Materials Research. 2010; 13(2): 265-271 © 2010

Effect of Particle Size in the TL Response of Natural Quartz Sensitized by High Dose of Gamma Radiation and Heat-Treatments

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Received: April 11, 2010; Revised: May 21, 2010

This work investigates the effect of particle size in the thermoluminescence (TL) response of a quartz crystal that was initially crushed and classified into ten size fractions between 38 µm and 5 mm. Aliquots of each size fraction were sensitized with a dose of 25 kGy of γ rays and heat-treatments at 400 °C. TL glow curves of sensitized and non-sensitized samples were recorded as a function of different test-doses of γ rays. For the non-sensitized samples, the TL peak near 325 °C increases with the decrease in particle size. In the case of sensitized samples, a strong TL peak near 300 °C increases with the increase in particle size up to mean grain size equal to 304 µm. Above 304 µm, an abrupt reduction in the TL intensity is noticed for the sensitized peak. These effects are discussed in relation to the specific surface area of quartz particles and the intensity of the electron paramagnetic resonance signal of the E'_1 center induced by the sensitization process.

Keywords: *natural quartz, particle size, thermoluminescence, EPR spectroscopy*

1. Introduction

Thermoluminescence (TL) of α-quartz has been the subject of numerous investigations in the last five decades since the discovery of its practical use for archeological and geological dating. Detailed descriptions of TL in quartz including numerous references are available in review papers by McKeever[1], Wintle[2] and Preusser et al.[3]. TL glow curves of quartz grains usually found in sediments and rocks or even prepared from single crystals are composed by several peaks appearing near 110, 170, 320 and 370 °C. The peak near 110 °C usually shows a high sensitivity compared to the other glow peaks. Zimmerman[4] was one of the first to report an increase in the sensitivity of this peak using γ doses of few hundred Gy and heat treatment at 500-900 °C. This procedure was further studied and let the extensive use of the 110 °C peak for dating and environmental dosimetry[5-8]. However, the TL signal of the 110 °C peak shows a fast anomalous fading at room temperature and due to this reason it is not used for TL dosimetry of X and γ rays[9-11]. Until now, the peaks appearing near 320 and 370 °C have been mainly used in dating protocols[2,3] but they are not used in TL dosimetry due to its low sensitivity. For instance, these peaks are not suitable for clinical dosimetry because for such kind of application the TL dosimeter (TLD) should assess a large range of doses from 10^{-6} to 10^{2} Gy[12].

Recently, the possibility to produce a strong TL peak near 300 °C in natural quartzes taken from different deposits was reported[13-15]. Combining high doses of γ radiation and heat-treatments, it was possible to increase the TL sensitivity of a 280 °C peak more than 1000 times. Using this procedure, it became possible to assess doses as low as 10^{-4} Gy using discs with a 6 mm diameter manufactured from a quartz block taken from the Solonópole district located in the Ceará State of Brazil[14]. It was also observed that the outcome of sensitization was related to the impurity content ratios of aluminum (Al^{3+}), lithium (Li^{+}) and hydroxyl (OH^{-}) which exist as impurities into the quartz lattice and varies from one deposit to the other. Lattice impurities usually give rise to precursors of point defects that act as electron traps or recombination centres during ionizing radiation and TL output. In addition, it was reported that the dispersion involved with the TL output around 300 °C for samples prepared from the same crystal is supposedly attributable to local variation in OH^{-}, Al^{3+} and Li^{+} concentrations[15]. The heterogeneity in the spatial distribution of lattice impurities is a common feature in natural single crystals but it can be reduced by powdering and homogenization procedures[16]. In particular, the non-uniform distribution of TL intensities observed in a lot of TLDs prepared from single crystals can be minimized when the TLDs are prepared from particles resultant from the powdering of the crystal[17].

As it is well known, Brazil has numerous natural deposits of raw quartz with different grades of optical quality and impurity content[18]. Looking for new applications of quartz resources, the sensitization process described above open the possibility to investigate the use of quartz particles in the production of TL dosimeters. Based on the detectable doses reported previously[13-15], it seems that dosimeters prepared from sensitized quartz particles may be suitable for clinical (medical) and industrial applications[17]. If this issue is pursued, the

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first point to take into account is the effect of particle size in the TL response of the sensitized quartz. Many TLD materials are produced using powdering procedures and it is known that TL intensities are affected by the particle size[17,19,20]. However, few studies were carried out with the objective to understand the TL response of a given material as a function of its particle size[19-22]. Thus, the aim of this study is to investigate the effect of particle size in the TL glow curves of natural quartz in non-sensitized and sensitized conditions.

