of these peaks, which was found to be affected strongly by competing electron traps, and the possibility to excite the TL(M) by a single irradiation. The single irradiation excitation provided a simple measurement of the binding energies of the M ions to the $\{\text{AlO}_4/\text{M}/h\}^+$ centers. These were found to be 0.25 eV and 0.31 eV for Li and Na, respectively.

Differences in the TL(M) intensities obtained by first irradiation at 250 K and second at low temperature and those obtained by the IW method were also investigated. Finally, the 3.2 eV X-ray induced luminescence is shown to be closely related to the TL(M) peaks.

Key Words: Quartz, defects, irradiation effects, thermoluminescence (TL), unconventional TL peaks, X-ray-induced luminescence, dose dependence.

Introduction

The advances in the research of defects in quartz dealt with in the present paper resulted from an unexpected effect observed in the thermoluminescence (TL) of quartz. A glow peak, which did not appear at all in the conventional glow curve excited by a single low temperature X-irradiation, appeared as a very strong TL peak after an excitation procedure involving a double X-irradiation. This peak appeared near 190 K (at a heating rate of 10°C per minute) and was often stronger by two orders of magnitude compared to the conventional glow peaks of the quartz sample. This strange looking effect was observed independently by two research groups. Malik *et al.* [16] observed that after a double irradiation of a quartz sample, first at a temperature below 300 K and then reirradiated at 95 K, the glow curve showed "a new extremely strong peak" at about 200 K. They described this as a most intriguing and unexpected effect. We (Halperin and Katz [6]) observed the unconventional TL peak near 190 K under a somewhat different procedure of double irradiation: namely, both X-irradiations were performed at 10 K but the sample was warmed to about 250 K between the two irradiations. The second irradiation could be performed at any temperature below about 170-180 K.

The full solution of the puzzling effect was obtained by a combined investigation of researchers of the Oklahoma State University (L.E. Halliburton and M.G. Jani) and the Hebrew University of Jerusalem (A. Halperin), including a closely correlated electron spin resonance (ESR) and TL study on samples taken from adjacent parts of the same quartz plate [13, 14]. The known conditions for the production of a very strong 190 K TL peak {in short, TL(Li) or TL(190)} and the high sensitivity of the TL measurements helped when an ESR spectrum due to $\{\text{SiO}_4/\text{Li}\}^0$ centers directly related to the TL(190) peak was observed. A short description of the transitions involved in the production of the $\{\text{SiO}_4/\text{Li}\}^0$ centers and the related TL(190) is given below. Then, we describe more recent results of research carried out in our laboratory. Some recent results on the properties of the $\{\text{SiO}_4/\text{M}\}^0$ ($M = \text{Li}$ or

Na) centers are also described in more detail.

Materials and Methods

The samples used in most of the investigations described below were cut from the +x-growth zone of electronic grade synthetic (Sawyer Research Products Inc., Eastlake, OH) quartz crystals. Samples for TL were usually 11 mm x 8 mm x 2 mm in dimensions, with the main faces perpendicular to the y-axis. These crystals contained Al impurities substituted for Si and mainly Li ions as charge compensators at the Al ($\{\text{AlO}_4/\text{Li}\}^0$ defect centers). In some samples, the Li ions were replaced by Na ions by electrical sweeping at about 530°C (803 K) between two graphite electrodes pasted with NaCl. An electrical field of 400 V/cm was applied along the c-axis of the quartz sample. The sweeping was continued until a charge of 4-5 C/cm³ was passed through the sample, which was found to replace practically all the Li by Na.

Some experiments were performed on high-Q samples supplied by Thermo Dynamics (Shwannee Mission, KS) or Sawyer Research Products. These crystals contained much less Al and, of course, lower concentrations of the charge compensating ions. The dimensions of the samples differed somewhat from those given above. Otherwise, the experimental procedures were almost the same for all samples.

Samples were polished to nearly optical flatness, then cleaned and annealed for about 20 minutes at a temperature (up to 800 K) desired for the specific experiments. They were then mounted in a bore in the cold finger of a vacuum cryostat. The sample was clamped tightly in order to secure good thermal contact to the cold finger. A liquid nitrogen cooled cryostat fitted for TL measurements was used for the temperature range 80-750 K. A Displex double stage refrigeration system (Air Products and Chemical Inc., Allentown, PA) was used for lower temperatures. It enabled TL measurements in the range 10-370 K.

The cryostats were provided with Spectrosil (Thermal Syndicate Ltd., Wellsend, England) fused silica windows, a thin (0.3 mm) Al window for X-ray transmission, a heater and suitable thermocouples. The Displex system also had suitable low temperature sensors for the precision temperature controller.

Unless specified otherwise, the samples were X-irradiated from a tungsten target at 55 kVp (kVp = kilovolts peak, meaning the maximal voltage in each rectified half cycle of the high voltage supplied by the X-ray tube) - 18 mA located at about 6 cm from the quartz sample.

The TL signal was focused on the photocathode of a photomultiplier by a quartz lens, then amplified by a

610C electrometer (Keithley Instruments, Inc., Cleveland, OH) and recorded on a chart recorder.

A 9658R photomultiplier (E.M.I. Industrial Electronics Ltd., Middlesex, England) cooled to -25°C (248 K) was used for measurements not exceeding 500 K. When reaching higher temperatures, the photomultiplier was replaced by an E.M.I. 6256 S, which is not sensitive at wavelengths above about 600 nm. In addition, a Corning (Corning Glass Works, Corning, NY) 1-69 heat absorbing filter was placed in the optical path between the cryostat and the photomultiplier. This reduced black body radiation, which enabled measurements up to about 750 K.

A suitable monochromator enabled scanning of the spectrum in the range 300 nm to 650 nm in less than one minute. It was put in the optical path between the cryostat and the photomultiplier for spectral measurements of the emitted TL. In these measurements, the rate of heating was only 2.5°C/min, which minimized the changes in the TL intensity during each scan of the spectrum. In regular undispersed TL measurements, the heating rate was 10°C/min.

Some experimental details specific to individual measurements will be given in the text.

