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Characterization of amethyst applied to TL and OSL dosimetry

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ABSTRACT

The amethyst is a gemological variety of quartz (SiO_2) and it can be found abundantly in Brazil. It is known that quartz exhibits an intense luminescence that is used in sediments dating and it is easily observed in the nature, due to these characteristics it was chosen to perform Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) analysis to verify its dosimetric properties. The morphological characterization was done by means of X-rays diffraction (XRD) technique and it was confirmed that the sample is a pure alpha quartz. Total and traces elements were determined using Total Reflection X-Ray Fluorescence (TXRF) technique and several impurities were found as P (11148 ppm), S (27.1 ppm), K (10.35 ppm), Ca (47.84 ppm), Fe (13.69 ppm), Cu (2.383 ppm) and Zn (11.082 ppm), also some trace impurities, as Cr (0.746 ppm), Mn (0.186ppm) and Ni (0.321 ppm) were determined and they may have important role in the luminescent emission. Sample in powder form was irradiated with crescent doses of beta particles, in an interval of 0.89–26.70 Gy and showed TL peaks at approximately 110, 240 °C. OSL response was verified with pellets produced with amethyst and Teflon, the pellets supplied an excellent OSL response. Ours results showed that amethyst can be used for OSL and TL dosimetry.

Keywords: Thermoluminescence dosimetry 1, OSL dosimetry 2, Amethyst 3.

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1. INTRODUCTION

Quartz is widely used in the dating of archaeological materials such as ceramics, ashes of fires, archeological soils and in the dating of Quaternary sediments [1-3]. However, it can also be used as a natural dosimeter [4]. In the case of the amethyst its TL property has been studied after different thermal treatments and high pre dose irradiation [5].

Luminescent dosimetry is based on the theory of the interaction of matter with ionizing radiation. When the ionizing radiation penetrates the crystal, charge carriers are released in crystalline net and can be trapped in traps (impurities and punctual defects), forming metastable states within the crystal lattice. Then, if the crystal is heated, these charges are released and can recombine in a luminescence center and emit light, which is termed Thermoluminescence (TL). In this way, the intensity of the TL emitted will be proportional to the ionizing radiation dose that had deposited in the crystal.

If instead of heating the crystal, it is optically excited, the charges can also be released from their traps, they can recombine and emit light, which in this case will be called Optically Stimulated Luminescence (OSL).

The present work aims to make a detailed investigation of the crystalline phase of the amethyst and its luminescent response by TL and OSL, after previous irradiation with beta radiation.

2 MATERIALS AND METHODS

Brazilian violet amethyst crystals (Figure 1) of approximately 5.8 cm, from State of Rio Grande do Sul, Ametista do Sul city, were properly crushed and sieved with granulometry, approximately of 0.075 and 0.150 μm, the powder sample was put in the oven at 500 °C for 5 minutes placed on the glass plate for X-ray diffraction analysis.

Pellets were made with 60% amethyst and 40% Teflon measured in mass to be used in OSL measurements. A mass of 1.5 mg of the mixture was placed in the home-made steel mould and pressed with 2 tons for 2 min and at room temperature.

Figure 1: *Brazilian amethyst crystal*

Source: Photo of Author.

The irradiations were made with beta source, $^{90}Sr/^{90}Y$, dose rate 0.089 Gy/s, with 1.5% systematic error approximately and with dose interval of 0.89-26.70 Gy. TL and OSL measurements of the samples were carried out with automatic TL / OSL reader, DA-20 model of Risoe. For TL measurements the heating rate used was 5 ^{o}C/s, N_2 atmosphere and optical filter was BG-39. OSL measurements were performed with blue excitation centered at 470 nm, in constant mode of illumination (CW-OSL) during 40 s, at 60 ^{o}C and 90 % of power, the detection filter was U-340. All the measurements were made with 5 aliquots and the results were the average.

XRD measurement was performed with a spectrometry MiniFlex 300 of Rigaku, with CuKα radiation and the data were scanned for 14 minutes and 50 seconds. The analysis of the majors and traces elements was done with the S2 PICOFOX of Bruker.

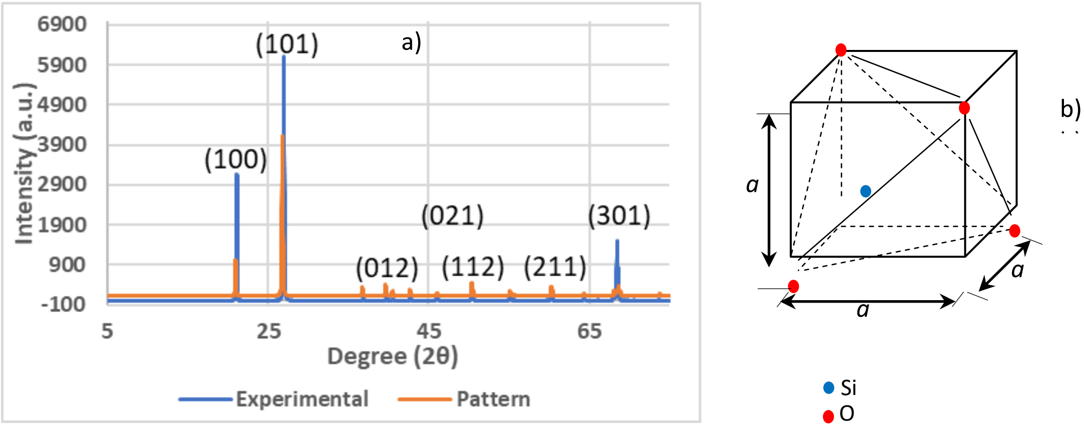
3 RESULTS AND DISCUSSION

3.1 Morphological study

Figure 2a shows X-ray diffraction spectrum obtained with the powdered sample, which agrees with the diffraction spectrum of quartz crystal, this crystal has a hexagonal crystal system (reference code 01-083-2466, the database is PDF-2 2003, from International Centre for Diffraction Data).

