Effect of particle size in the TL response of natural quartz sensitized with high gamma dose

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Abstract. The aim of this study is to investigate the effect of particle size in the thermoluminescence (TL) response of natural quartz sensitized with high gamma dose. For this, fragments of a single crystal taken from the Solonópole district (Brazil) were crushed and classified into ten size fractions ranging from 38 µm to 5 mm. Aliquots of each size fraction were sensitized with 25 kGy of gamma dose of ⁶⁰Co and heat-treated in a muffle furnace at 400°C. The non-sensitized samples were exposed to test doses between 50 Gy and 5 kGy and the sensitized samples were exposed to a unique test dose equal to 50 mGy. For non-sensitized samples, the TL peak near 325 °C increases with the particle size decreasing. However, in the case of sensitized samples, the TL output near 280 °C increases with the increasing of particle size up to mean grain size equal to 308 µm. Above 308 µm, an abrupt reduction in the TL intensity was noticed. These effects are discussed in relation to the specific surface area and the different interaction of high gamma doses with fine and coarse particles of quartz.

1. Introduction

Many natural crystals exhibit thermoluminescent (TL) properties that are suitable for TL dating amongst which quartz is one of the most important ones because it is currently found in fragments of ancient ceramics and geological sediments [1,2]. Recently, natural quartz has been investigated for TL dosimetry applications [3]. Even though there is a large number of studies dealing with TL properties of quartz and silica, it is believed that natural quartz has not been used as a dosimeter for ionizing radiation. The reason for this is that its glow curve is very dependent on the geological conditions in which quartz was grown [1,3]. In addition, the point defects acting as electron traps and recombination centers in crystalline quartz are not yet fully characterized.

An important effect that can be observed in quartz is the increase in the sensitivity of a given glow peak following the absorption of high radiation doses. This sensitization process, also known as pre-dose effect, is an important feature in radiation dosimetry where the enhancement in sensitivity is highly desirable. Until now, systematic studies on the sensitization in quartz have been restricted to the first glow peak around 110 °C by ionising radiation and heat-treatment. This sensitization process was explained using a phenomenological model, which involves an increase in the probability of radioactive recombination at the luminescence sites [4,5]. On the other hand, a recent study reported...
the sensitization of a peak between 250 and 300 °C induced by high gamma irradiation [6]. This study showed that the sensitization of the peak near 280 °C allows the detection of doses in range of few mGy. Thus, the sensitization of quartz glow peaks appearing above 110 °C can be useful for applications in TL dosimetry due to the no effect of thermal fading.

There are several materials produced for TL dosimetry using powdering procedures and it is well known that TL intensities are affected by the particle size [7-9]. Studies have been performed with the objective to understand the behavior of TL materials of different grain sizes [8,10,11]. In the case of silica powders, it was reported that the intensity of the TL peak at 180 °C increases with decreasing grain size when silica is irradiated with gamma doses of 23 Gy [11]. In addition, efforts have been made to produce TL dosimeters using quartz grains prepared from sensitized natural quartz [12]. Therefore, it seems important to better understand the behavior of TL glow curves as a function of quartz particles with different grain sizes. Thus, the aim of this study is to investigate the effect of particle size in the TL response of non-sensitized and sensitized quartz particles.

2. Experimental procedure
For this study, a quartz single crystal extracted from the Solonópole district located in the Ceará State of Brazil was used. Crystal plates cut with a diamond saw were manually crushed using an agate mortar and pestle. After crushing, the particles were classified into fine (300x425 µm, 150x315 µm, 150x300 µm, 75x150 µm, 38x75 µm and < 38 µm) and coarse fractions (2.8x4.8 mm, 2.0x2.8 mm, 1.4x2.0 mm and 0.85x1.7 mm) by using standard Tyler sieves. The particle size distributions 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 (Dm) corresponds to the aperture associated with 50% of passing material. For the coarse fractions, Dm corresponds to the average of the lengths measured along three directions with a digital microscope.

Aliquots of fine and coarse grains were sensitized with 25 kGy of 60Co in a gamma cell irradiator with a dose rate of 10 kGy h⁻¹. Three heat treatments were successively performed in order to guarantee the release of charge carriers from the trap levels. The heat-treatments were 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 was adopted as the standard procedure throughout this work. This heat-treatment was performed only once for non-sensitized samples.