The Transitions Involved in Formation of TL(M) (M = Li or Na) and Some of Their Characteristics

In this section, we shall give, in short, the explanation of the formation of the TL(190) and of the analogous TL(200) observed in Na containing samples. This short review is necessary for a better understanding of the more recent results described below.

A careful examination of the ESR spectrum of our quartz samples under the procedures which caused the TL(190) to appear at high intensity proved successful when an ESR spectrum of the $\{\text{SiO}_4/\text{Li}\}^0$ center was revealed [14]. Further work on the ESR and TL resulted in a close correlation between the TL(190) and the $\{\text{SiO}_4/\text{Li}\}^0$ center [13]. Figure 1 shows that the emission of TL(190) is accompanied by a drop down to zero of the ESR spectrum related to the $\{\text{SiO}_4/\text{Li}\}^0$ centers. The drop in the ESR near 110 K may be related to a TL peak at about 110 K. This, however, was not investigated further, and the nature of the centers related to this drop in the ESR is still unknown.

The process of the formation of the $\{\text{SiO}_4/\text{Li}\}^0$ centers and their cancellation with the emission of the TL(190) is as follows:

(1). Holes provided during the first low temperature X-irradiation get trapped at the $\{\text{AlO}_4/\text{Li}\}^0$ centers, thus forming $\{\text{AlO}_4/\text{Li/h}\}^+$ centers.

(2). The Li^+ ions are bound loosely to the $\{\text{AlO}_4/\text{Li/h}\}^+$ centers. So, on warming to, let us say

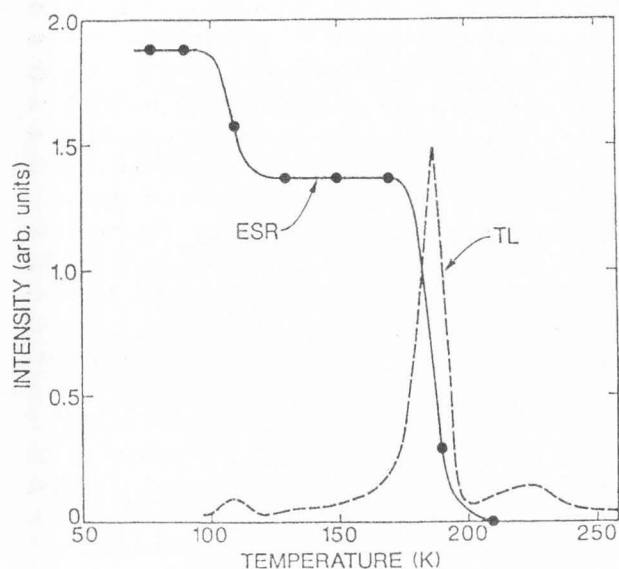


Figure 1. Thermal anneal of the ESR spectrum due to the $\{\text{SiO}_4/\text{Li}\}^0$ centers. The ESR is shown to drop down to zero with the emission of the TL(190) peak.

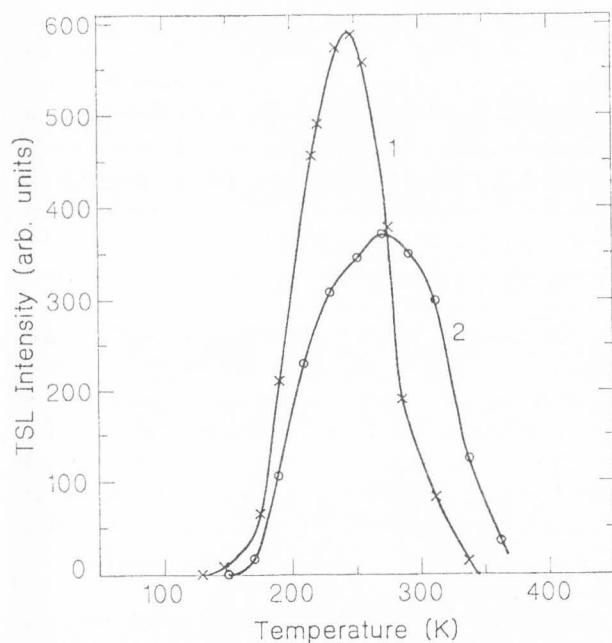


Figure 2. Formation curves for (1): TL(190), and (2): TL(200) peaks, obtained by the intermediate warming (IW) method. The abscissa gives the temperature reached by the intermediate warming.

250 K, they leave the Al-centers and migrate along the c-axis channels, where they get trapped near a regular silicon in the lattice, thus forming $\{\text{SiO}_4/\text{Li}\}^+$ electron traps. They leave behind $\{\text{AlO}_4/\text{h}\}^0$ centers.

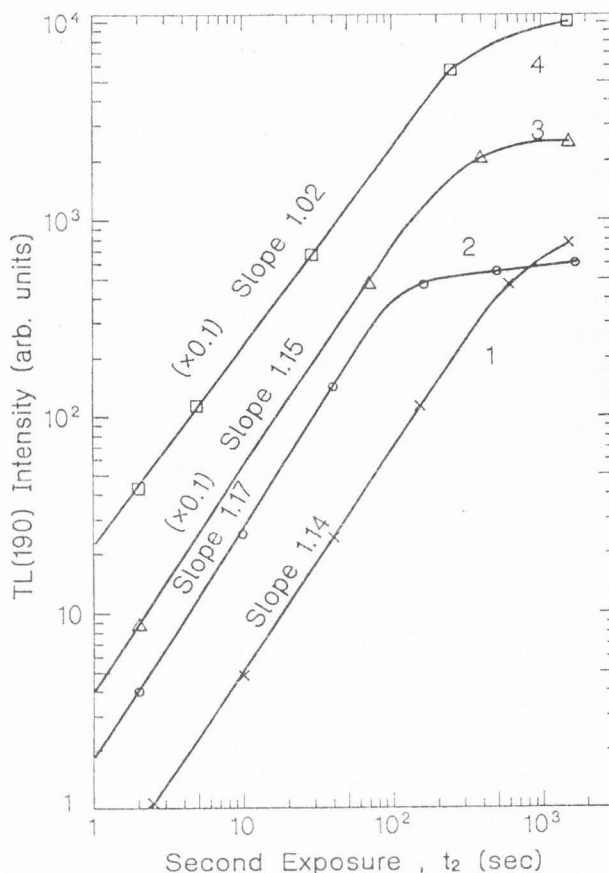


Figure 3. Dependence of TL(190) on the second irradiation time. Curves 1-4 were obtained after prolonged preirradiations at 700, 400, 310 and 260 K, respectively.

