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Sensitization of thermoluminescence in synthetic quartz - heat treatment and radiation effects

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Changes in the sensitivity to β dose of the 100°C TL peak in synthetic quartz powder have been studied. While the emission in the visible range (~450 nm) was separately measured, the sensitivity increased substantially by high dose (~100 Gy) irradiation. This sensitivity was found to be reduced by repeated heatings to about 300°C, followed by 8 Gy (test dose) irradiations. The reduction of sensitivity was down to a certain equilibrium value. Applying the test dose followed by heating to the same temperature repeatedly to an unirradiated portion of the same sample, caused an increase in the sensitivity which reached an equilibrium after several such cycles; usually the same equilibrium as before. A qualitative model, consistent with previously known facts concerning synthetic quartz is given. The possibility that remnants of this effect occur in previously fired samples may explain some anomalous results in the pre-dose effect of sensitization observed in natural quartz.

1. Introduction

Most kinds of natural quartz show an increase in sensitivity of the 110°C thermoluminescence (TL) peak resulting from β or gamma irradiations followed by thermal activation at 350–900°C [1]. A model has been given by Zimmerman [2] which explains this sensitization as being due to a filling of a hole "reservoir" by the radiation, followed by the transfer of the holes into the recombination centers by the thermal activation. Chen [3] has modified this model showing that a necessary condition for it to be consistent with the experimental results is the presence of a competing radiationless center. In addition, it has been shown [4] that in synthetic quartz, the initial sensitivity is relatively low, and it can be substantially increased by firing the sample at the same range of temperatures. This effect has been shown to be closely related to the strong superlinearity found in the excitation of the 110°C TL peak [4], the explanation of which requires the occurrence of the same kind of competitor. Further results on this superlinearity were given by Kristianpoller et al. [5]. Yang and McKeever [6], following previous work [7,8] identified the electron trap with $(GeO_4)^-$ centers and the hole centers with $(AlO_4)^0$ yielding ~470 nm light. They also concluded, using combined TL and ESR measurements that the 380 nm emission is related to $(H_3O_4)^0$ hole centers. It is to be noted that a 470 nm emission band was found by Itoh et al. [9] in the electron excited luminescence of the same synthetic quartz, and was explained as being due to the recombination of self-trapped excitons. Kristianpoller [10] reported emissions at ~380 nm, ~450 nm as well as ~320 nm in photoluminescence and TL of synthetic quartz. Many authors reported that the main emission in the 100°C peak, namely, the 380 nm, was the one associated with the increase in sensitivity due to irradiation followed by thermal annealing.

In the present work we concentrate on some new results of changes of sensitivity, related mainly to the 450 nm emission.

2. Experimental procedure

For our measurements, synthetic "Premium Q" grade quartz from Sawyer Research Products was used. For most of the experiments, powder samples were used. The synthetic single crystals were crushed, ground and sieved. Recent measurements have shown that the TL sensitivity as well as the

dose dependence vary with the size of the grains [5]; therefore, grains of size ~30 μm were used for the measurements in the present work. 4–10 mg of powder were placed in a stainless steel dish, which was heated on a nichrome strip in a dry nitrogen atmosphere. The heating rate of 5°/s was monitored and kept constant by an electronically controlled system. The maximal preset heating temperatures varied from 150 to 550°C. The TL glow curves were recorded with an EMI 6255 photomultiplier; amplified and recorded with a Keithley 410 micro-micro-ammeter and an x-y recorder. The temperature was measured with a chromel-alumel thermocouple.

For spectral decomposition of the TL emission, appropriate optical filters were used. Optical filters were also applied to reduce black body radiation, especially at the high temperature range. For more precise spectral analysis of the light emitted at the various glow peaks, the samples were mounted in a vacuum cryostat, and the emission spectra were measured with a special fast-scanning device, which allows simultaneous measurements of the total TL emission and of their emission spectra. The here given emission wavelengths were not corrected for the instrumental response. Further details on this procedure and on the experimental equipment have been given elsewhere [11]. For these spectral measurements, the heating rate was 20°C/min compared to 5°C/s in the measurements with filters. This resulted in a shift in the peak temperatures. Due to the relatively low light intensities of the spectral bands obtained by this method, much higher radiation doses were required in order to obtain measurable spectral bands. These high doses influenced the TL emission due to the nonlinear dose dependence of some of the glow peaks.

For irradiation, a ^{90}Sr β source was used. The samples were irradiated at room temperature and the test dose varied generally between 1 and 12 Gy. The different doses were achieved using different irradiation times. In order to investigate the influence of previously absorbed radiation on the TL sensitivity, the samples were first exposed to relatively high doses, of the order of 100 Gy, and then heated to various temperatures. Subsequently the sample was exposed to the regular test dose and TL was measured in repeated cycles, consisting of exposure to a certain test dose and TL measurements. In the course of this study, the effects of thermal pretreatment on the TL sensitivity was also investigated. The samples were annealed in air in a furnace for about one hour and then slowly recooled to room temperature.