For the study of TL response as a function of particle size, batches containing three aliquots of non-sensitized and sensitized samples were prepared. The mass of each aliquot (~ 5 mg) was determined with an analytical balance accurate to 0.0001 g. The non-sensitized samples were exposed to test doses of 0.05, 0.5, 2 and 5 kGy of 60Co called here test doses to distinguish them from the sensitization doses. The sensitized samples were exposed to test doses of 50 mGy. The TL glow curves were record from 50 to 400 °C using a Harshaw 3500 reader with a heating rate equal to 2 °Cs⁻¹. The TL signal was normalized regarding weight and dose. The TL intensities were obtained integrating the TL glow curves between 175 and 390 °C.

To analyze the severity of the crushing procedure on the crystalline structure of quartz particles, aliquots of three fine fractions (75x150 µm, 38x75 µm and < 38 µm) were examined by X-ray diffraction (XRD). Standard XRD patterns were obtained with a 0-20 diffractometer between 10° and 60° using Cu-Kα radiation and the full width at half maximum (FWHM) of the diffraction peaks related to (10 1 0), (10 1 1) and (1 1 2 2) were measured. Afterwards, scanning electron microscopy (SEM) was used to observe the shape and the fracture pattern of crushed particles.
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 which 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 1 shows the characteristic TL curves for samples with different particle size irradiated with 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 2. 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 1. TL glow curves of quartz particles with different sizes exposed to 50 Gy.

Figure 2. TL glow curves of quartz particles with different sizes exposed to 500 Gy.

Figure 3 summarizes the behavior of the TL intensity integrated from 175 to 390 °C as a function of the mean particle size. In this figure, the TL intensity was normalized in relation to the intensity measured for the size fraction < 38 µm. According to Figure 3, the samples irradiated with 50 and 500 Gy show a similar behavior in relation to the mean particle size (D_m), 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 2, this peak increased with increasing particle size. Thus, the increase of the 325 °C peak with decreasing 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 sensitized samples were divided in two groups. Figure 4 shows the TL glow curves for fine fractions and Figure 5 shows the TL glow curves for coarse fractions. In Figure 4, 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 2). 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 4 and 5 cannot be explained by the effect of the 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 irradiated with high gamma doses.

![Figure 3](image3.png)

**Figure 3.** Relationship between TL intensity integrated from 175 to 390 °C and the mean particle sizes (D_m) for non-sensitized quartz.

![Figure 4](image4.png)

**Figure 4.** TL glow curves of fine particles of sensitized quartz (test dose: 50 mGy).

![Figure 5](image5.png)

**Figure 5.** TL glow curve of coarse particles of sensitized quartz (test dose: 50 mGy).

Figure 6 shows the TL signals integrated from 175 to 390 °C as a function of the mean particle size for sensitized quartz. It can be seen that the TL intensity increases as the particle size increases from 17 to 308 μm. For particles larger than 308 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 mm and 1 mm thick. This disc was prepared directly from the crystal plate and it was not submitted to the crushing procedure. 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 crystal structure when fine quartz grains are submitted to high pressures [13,14]. However, any change in the width of the (1010), (1011) and (1122) diffracting peaks was observed with the FWHM analysis carried out in 75x150, 38x75 and < 38 µm particle fractions. Based on this analysis, the assumption that the decreasing TL intensity for \( D_m < 308 \mu m \) shown in Figure 6 would be associated with amorphization or mechanical damage can be ruled out. Similarly, the SEM analysis did not reveal any substantial difference in the morphology of the quartz particles. For instance, figures 7 and 8 show typical images obtained with particle sizes of 308 µm and 432 µm mean grain sizes. Besides the size range and the presence of very fine grains deposited on the surface of 308 µm particles, no difference is observed in fracture patterns that could be associated with the abrupt change of TL intensity shown in Figure 6. It is observed that brittle microcracking was the principal mechanism of size reduction related to the crushing procedure performed here.

Figure 6. Relationship between the TL intensity integrated from 175 to 390 °C and the mean particle size of sensitized quartz (test dose: 50 mGy).

Figure 7. SEM micrograph of quartz particles with \( D_m = 308 \mu m \).

Figure 8. SEM micrograph of quartz particles with \( D_m = 432 \mu m \).
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. Figure 9 shows the relationship between the TL intensity and the specific surface area of several particle fractions. For test doses 50 and 500 Gy, it is observed that the TL intensity increases with increasing specific surface area. A similar behavior was previously reported for particles of potassium iodate (KI) and amorphous silica exposed to similar doses \([10,11]\). 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 administrated to quartz grains due to the onset of peak near 215 °C. As shown in Figure 2, this peak increases with increasing particle size.