(3). The second low temperature X-irradiation provides free electrons, and some of them get trapped at the $\{\text{SiO}_4/\text{Li}\}^+$ electron traps, forming the $\{\text{SiO}_4/\text{Li}\}^0$ centers observed in the ESR spectrum.

(4). Finally, warming the sample to 190 K releases the electrons from the $\{\text{SiO}_4/\text{Li}\}^0$ centers when the related ESR spectrum disappears. The released electrons recombine at luminescence centers with the emission of TL(190). At the end of the process, the Li ions return to the Al centers at which the positive holes were canceled by recombination with the electrons released from the $\{\text{SiO}_4/\text{Li}\}^0$ centers.

When the first X-irradiation takes place at suitable higher temperatures, let us say 250 K, the Li ions leave the $\{\text{AlO}_4/\text{h}\}^+$ centers immediately when the $\{\text{SiO}_4/\text{Li}\}^+$ traps are formed.

An unconventional TL peak was observed also in Na-swept samples [7]. In this case, the peak appeared near 200 K {TL(200)}. Its intensity was very close to that of the TL(190) in the original sample before the Na-sweeping. The emission spectra of both the TL(190)

and TL(200) were identical (about 3.2 eV, 380 nm) [8]. The formation curves for the Li and Na containing samples are shown in Figure 2, where the abscissa gives the temperature reached in the intermediate warming between the two low temperature irradiations. The formation curve for the Na-containing sample is seen to have its maximum at about a 15-20 K higher temperature compared to the Li-containing sample.

Attempts to reveal the ESR spectrum related to the $\{\text{SiO}_4/\text{Na}\}^0$ centers were, until now, unsuccessful. The reason for this is not clear. Balley and Weil [1] have observed the $\{\text{SiO}_4/\text{Li}\}^0$ center in natural rose quartz but could not observe any ESR spectrum of the $\{\text{SiO}_4/\text{Na}\}^0$ centers. More than that, on replacing the Na back by Li, even the $\{\text{SiO}_4/\text{Li}\}^0$ center disappeared. There were also other differences in the $\{\text{SiO}_4/\text{Li}\}^0$ centers of the natural rose quartz compared to our synthetic samples. In the rose quartz, the $\{\text{SiO}_4/\text{Li}\}^0$ center was observed after one X-irradiation at 77 K, which was not the case in our samples. In addition, the rose quartz gave a single drop in the ESR at 190 K, and no drop was observed at 110 K (see, Fig. 1). These differences seem to be related to the more complicated centers present in the rose quartz. No TL related to the $\{\text{SiO}_4/\text{Li}\}^0$ centers in rose quartz has been measured until now. We plan to do it in the future, and it is believed that careful examination of the TL in close correlation with the electron paramagnetic resonance (EPR) of the samples will provide information leading to a better understanding of the observations.

Some Physical Properties of the TL(M) Peaks Related to the $\{\text{SiO}_4/\text{M}\}^0$ Centers

In this section, we shall describe and discuss some of the characteristics of the $\{\text{SiO}_4/\text{M}\}^0$ defects investigated in our laboratory since 1987. Most of the results have been published elsewhere and are only described briefly along with results of very recent measurements. In addition, the more general outlook enabled by the accumulation of more experimental facts in the last few years has helped in establishing and even improving the interpretation of the observed phenomena. Such revised explanations and their justification is given below in some detail. The results of some physical properties under investigation are given in the following sub-sections.

Dose dependence of the TL(M) intensities

In conventional single excitation of TL, the dose dependence curves rise linearly (slope of 1) at low doses and tend to saturate at higher doses. It has been shown that in the presence of an active competing trap, the dose dependence may show super-linearity [15]. Things are different in the double excitation of the TL(M) of

quartz. Preliminary experiments have given slopes varying between zero and two. The complications arise from the existence of many deeper electron traps in quartz, which compete with the $\{\text{SiO}_4/\text{M}\}^+$ traps for the electrons. The competition depends on the concentration of empty competing traps which, in turn, depends on the preirradiation and preheating in the history of the examined sample. This explains the variety of slopes observed in the preliminary experiments. Some of the competing traps are also filled up during the first and second irradiations, which also affects the measured slopes. The reader is referred to the published work on the dose dependence [5, 12]. In the following, we only give examples demonstrating the competition effect.

The curves in Figure 3 give the dependence on the dose of the X-irradiation of the TL(190) peak. The dose was varied by changing the second exposure time (t_2). In this case, the first irradiation time (t_1) was kept at 2 seconds. Curves 1-4 in Figure 3 were obtained after prolonged preirradiations at 700 K, 400 K, 310 K and 260 K, respectively, thus eliminating from the competition the traps stable above these temperatures which were filled up by the preirradiation.

All the curves in Figure 3 rise somewhat super-linearly (slopes up to 1.17) up to above $t_2 = 10^2$ seconds and then tend to saturate. The TL(190) intensities were very low in curve 1, in which case all the electron traps stable up to 700 K were empty. Filling up more and more traps, the TL(190) intensities go up, and with all the electron traps stable above 260 K filled up {curve 4, given on a reduced ($\times 0.1$) ordinate scale}, the TL(190) intensities are higher by about 2.5 orders of magnitude compared to those in curve 1.

Another point which follows from Figure 3 is that in spite of the very short first irradiation ($t_1 = 2$ seconds), the curves rise with a practically constant slope up to t_2 values above 10^2 seconds. This means that the $\{\text{SiO}_4/\text{M}\}^+$ electron traps formed during the 2 seconds irradiation need more than 10^2 seconds of the second irradiation to get filled up. The saturation of the curves in Figure 3 occurs when the filling up of the $\{\text{SiO}_4/\text{M}\}^+$ traps reaches equilibrium.