3. Results

Figure 1 depicts some representative results of the ~450 nm spectral band emitted at the 110°C TL peak. In each measurement, the sample was heated to 300°C before cooling back to RT for the next irradiation. Curves (a_1), (b_1) and (c_1) show the decrease of sensitivity following a 100 Gy initial irradiation, where test doses of 4, 8, and 12 Gy, respectively, are used for each measurement. Since different portions of the sample were used, the specimens were weighed and the results normalized by dividing the TL intensity by the weight. The term "sensitivity" should be used with some caution since different test doses are used in the three cases. If a normalization is performed by dividing the results by the appropriate doses, the equilibrium level reached varies to some extent with the test dose used, slightly increasing with these doses. Curves (a_2), (b_2) and (c_2) are found following excitations with the same doses of 4, 8, and 12 Gy respectively, without the prior high dose (100 Gy) irradiation. As seen in parts (b) and (c) of the figure, the increasing and decreasing curves come to about the same equilibrium value following a large number of cycles. As for (a), the general behavior is similar, but a small gap still remains between the levels after 12 cycles. It is not clear whether the gap will close following a much larger number or cycles. These effects were observed for the ~450 nm emission only and did not appear in the ~380 nm emission. Analogous measurements for this emission band showed a constant level of sensitivity in repeated cycles with and without previous initial irradiation.

Figure 2 shows the decrease of the sensitivity following the same initial irradiation of 100 Gy, but after heating to different temperatures in each cycle. Again, a filter transmitting the ~450 nm

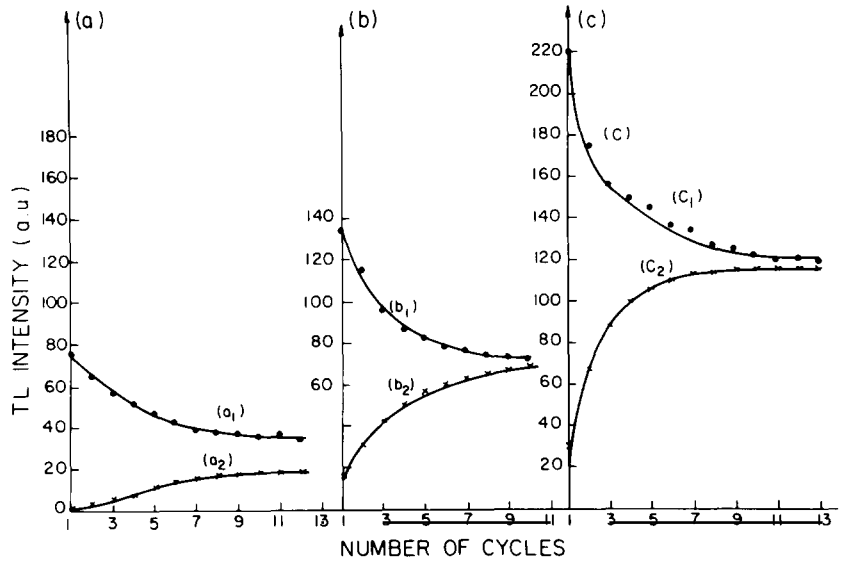

Fig. 1. The intensities of TL peaks at about 110°C in previously 100 Gy irradiated samples (a_1, b_1, c_1) and non-irradiated (a_2, b_2, c_2) in cycles of heating to 300°C followed by irradiations of 4, 8, and 12 Gy in a, b and c respectively. (All given data are of the ~450 nm spectral band. All irradiations were performed at RT.