**Figure 9.** Relationship between TL intensity integrated from 175 to 390 °C and the specific surface area of non sensitized quartz samples with different particles sizes.

For sensitized samples, no additional information beyond that shown in Figure 6 was observed when the integrated TL signal was plotted against the specific surface area. A small increase in TL intensity is observed when the TL responses of single crystal and fragments of few millimeters are compared with the response of particles with \(D_m = 400 \mu m\). This effect can also be associated with the increase of the specific surface area. In the sequence, the abrupt increase in TL response for \(D_m = 308 \mu m\) and the subsequent decrease noticed for finer grains 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 gamma doses. For some reason that is not clear, the sensitization with 25 kGy is much more effective to create paramagnetic centers acting as electron traps and recombination centers in those particles with to \(D_m = 308 \mu m\). It is believed that finer particles do not absorb the radiation in the same way as particles with grain size larger than 308 \(\mu m\). Thus, the 280 °C TL peak noticed for quartz particles with \(D_m = 308 \mu m\) could be explained by the concomitant effects of the absorption of high gamma doses and the specific surface area of the particles within this size range.
5. Summary
For non-sensitized quartz of fine grain sizes, the increase in TL intensity integrated from 175 to 390 °C is associated with the increase of the peak near 325 °C and can be explained by the increase of the specific surface area. In this study, this effect was clearly observed at 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 was not observed due to the onset of an additional peak near 215 °C. After sensitization, the effect of the specific surface area was noticed only when the TL intensity of fragments of a few millimetres is compared to that particles of mean grain size close to 300 µm. The subsequent decrease in TL intensity observed for finer particles was tentatively explained by their lower effectiveness in absorbing high gamma doses during the sensitization process. Solonópole quartz with grain size near to 300 µm has suitable properties for future use in TL dosimetry.

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References
[1] McKeever S W S 1984 Thermoluminescence in quartz and silica Radiat. Protec. Dosim. 8 81
[2] Wintle A G 1997 Luminescence dating: laboratory procedures and protocols Radiat. Meas. 27 769
[3] Guzzo P L, Khoury H J, Souza C P, Souza A M, Souza Jr, Schawrrtz M O and Azevedo W M 2006 Defect analysis in natural quartz from brazilian sites for ionising radiation dosimetry Radiat. Protec. Dosim. 119 168
[4] Zimmerman, J 1971 The radiation-induced increase of the 110°C thermoluminescence sensitivity of fired quartz J. Phys. C 4 3265
[5] Yang X H and McKeever S W S 1990 The pre-dose effect in crystalline quartz J. Phys. D. Appl. Phys. 23 237
[6] Khoury H J, Guzzo P L, Brito S B and Hazin C A 2007 Effect of high gamma doses on the sensitisation of natural used for thermoluminescence dosimetry Radiat. Effects & Defects in Solids 162 101
[7] Mahesh K, Weng P S and Furetta C 1989 Thermoluminescence in solids and its applications Nuclear Technology Publishing 306
[8] Driscoll C M H and McKinlay A F 1981 Particle size effects in thermoluminescent lithium fluoride Phys. Med. Biol. 26 321
[9] Carlson G A and Lorence L 1990 Particle size effect in CaF₂:Mn/Teflon TLD response at photons energies from 5-1250 keV IEEE Trans. on Nuclear Sci. 37 1560
[10] Dhoble S J, Sahare P D and Moharil S V 1991 Thermoluminescence and colour centres in KI: particle size effect J. Phys. 3 1189
[11] Ranjbar A H, Durrani S A and Randle K 1999 Electron spin resonance and thermoluminescence in powder form of clear fused quartz: effect of grinding Radiat. Meas. 30 73
[12] Carvalho Jr A B, Guzzo P L, Khoury H J 2007 Obtenção de discos policristalinos de quartzo natural para dosimetria das radiações ionizantes XII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa 767
[13] Hazen R M, Finger L W, Hemley R J, Hemley R J and Mao H K 1989 High-pressure crystal chemistry and amorphization of α-quartz Solid State Communications 72 507
[14] Kingma K J, Meade C, Hemley R J, Mao H and Veblen D R 1993 Microstructural observations of α-quarz amorphization Science 259 666