Figure 4, again for the TL(190), gives the dose dependence curves as function of t_1 with t_2 fixed (5 seconds). Curves were again obtained by gradually reducing the competition of deeper electron traps by prolonged preirradiations at 700 K, 400 K, 300 K and 250 K for curves 1-4, respectively. Curves 1 and 2 in Figure 4 rise almost linearly up to above $t_1 = 10^2$ seconds. This time, however, the rise of the TL(190) is caused by the gradual filling up of the empty competing traps during the exposures along each of the curves. This effect is very small in curves 3 and 4, where the concentration of the remaining empty competing traps is very low, and

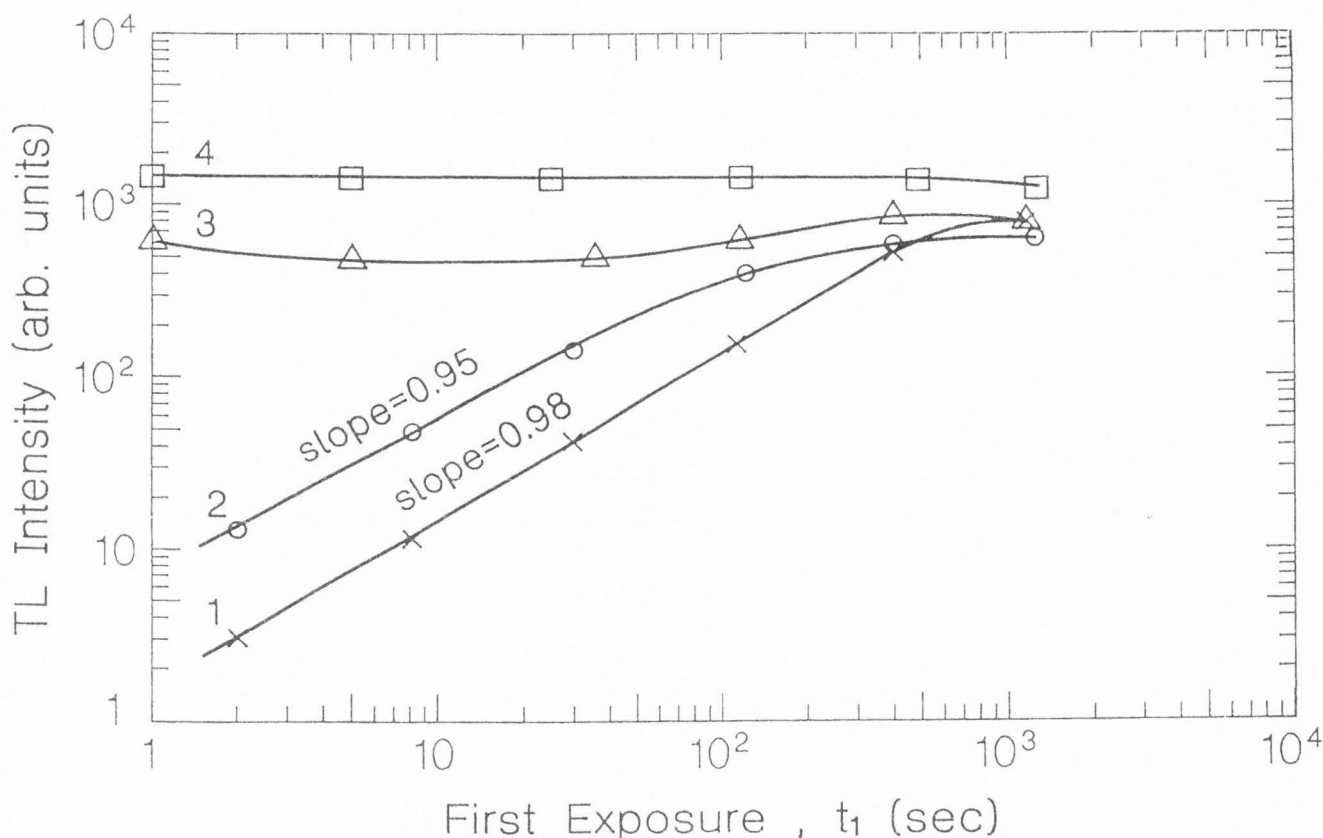


Figure 4. Dependence of TL(190) on the first irradiation time. Curves 1-4 after prolonged preirradiation at 700, 400, 300 and 250 K, respectively.

hence, the curve have slopes close to zero. The saturation intensities of the curves in Figure 4 give a measure of the concentrations of the $\{\text{SiO}_4/\text{Li}\}^0$ centers filled up by electrons during the second irradiation under conditions of negligible competition.

All the curves in Figures 3 and 4 were obtained with both irradiations performed at 80 K and an intermediate warming to 250 K between the two irradiations. Qualitatively similar results (with somewhat different slopes) were obtained with the first irradiation carried out at 250 K and the second at 80 K; Na-containing samples behaved similarly. The curves in Figures 3 and 4 do not give, therefore, the true dependence on the dose of excitation. To illustrate this, Figure 5 shows a few curves in which the excitation dose was fixed for all the TL measurements. The slopes of the curves in Figure 5 are obviously not zero.

For each point in Figure 5, the first excitation ($t_1 = 40$ seconds) was carried out at 250 K and the second ($t_2 = 2$ seconds) at 80 K. The abscissa gives now the accumulated exposure time for each curve (Σt_1 , neglecting the low, $t_2 = 2$ seconds, exposures). For each curve, the sample was preheated to 700 K, thus emptying all

the shallower traps unstable at 700 K. In recording the glow curves, the sample was heated to a different temperature for each curve. These temperatures were 620, 500, 400 and 320 K for curves 1-4, respectively.

Curve 1 in Figure 5 shows a very small increase in the TL(190) with the increase of Σt_1 . This is because in each TL measurement, the electron traps stable up to 620 K were emptied, and for longer Σt_1 values, an equilibrium is reached between the emptying and the filling up of the electron traps. With the gradual reduction of the emptying of the competing traps by reducing the temperature reached in each TL measurement, the remaining competing traps are filled up faster when the rise in the curve becomes steeper. Thus, in curve 4 (warming up to 320 K), equilibrium takes place only after an increase of TL(190) by nearly a factor of 10, compared to that at $\Sigma t_1 \approx 0$.