2. Experimental

The natural quartz used in the present study was a single crystal extracted from one deposit located in the district of Solonópole (Ceará State, Brazil). Fragments of this crystal were cleaned with acetone for 15 minutes using an ultrasonic bath and then were manually crushed using an agate mortar and pestle. After crushing, the particles were classified into fine (300 × 425 μm, 150 × 315 μm, 150 × 300 μm, 75 × 150 μm, 38 × 75 μm and < 38 μm) and coarse fractions (2.8 × 4.8 mm, 2.0 × 2.8 mm, 1.7 × 2.0 mm and 0.85 × 1.7 mm) by using standard Tyler sieves. The particle size distributions and the specific surface area of the fine fractions were measured with a laser particle size analyzer, model Malvern Mastersizer 2000 with the Hydro 2000MU sample dispersion accessory. For these fractions, the mean particle size (D_m) corresponds to the aperture associated with 50% of passing material. For the coarse fractions, D_m corresponds to the average of the lengths measured along three directions of quartz grains with a digital microscope.

Aliquots of each size fraction were sensitized with a dose of 25 kGy of ^{60}Co in a γ-cell irradiator with a dose rate close to 10 kGy/h. After, three heat-treatments were successively performed in a muffle furnace as follows: continuous heating up to 400 °C, annealing for one hour at 400 °C, cooling, annealing for two hours at 100 °C and cooling. This thermal cycle completed the sensitization process and it was adopted as the standard annealing procedure throughout this work. For non-sensitized samples, this heat-treatment was also performed in order to remove the TL signals caused by previous exposure to natural radiation.

For the study of TL response as a function of particle size, three aliquots of 5 mg were prepared for fine size fractions (< 425 μm). In the case of coarse particles (> 850 μm), the TL measurements were carried out in individual particles. The weight of each particle was ranged from 5 to 25 mg according to its size. In order to compare with our previous data, the TL response was also read at three single crystals extracted from the same block. These samples are discs with 6 × 1 mm^2 which were sensitized with the same conditions described above. The non-sensitized samples were exposed to doses of 0.05, 0.5, 2 and 5 kGy of ^{60}Co called here test-doses to distinguish them from the sensitization dose (25 kGy). The sensitized samples were exposed to single test-doses of 50 mGy. The TL glow curves were recorded from 50 to 400 °C using a Harshaw 3500 reader with a heating rate equal to 2 °Cs^{-1}. The TL signals of each aliquot were normalized into respect with the sample weight and test-dose. The mean TL intensities of the three measurements were obtained integrating the TL glow curves between 175 to 390 °C.

In order to check the induction of lattice distortions in the crystal structure of quartz grains due to the severity of the manual crushing, standard X-ray diffraction (XRD) analyses were carried out in samples of very fine size fractions, i.e., 75 × 150 μm, 38 × 75 μm and < 38 μm. For this, XRD patterns were obtained with a 2θ diffractometer between 10 to 60° using Cu-Kα radiation. The full width at half maximum (FWHM) of the diffraction peaks related to $(10\bar{1}0)$, $(10\bar{1}1)$ and $(11\bar{2}0)$ planes were measured. Afterwards, scanning electron microscopy (SEM) was also used to observe the shape and fracture patterns of the crushed particles classified in several size fractions.

The electron paramagnetic resonance (EPR) spectroscopy was carried for the fine size fractions (< 425 μm). The samples (200 mg) were placed into fused quartz tubes with inner diameter equal to 3 mm. For each sample, three measurements were carried out in a Bruker EMX 10-Plus spectrometer operating at the X-band (~9.83 GHz) provided with a high sensitive cylindrical cavity. Initially, the magnetic field was swept from 1000 to 5500 G. Then, the EPR intensity was recorded at room temperature by sweeping the magnetic field from 3400 to 3530 G setting the parameters as follows: modulation amplitude of the magnetic field: 1 G; modulation frequency: 100 kHz; time constant: 10.24 ms; conversion time: 20 ms; receiver gain: 1 × 10^4; number of scans: 10. For specific magnetic field intervals, the signal was recorded as a function of the microwave power ranging from 0.002 to 63.25 mW. The peak-to-peak intensities of EPR signals were measured in non saturated conditions.