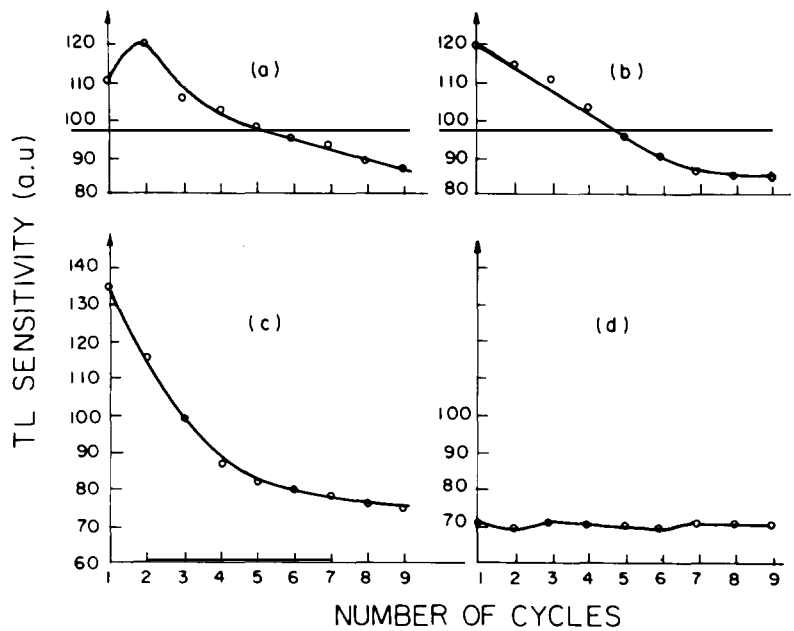

Fig. 2. Sensitivity to 8 Gy test dose in a previously 100 Gy irradiated samples. The heating in each cycle was to 150°C, 200°C, 300°C and 400°C in (a), (b), (c) and (d), respectively.

emission was used. The test dose used for all these measurements was 8 Gy. Curve (a) depicts the results while heating to 150°C. The sensitivity increased in the second cycle which is unusual compared to the other results. Curves (b) and (c) show the decrease of the sensitivity with heatings to 200 and 300°C, respectively. Curve (c) is the same as (b_1) in fig. 1. Curve (d) shows the results while heatings were to 400°C. The measured sensitivity was practically constant for all the cycles. It is to be noted that the final sensitivity following several cycles was nearly the same (between 70 and 90 units) in all the measurements.

4. Discussion

The main effect to be explained is the sensitization and desensitization of the ~450 nm emission by irradiations and thermal treatment of the samples. It is to be mentioned that, as opposed to the "classical" sensitization of the 100°C peak (at ~380 nm) in which the change of sensitivity was induced by the combined effect of irradiation and heating (to, e.g. ~500°C), here the heating (to, e.g. ~300°C) has a different role. Thus, we do not need to presume in the present context that holes are first accumulated in a reservoir and then transferred to the center but rather, that the 450 nm centers are directly filled by the free holes generated during the irradiation. On the other hand, as shown below, the other important element associated with the model of sensitization, namely, the occurrence of a center which competes for free electrons during the heating stage [13], is still of importance. Let us discuss first the accumulated sensitivity seen by, e.g. repeated irradiations of 8 Gy. It is to be noted that, since the sensitivities described here are much lower than those at 380 nm seen in natural quartz the test dose used here is by far higher than that utilized in archaeological dating. In many cases related to TL, one can assume that both electrons in traps and holes in centers (as appropriate in the present case) are accumulated in proportion to the excitation dose. This does not mean that the initial concentrations (following excitation) of electrons in traps and holes in centers are equal. Normally, one would expect the TL to depend on $\min(n_0, m_0)$ [12] where n_0 and m_0 are the initial concentrations of electrons and holes, respectively (as mentioned above, probably in $(GeO_4)^-$ and $(AlO_4)^0$ centers, respectively). This explains the normal linear dose dependence of different peaks. As explained, however, by Kristianpoller et al. [13], the presence of a competitor may cause the TL to depend on $n_0 m_0$, which has been used [4] for explaining the strong superlinearity in the 110°C peak in synthetic quartz. Following this reasoning, one may conceive a situation in which, at the end of the irradiation (by, e.g. 8 Gy), one has $m_0 > n_0$. Heating the sample above the 110°C peak depletes the electrons off the traps and reduces the number of trapped holes. During the next irradiation by 8 Gy, about the same number of electrons accumulate in the traps, but m_0 at the end of this excitation is larger than before due to the residue of holes from the previous excitation. One can see a sensitization which is related to the increase of the concentration of holes from step to step, again, under the assumption that a competitor exists [13]. The temperature to which the sample is heated does not appear to influence dramatically the results up to ~350°C, although some changes in the decrease rate and final equilibrium sensitivity are seen in fig. 2. Heating even once to 400°C reduces the sensitivity to its equilibrium level. Preliminary results show that beyond this temperature, there is an increase in the sensitivity even without prior irradiations. This is mainly in the 320 and 380 nm emissions [4,5], but appears to have some effect of the same kind on the 450 nm emission as well.

Starting from high sensitivity, the effect is reversed as seen in fig. 1, namely, the sensitivity reduces with the cycles of test dose plus heating. It appears that the main reason for this reduction is the heating in each cycle. It seems that following the high dose irradiation, the occupancy in the hole centers is close to saturation so that the additional test dose does not increase it substantially. The released electrons from the 110°C related trap (and traps related to higher temperature ones, if the sample is heated higher) recombine preferably with these luminescent centers (rather than the competitors), which reduces the sensitivity for a subsequent cycle. It seems to have been established that the basic factor in the increase of sensitivity

is the irradiations whereas the reason for the decrease, is the annihilation of holes via recombination with thermally released electrons. The steady state level seen in fig. 1 is a result of an equilibrium between the two effects. This level is seen to depend slightly on the size of the test dose used, as can be understood from the above explanation.

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