The investigation of these effects is now underway. Results reached, up to now, show that under certain conditions, the effect of the accumulated filling up of the competing electron traps can be dominant.

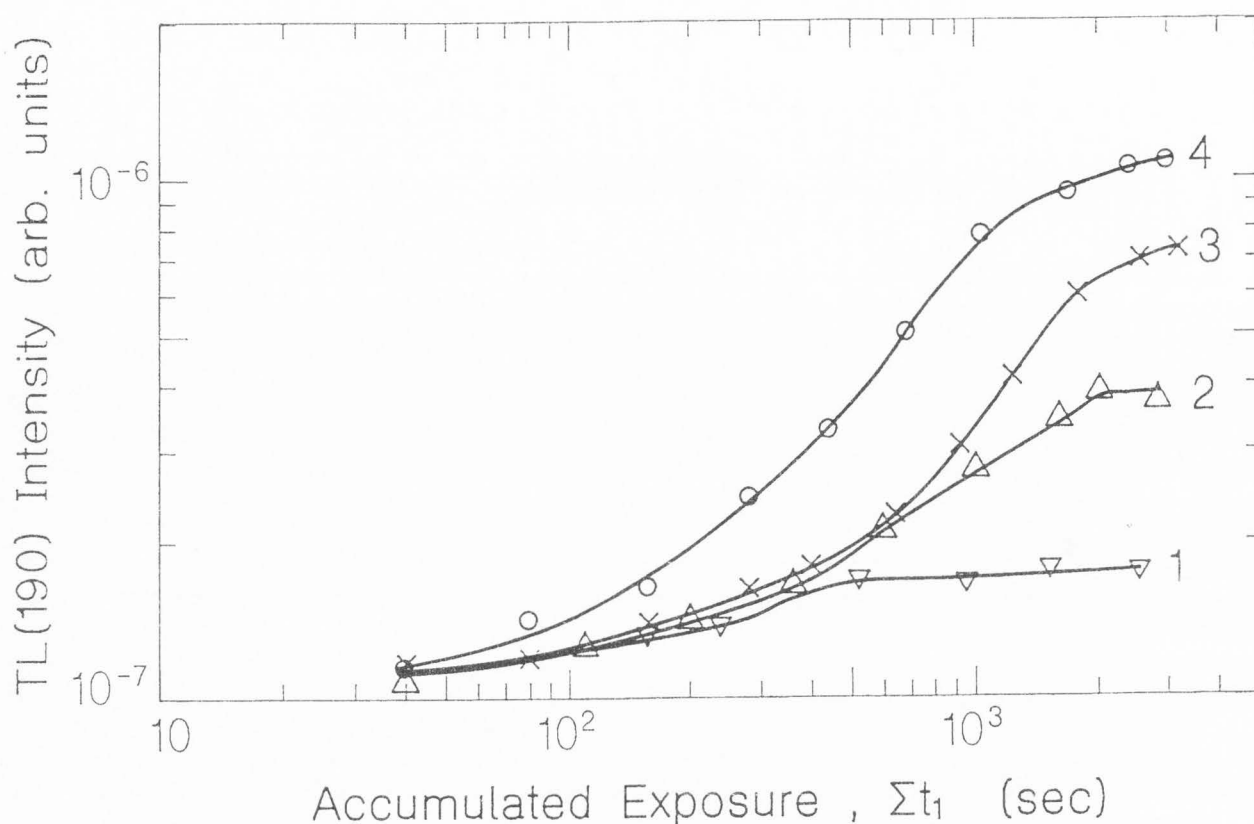


Figure 5. TL(190) as function of the accumulated first exposure (Σt_1). Sample was warmed to 750 K before starting each curve. The temperatures to which the samples were heated in each TL measurement (each point) were 620, 500, 400, 320 K for curves 1-4, respectively.

Single irradiation excitation of TL(M)

It has been stated above that a double irradiation is necessary for the excitation of the TL(M) peaks. This remains true with some restriction. It has been realized that in a small temperature range, the TL(M) peaks can be obtained by a single irradiation, though at intensities much lower compared to those reached by a double irradiation.

It is clear that the upper temperature limit for a single irradiation excitation should be below about 190 K, where the TL(M) related traps are still stable. On the other hand, the irradiation should be in the range of the formation curve of the TL(M), at which the M ions can be released from the Al and form $\{\text{SiO}_4/\text{M}\}^+$ traps (see, Fig. 2). This limits the possibility for a single irradiation excitation of the TL(M) to the range 150-180 K. This temperature range lies on the left tail of the formation curves (Fig. 2) where the TL(M) intensities are low compared to those at the maxima of the formation curves (at about 250-260 K).

Some characteristics of the single excitation TL(M) peaks were reported earlier [3, 10]. These are described

in brief here. However, results on the nature of the double excitation process accumulated since 1991 suggest a revision in the interpretation of dose dependence of the single excitation TL(M) peaks as given below.

Figure 6 presents (on a log ordinate) the intensity of the TL(190) peak as function of the reciprocal temperature. The various curves in the figure are for different exposure times, as indicated on the curves. The curves before saturation give a thermal activation energy of 0.25 ± 0.02 eV, which is the binding energy of the Li ions at the $\{\text{AlO}_4/\text{Li}/h\}^+$ centers. The bending down of the curves at temperatures above 180 K is caused by the instability of the TL(190) at these temperatures.