3. Results

The TL curves of the non-sensitized samples with particle sizes ranging from 38 to 425 μm show glow peaks near 90, 215 and 325 °C. An intense TL peak was observed at 90 °C that corresponds to the well-documented 110 °C peak of quartz. In the present study, the peak at 90 °C was not considered due to its unstable behavior at room temperature. Figure 1a shows the characteristic TL curves for samples with different particle sizes irradiated with a test-dose of 50 Gy. These results show that the TL intensity of the peak near 325 °C increases with decreasing particle size. The TL glow curves of samples irradiated at 500 Gy are shown in Figure 1b. Besides the 110 and 325 °C glow peaks, a new peak is observed near 215 °C. In this case, an opposite effect is observed with respect to particle size, i.e., the TL intensity at 215 °C decreases with decreasing particle size.

Figure 2 summarizes the behavior of the TL intensity integrated from 175 to 390 °C as a function of the mean particle size (D_m) for non-sensitized samples. In this figure, the TL intensity was normalized in relation to the intensity measured for the size fraction < 38 μm. According to Figure 2, the samples irradiated with 50 and 500 Gy show a similar behavior in relation to the mean particle size, i.e., the increase in TL intensity is observed for samples with D_m < 150 μm. In case of samples irradiated at 2 and 5 kGy, the TL intensity is not clearly correlated with D_m due to the increase of the peak near 215 °C. As shown in Figure 1b, this peak increase with the increase in particle size. Thus, the increase of the 325 °C peak with the decrease in particle size was completely surpassed by the increase of the 215 °C peak.

In order to better observe the effect of particle size in the TL response, the glow curves of the sensitized samples were divided in two groups. Figure 3a shows the TL glow curves for fine fractions and Figure 3b shows the TL glow curves for coarse fractions. In Figure 3a, an increase in the TL intensity of the peak near 300 °C is observed for larger particle sizes. This behavior is similar to that observed for the peak near 215 °C occurring in non-sensitized samples (Figure 1b). In addition, it is observed that the TL peak near 300 °C shifts to 280 °C for particles classified as coarse fractions. In principle, it would be expected that this shift should be noticed in the opposite sense because it is believed that the temperature set is reached in a smaller amount of time when fine particles are distributed over the heating planchet of the TL reader. This statement is based on the assumption that the heating flow rate through a mass of insulating material is higher for fine grains. In this way, the onset of the luminescence should occur at lower temperature for fine grains. Therefore, the temperature shift shown in Figures 3a and b cannot be explained by the effect of the