Log-log plots of the TL(190) intensity as function of excitation time taken at a fixed temperature (dose dependence curves) give a constant slope of 2 up to excitation times of about 10^2 seconds and tend to saturate at longer exposures (see, Fig. 3 in ref. [3]). Because of the comparatively low excitation times and the low intensities of the TL(190) peak in the single irradiation excitation, the concentration of the empty competing traps remains almost unchanged and so does not affect

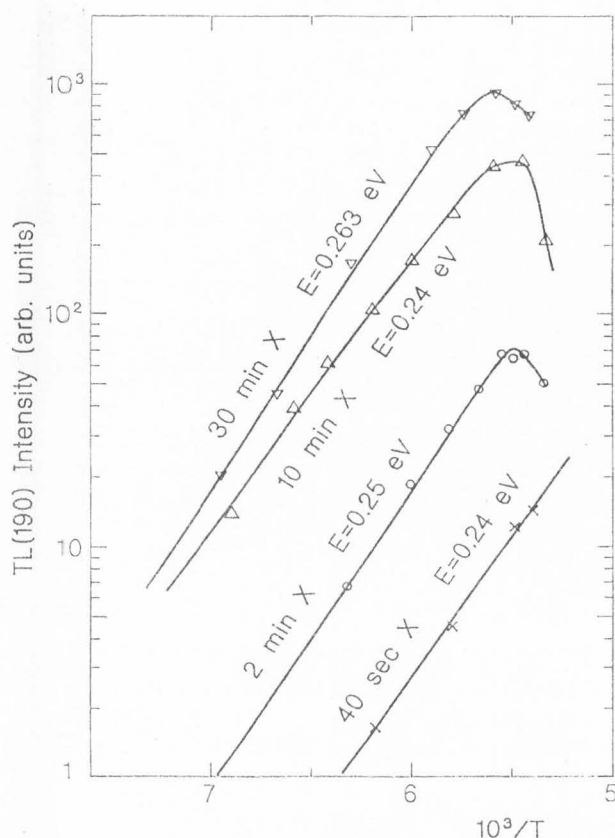


Figure 6. TL(190) intensity as function of $10^3/T$. Exposure times varied from one curve to another as indicated.

the measured slopes.

The quadratic dose dependence in this case is explained as follows: it was shown above that the release of the M ions from the Al centers is much faster than the filling up of the formed $\{\text{SiO}_4/\text{M}\}^+$ traps by electrons during the second irradiation. More than 10^2 seconds of the second irradiation were needed to supply the electrons for all the $\{\text{SiO}_4/\text{M}\}^+$ traps provided by the 2 second first irradiation. This implies that in a single irradiation procedure, and as long as saturation is not approached, the concentration of the released M ions and, as a consequence, the production of $\{\text{SiO}_4/\text{M}\}^+$ electron traps will grow linearly with the dose. On the other hand, the filling up of these traps will depend on the amount of free electrons getting trapped at the $\{\text{SiO}_4/\text{M}\}^+$ traps which also grows linearly with the time of irradiation. Therefore, the TL(M) intensity has to grow with t^2 as observed.

The present argument seems to give the true justification for the quadratic dose dependence observed in the TL(190) peak.

Na-swept samples gave similar results. In this case,

the binding energy of the Na ions to the $\{\text{AlO}_4/\text{Na}/\text{h}\}^+$ centers was found to be 0.31 ± 0.03 eV.

The release of M-ions from the Al centers

It has been shown above that the TL(M) peaks can be formed by two low temperature irradiations with an intermediate warming to, let us say, 250 K between the two irradiations. A second method of formation of the TL(M) is that of the two temperature irradiation (TTI) with the first irradiation at 250 K and the second one at a low temperature. By the IW method, the first low temperature irradiation was described as producing $\{\text{AlO}_4/\text{M}/\text{h}\}^+$ centers (see above) when the intermediate warming can easily remove the M ions from the Al-sites. It seems clear that under the strong Coulomb attraction of the M ions at the $\{\text{AlO}_4/\text{M}\}^0$ centers, such a release is impossible even at much higher temperatures. The above model differs from that given generally in literature, claiming that radiation above 200 K releases the M ions from the $\{\text{AlO}_4/\text{M}\}^0$ centers, and only then, positive holes get trapped at the Al sites [2, 17].

Our observations showed that with the same doses (t_1 and t_2) used for the excitation of the TL(M) peaks, the TTI method gives TL(M) intensities higher, often by a factor of 3 or even 4, compared to those obtained by the IW method. More than that, it was observed that both the TL(M) and the related ESR spectrum obtained by the TTI method were higher by a factor of 3 compared to those obtained by the IW method (see Figs. 4 and 5 in ref. [13]). It has been assumed by us that the dynamic process of formation of $\{\text{AlO}_4/\text{M}/\text{h}\}^+$ centers and their canceling by the release of the M ions when irradiating at 250 K gives a more efficient release of the ions from the Al-sites. Preliminary experiments show that this is not the case, and, in fact, the efficiency of release of the M ions is the same for the two methods.

This is shown in Figure 7, which gives the TL(190) intensities obtained by the IW method (x) and by the TTI method (o) for all the points $t_1 = t_2 = 100$ seconds. The numbers on the curve give the chronological order of the measurements, passing alternately from one irradiation method to the other. By this arrangement, the concentration of the empty competing electrons was nearly the same for each pair of points. The fact that all points in Figure 7 lie on the same curve suggests that the higher observed TL(M) intensities obtained by the TTI method compared to the IW method result from more efficient filling of the competing electron traps by the first method than by the second one. This suggestion must be checked further experimentally by comparing the filling process of the competing traps, and the corresponding TL(M) intensities obtained by the two methods.