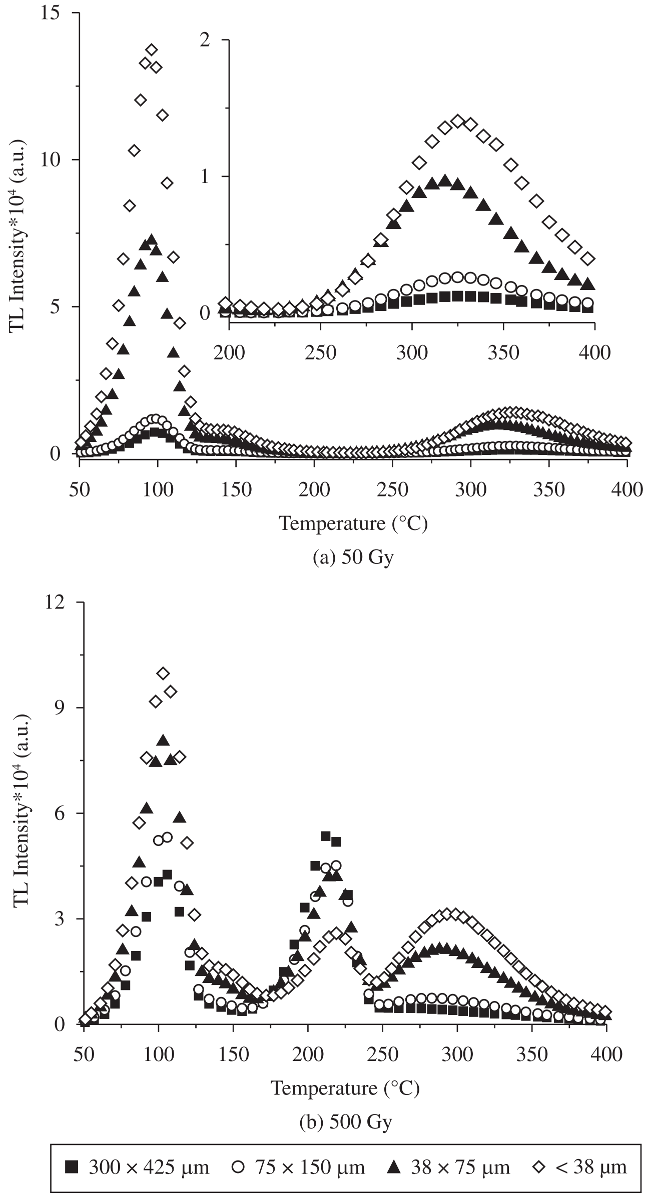


Figure 1. TL glow curves of quartz particles exposed to different test-doses of γ radiation.

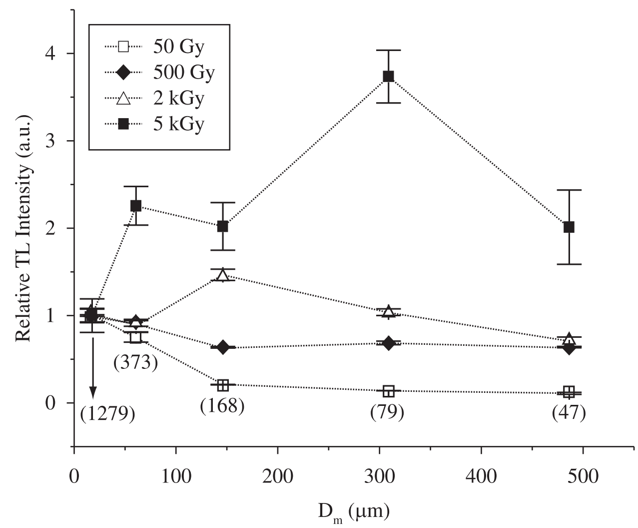


Figure 2. Relationship between TL intensity integrated from 175 to 390 °C and the mean particle size (D_m) for non-sensitized quartz. Values between parentheses are the specific surface area measured in cm^2g^{-1}.

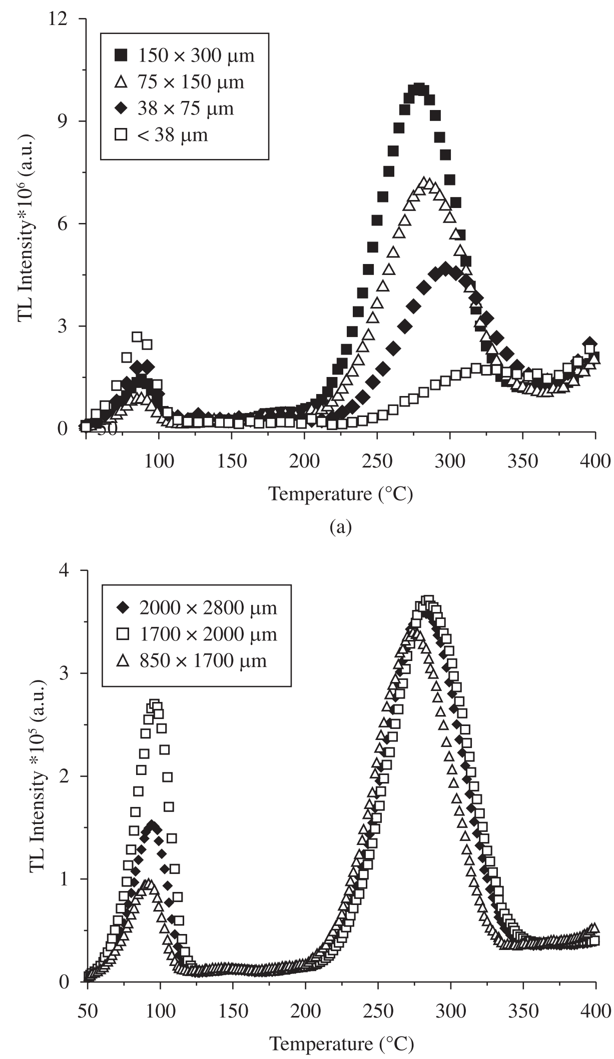


Figure 3. TL glow curve of quartz particles sensitized with 25 kGy of γ radiation and heat-treatments at 400 °C (test dose: 50 mGy).

particle size on the heat flow during the TL readings. Certainly, the temperature shift of the second peak is connected with the sensitization of a broad TL peak occurring between 200 and 300 °C when quartz is treated with high γ dose and heat. In addition, Figure 3 shows that the peak at 90 °C shows different intensities that can be explained by the anomalous fading[9-11], which occurs during the interval of TL readings. On the other hand, the intensity of the TL peak near 300 °C seems to be very stable as a function of time.