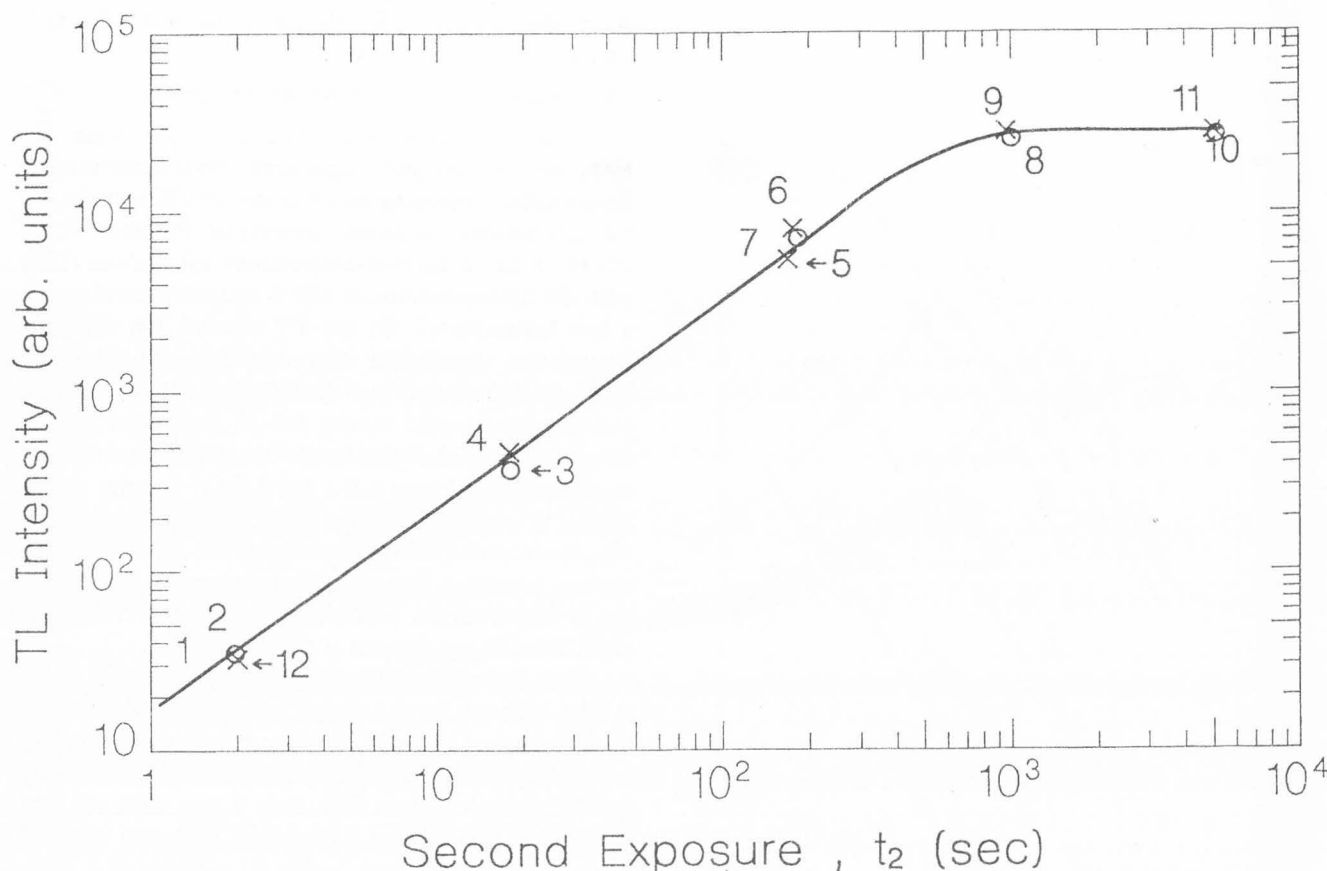


Figure 7. TL(190) intensities obtained by the IW method (x-s) and by TTI method (o-s). The numbers at the points give the chronological order of the measurements.

Temperature dependence of X-ray induced luminescence (XL) in quartz

The Li containing samples (Sawyer, electronic grade) showed mainly three emission bands peaking at about 2.4, 2.8 and 3.2 eV [4]. The Na-swept samples also showed three emission bands. The two low energy bands appeared, in this case, at somewhat lower energies, but the high energy one (3.2 eV) was identical with that in the Li-swept samples [11]. More than that, the 3.2 eV band observed in the XL was also identical with that observed for the TL(M) peaks. This suggests a close relation between the 3.2 eV XL and the TL(M). We shall concentrate below on the 3.2 eV XL and describe some of the results supporting its relation to the TL(M). A Wratten 18A filter (Eastman Kodak Co., Rochester, NY), having its maximum transmission at 360 nm and cutting off light above 400 nm, was used to isolate the 3.2 eV XL.

Figure 8 gives the temperature dependence of the 3.2 eV XL for a Li-swept sample. The exposures to X-rays were, in this case, kept below 1 second each

(probe exposures). This kept the concentration of the various electron traps (including the $\{\text{SiO}_4/\text{Li}\}^+$ traps) almost unchanged for all the points on each curve.

Curve 1 in Figure 8 gives the 3.2 eV XL obtained after preheating the sample to 750 K, thus emptying all the electron traps unstable at this temperature. The curve exhibits a steep drop in the XL starting at about 170 K. We label this drop as Stage II [4]. Curve 2 was obtained after a 30 minute preirradiation at 270 K. There then appears a considerable increase of the XL in the range 220-300 K (Stage III XL). Curve 3 was obtained after 1 hour preirradiation at 410 K. This preirradiation produced XL in the temperature range 280-450 K (Stage IV XL).

Na-swept samples showed similar effects with Stages III and IV shifted to higher temperatures [11]. Figure 9 gives the formation curves for Stage III XL, for a Li-swept sample (curve 1) and a Na-swept one (curve 2). The XL formation curves follow closely those obtained for the TL(M) peaks (Fig. 2). This suggests that the 3.2 XL is associated with the TL(M) related $\{\text{SiO}_4/\text{M}\}^+$ traps.