Figure 4 shows the TL signals integrated from 175 to 390 °C as a function of the mean particle size for sensitized quartz samples. It can be seen that the TL intensity increases as the particle size increases from D_m = 18 to D_m = 304 µm. For particles larger than 304 µm, an abrupt decrease in the TL intensity is noticed and no important change in TL intensity is observed for particle sizes larger than 2 mm. In this figure, the sample with the largest D_m is a solid disc with diameter of 6 and 1 mm thick. This disc was prepared directly from the crystal plate and it was not submitted to the crushing procedure.

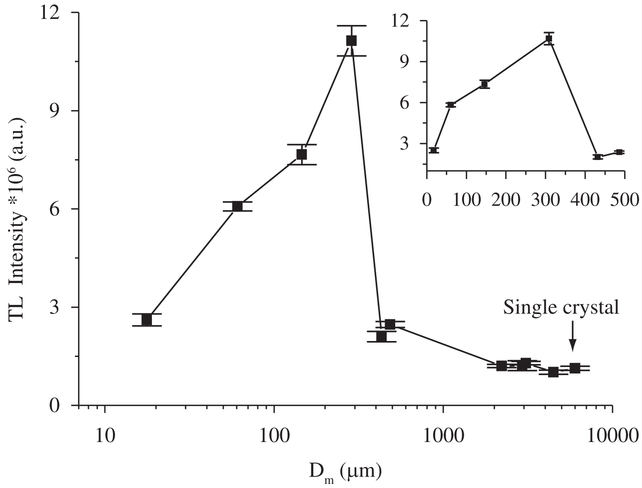
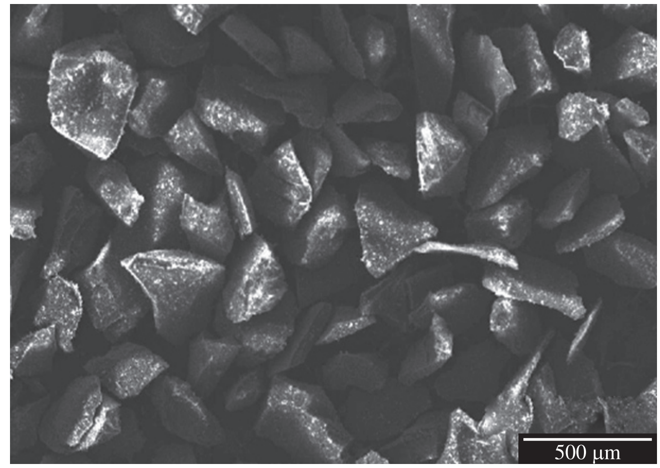
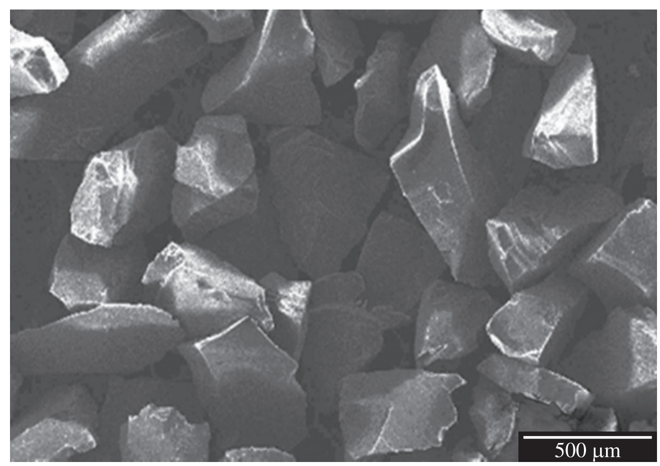


Figure 4. Relationship between TL intensity integrated from 175 to 390 °C and the mean particle size (D_m) for sensitized quartz (test dose: 50 mGy). The inset plot corresponds to the initial part of the figure in a linear scale.