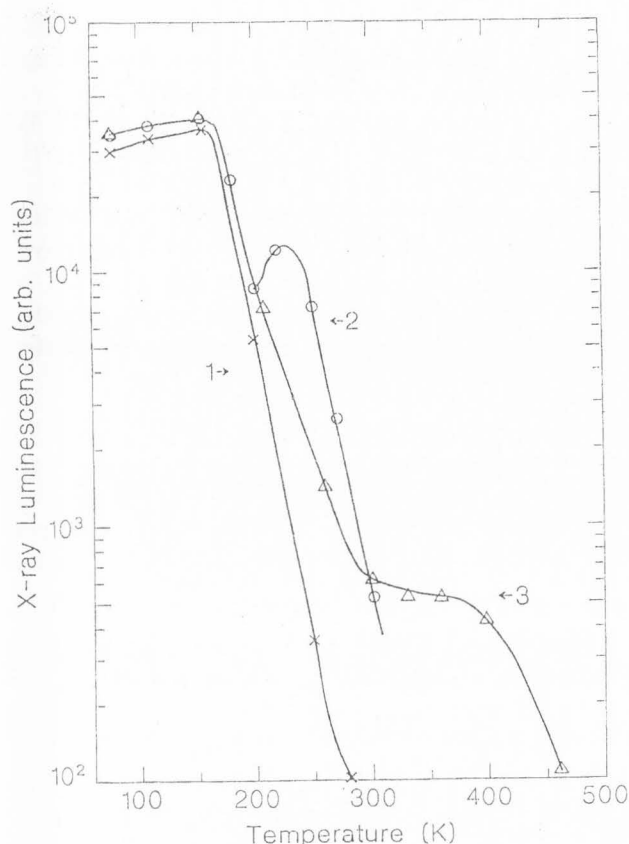


Figure 8. Temperature dependence of the 3.2 eV XL for a Li-swept sample. (1): After preheating to 750 K; (2): after 30 minutes preirradiation at 270 K; and (3): after 1 hour preirradiation at 410 K. Exposures for each point were limited to less than 1 second.

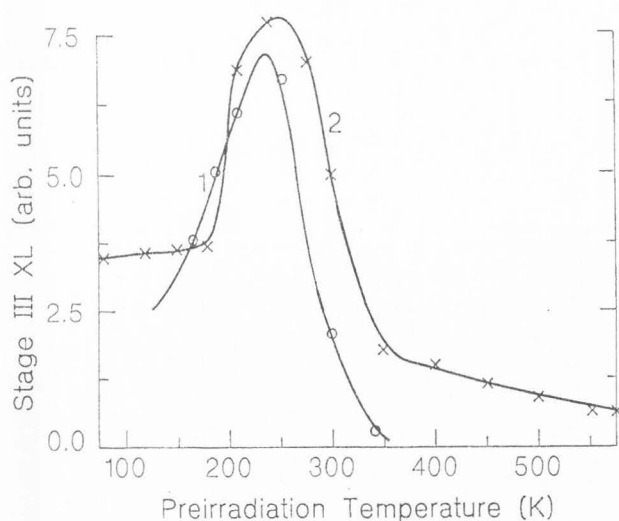


Figure 9. Formation curves for Stage III XL. (1): For a Li-swept sample; and (2): for a Na-swept one.

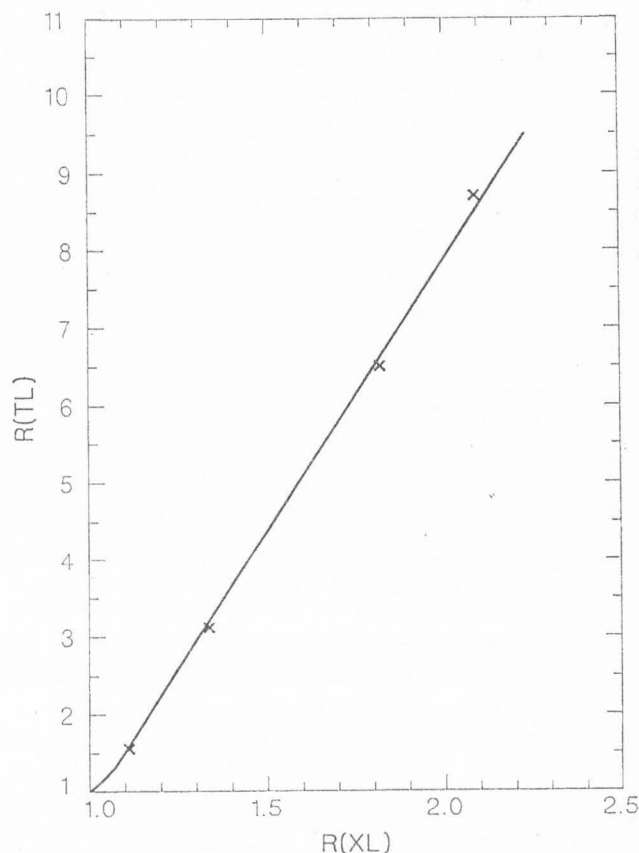


Figure 10. Relation between Stage III 3.2 eV XL and the TL(190) peak. $R(TL)$ gives the relative increase in TL(190) on increasing Σt_1 from 50 to 2500 seconds. $R(XL)$: analogous relative increase in the 3.2 eV XL.

The Stage IV 3.2 eV XL gives a formation curve closely related to a TL(Li) peak at about 180 K. This peak was found to replace the TL(190) peak after prolonged X-irradiation in the range of the formation of the Stage IV XL. The TL(180) peak has been assumed to be associated with centers similar to the $\{SiO_4/Li\}^0$, but with the Li ion trapped at unidentified defects X, thus forming $\{X/Li\}^0$ centers [9].

It has been shown above that with the first X-irradiation taking place at 250 K, the TL(190) peak rises with the accumulated exposure time (Σt_1). This rise of TL(190) depended on the rates of filling and emptying of the competing electron traps in each TL measurement (curves 1-4 in Fig. 5). Similar increases in intensity were also observed in the XL obtained in the 250 K first X-irradiation used to excite the TL(190). The 250 K irradiation, in fact, gives the rise in the Stage III XL with the dose (t_1).

The rise in the two quantities {XL and TL(190)} was found to show a linear relation, as depicted in Fig-

ure 10. In this figure, the ordinate gives the ratio, $R(TL)$ of the TL(190) intensity at saturation ($\Sigma t_1 \approx 2500$ seconds) to that at $\Sigma t_1 \approx 40$ seconds. The ordinate values in Figure 10 were obtained from these ratios as calculated from curves 1-4 in Figure 5. The abscissa values in Figure 10 give the analogous intensity ratios for corresponding XL intensities obtained at the 250 K X-irradiation used to excite the TL(190), $R(XL)$. The straight line obtained in Figure 10 gives further support to the close relation between the Stage III XL and the TL(190). Qualitatively similar results were observed for the TL(200) peak in Na-swept samples.

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