(a) D_m = 304 mm



(b) D_m = 486 mm

Figure 5. SEM micrographs of quartz particles with different mean grain sizes.

These measurements suggest a reliable similarity between the TL responses of coarse particle sizes and the TL response of a single crystal prepared from the same sensitized quartz.

4. Discussion

Previous studies showed that the manual crushing of quartz particles with mortar and pestle can induce mechanical damage or amorphization into the crystalline structure when fine grains are submitted to high pressures[23-25]. However, no change in the width of the $(10\bar{1}0)$, $(10\bar{1}1)$ and $(11\bar{2}0)$ diffracting peaks was observed with the FWHM analysis carried out in 75 × 150 µm, 38 × 75 µm and < 38 µm size fractions. Based on this analysis, the assumption that the decreasing TL intensity for D_m < 304 µm shown in Figure 4 would be associated with amorphization or mechanical damage into the crystalline structure of quartz grains can be ruled out. Similarly, the SEM analysis did not reveal any substantial difference in the morphology of the quartz particles. For instance, Figure 5 shows typical images obtained for particles with D_m equal to 304 and 486 µm. Besides the size range and the presence of very fine grains deposited on the surface of 304 µm particles, no difference is observed in fracture patterns that could be associated with the abrupt change of TL intensity shown in the Figure 4. It is observed that brittle micro-cracking is the principal mechanism of size reduction related to the crushing procedure performed here.

The effect of the particle size in the TL response of non-sensitized quartz can be explained by the increase in the specific surface area for fine quartz grains. For test-doses 50 and 500 Gy, it was observed that the TL intensity increases with decreasing particle size when D_m < 150 µm. As shown in Figure 2, the specific surface area for size fractions < 38 µm and 38 × 75 µm are larger than the others. A similar behavior was previously reported for particles of potassium iodate (KI) and amorphous silica exposed to similar test-doses[21,22]. As stated before, the TL output increases with decreasing particle size because a much higher surface area of material is exposed during the TL reading. The effect of the specific surface area on the TL intensity was not observed when test doses such as 2 and 5 kGy were administered to quartz grains due to the onset of the peak near 215 °C. As shown in Figure 1b, this peak increases with the increase in particle size and this effect is probably associated with the beginning of the sensitization process responsible for the strong peak near 300 °C.

For sensitized samples, the small increase in TL intensity observed in the right side of Figure 4, when TL intensities of the single crystal and fragments of few millimeters are compared with that of particles with $D_m \approx$ 450 µm, can also be attributed to the increase of the specific surface area. In the sequence, the abrupt increase in TL response for D_m = 304 µm and the subsequent decrease noticed for finer particles cannot be merely explained by the effect of specific surface area. As a first approximation, these results can be explained by the effect of particle size during the irradiation of quartz with high dose of γ radiation. For some reason that is not clear, the sensitization with 25 kGy is more effective to create paramagnetic centers acting as electron traps and recombination centers in those particles with D_m = 304 µm. It is believed that finer particles do not absorb the radiation in the same way as particles with grain size larger than 304 µm. Thus, the 280 °C TL peak noticed for quartz particles with D_m = 304 µm could be explained by the concomitant effects of the absorption of high γ dose and the specific surface area of the particles within this size range. In order to examine this hypothesis in more detail, the fine size fractions of sensitized quartz were further investigated with EPR spectroscopy and the most important results are described below.

The EPR spectra shown in Figure 6 illustrate typical derivative lines of the EPR signals recorded for the fine size fractions of quartz particles measured before and after the sensitization process. In the Figure 6a, the EPR lines observed in the region between 3400 and 3520 G, characterized by the g factors at 2.0496, 2.0072 and 2.0037, were assigned to paramagnetic centers related to silicon vacancies. The existence of silicon vacancies in the quartz structure is expected to lead to hole trapping by two oxygen ions with the formation of various O_2^{3-} centers. In this case, the values of the *g* factors mentioned above corresponds to the presence of O_2^{3-}/M^+ centers (where $M^+ = Li^+, Na^+$) in the quartz structure[26-28]. It was reported that these centers are stable at room temperature and can be observed up to 350 °C[26,28]. Because the sample of Figure 6a was not irradiated, it is suggested that the Si-vacancy centers observed in Solonópole quartz were originally created during the crushing procedure but the intensity of the EPR lines of these centers remarkably increased after the sensitization with 25 kGy and heat-treatment at 400 °C, as can be seen in Figure 6c.

As shown in Figure 6b, no EPR signals were observed for non sensitized samples in the field range of 3508 and 3525 G. In case of sensitized samples, definite EPR signals appeared in this field range for all size fractions that was investigated. As shown in Figure 6d, these signals, characterized by g values equal to 2.0012, 1.9950 and 1.9940, were previously detected in synthetic quartz crystals doped with germanium. These signals were assigned to E'_1 centers perturbed by a Ge^{4+} substituting for Si^{4+} in the SiO_4 tetrahedron[29,30]. The accepted model for the E'_1 center corresponds to an oxygen vacancy with an unpaired electron in the sp^3 hybrid orbital extending into the vacancy from an adjacent Si atom[30,31].

The relationship between the intensity of the central signal ($g_2 = 1.9950$) related to E'_1 center and D_m is shown in Figure 7. It is observed that the intensity of this signal initially increases and then decreases with the increase in D_m. It is also observed that the size fractions with D_m equal to 138 and 304 µm show similar EPR intensity values for this defect centre. Compared to the TL response shown in the inset plot of Figure 4, one observes that the decrease in both signals (TL and EPR) occurs for particles with similar sizes. Previously, several authors suggested that paramagnetic centers of the E' family play the role of electron traps during quartz irradiation[32-34]. Thus, the results of the present study let us to suggest that the formation of E'_1 centers (perturbed by substitutional Ge species) by the sensitization process described above are dependent of the particle size and help to explain the relationship observed between the TL response of the 280 °C glow peak of Solonópole quartz and its particle size. Using a similar attempt to correlate the g_2 value of Si-vacancy centers, no clear relationship was found between this signal and the TL response of the sensitized peak. Further investigations are required to examine the effect of particle size in the creation of paramagnetic centers that act as recombination centers during the TL output such as the $[AlO_4]^0$ hole-centers. The EPR signals of this defect can be only detected at 100 K or at lower temperatures[1,31].

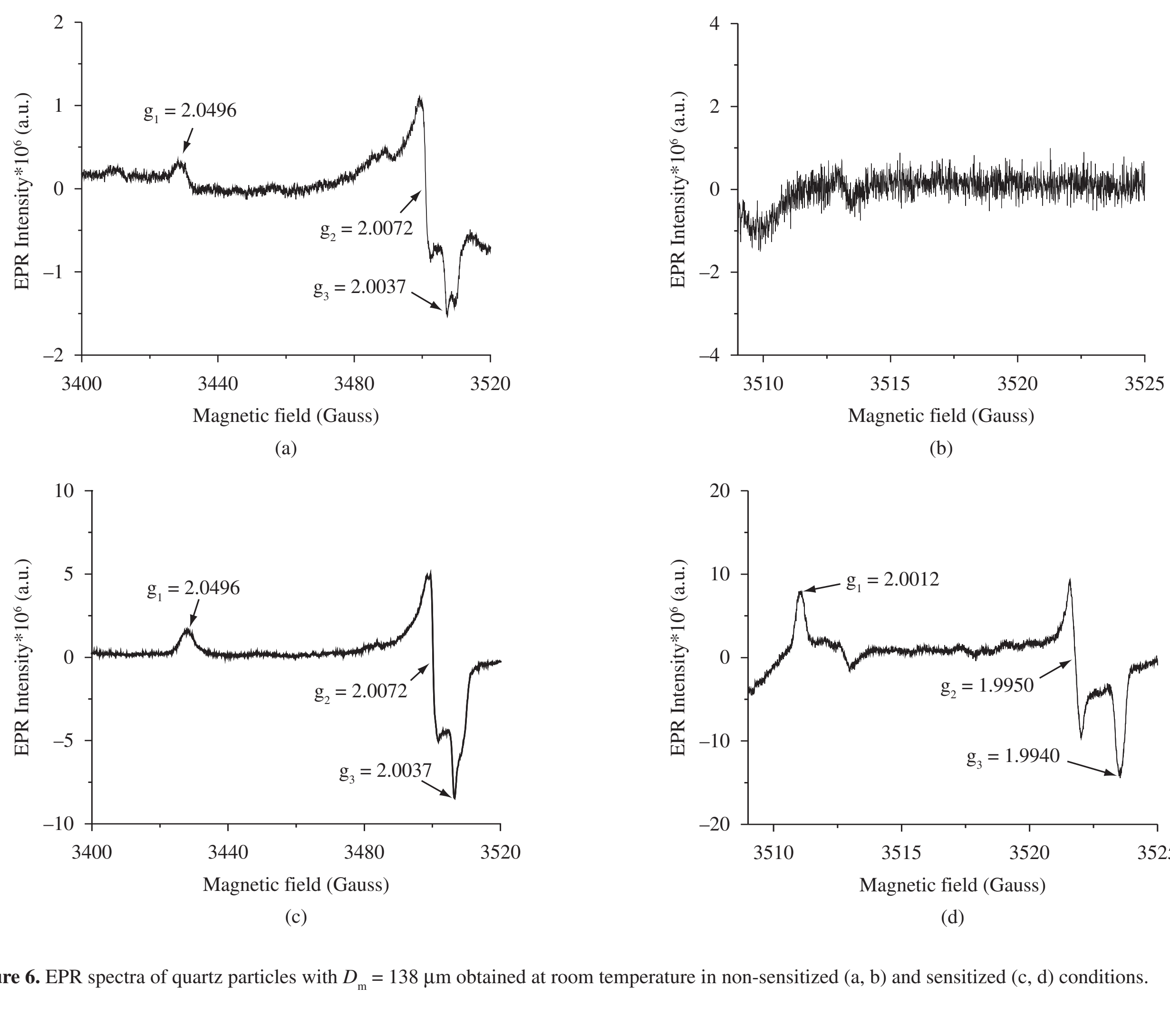


Figure 6. EPR spectra of quartz particles with D_m = 138 µm obtained at room temperature in non-sensitized (a, b) and sensitized (c, d) conditions.

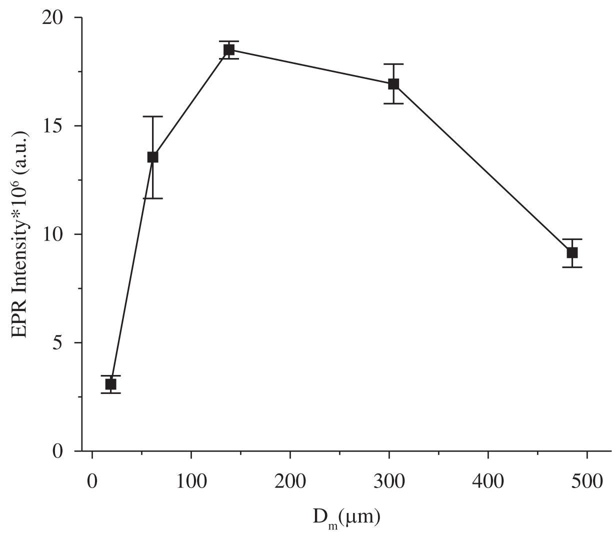


Figure 7. Relationship between the EPR intensity of E'_1 centers perturbed by substitutional Ge species and the mean particle size (D_m) of sensitized quartz.

5. Conclusion

For non-sensitized natural quartz extracted from the Solonópole district, the increase in TL intensity integrated from 175 to 390 °C with particle size decreasing is associated with the increase in the peak near 325 °C and this result is explained by the increase in the specific surface area. In this study, this effect was clearly observed using test-doses ranging from 50 to 500 Gy. For test-doses in the range of a few kGy, the effect of the specific surface area is not observed due to the onset of an additional peak near 215 °C, which showed an opposite behavior with particle size. After sensitization with 25 kGy and 400 °C, the effect of the specific surface area is noticed only when the TL intensities of fragments of a few millimeters are compared to those particles with mean grain size close to 300 μm. The subsequent decrease in TL intensity observed for particles with mean grain size < 300 μm can be explained by the inferior number in E'_1 centers perturbed by substitutional Ge created during the sensitization process, which probably act as electron traps during irradiation with test-doses. This work led to the conclusion that Solonópole quartz with mean particle size close to 300 μm has suitable properties for future use in TL dosimetry.

Acknowledgments

The authors are thankful to Prof[a]. Márcia Carvalho A. Fantini (IF-USP, São Paulo) for XRD analyses. One the authors (ABCJr.) is grateful to CAPES for the scholarship provided. This work was supported by CNPq and FINEP/INFRA-2005 (Brazil).

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