The quartz structure consists of SiO4 tetrahedra, so that each Si is bonded to four oxygens and each oxygen is bonded to two silicon atoms, as shown in Figure 2b [6].

Figure 2: *a) X-ray diffraction of amethyst powder sample, b) Quartz crystal structure [6].*



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Using the X-Ray Total Reflection Fluorescence (TXRF) several impurities were found as P , Ca, S, Fe, Zn, K and Cu, some of them with low concentrations, however, they may have important role in the luminescent emission were also determined, as Cr (0.75 ppm), Mn (0.19 ppm) and Ni (0.32 ppm) were found. All elements are listed in Table 1. However, it should not be forgotten that the oxygen vacancies that give rise to the E'- centers are primarily responsible for the luminescence of quartz, for example, E´-centre in a α-quartz consist of an oxygen vacancy with an unpaired electron located at the Si(I) site.

In addition, K^+ can modifier the system inducing non-bridging oxygen, without radiation exposure. Although Fe^{3+} is known as luminescence quenching, but in this case recent studies have shown that the amethyst coloration is due to ferrous impurities and the complex interaction between iron and aluminum is responsible by amethyst coloration [7].

It is well known that each technique of analysis has its limitations and that the amethyst in question must have more impurities, the rare earth elements and Al could not be identified with this analysis.

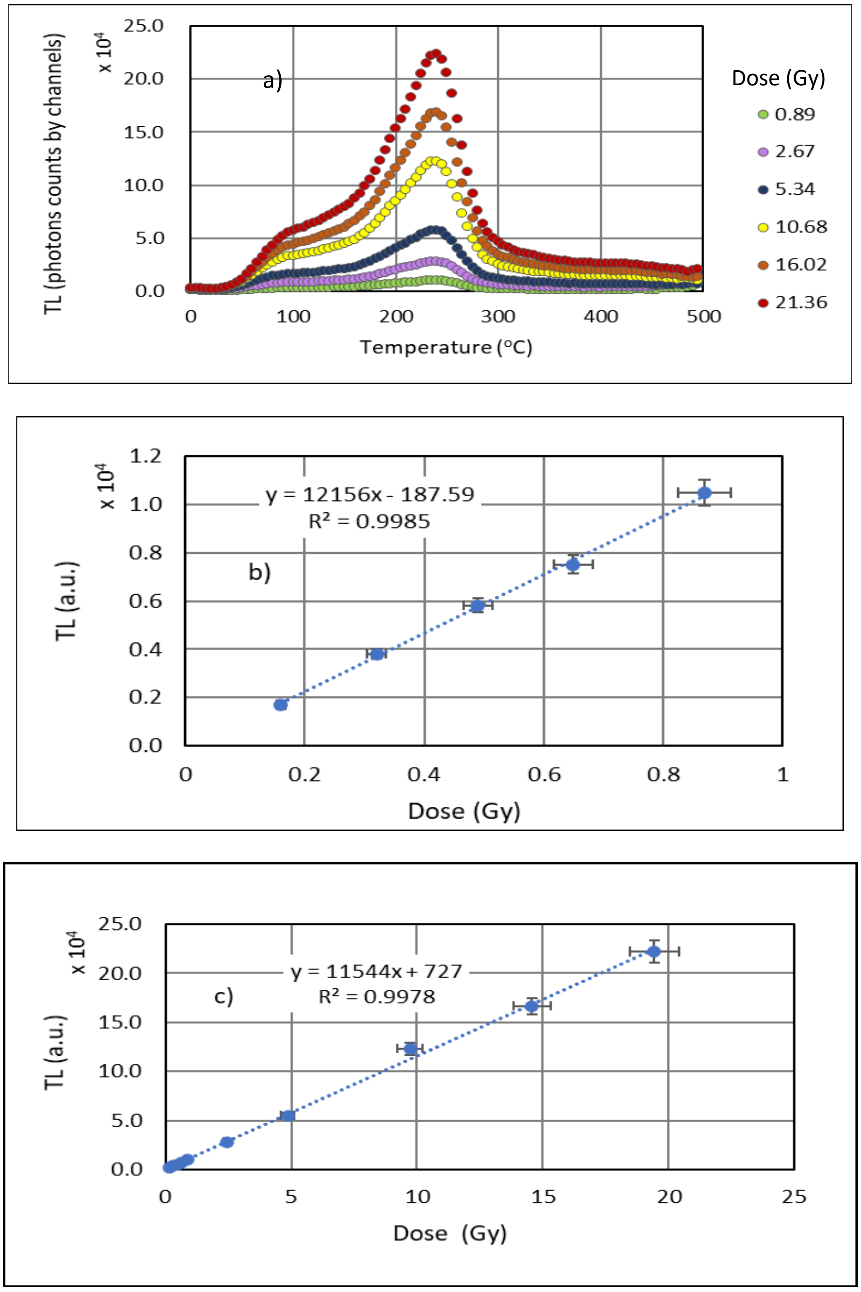
Table 1: Elements concentrations of Brazilian amethyst determined with TXRF.

Element	Concentration (ppm)	Sigma (ppm)
P	11148	18
Ca	47.8	0.4
S	27	1
Fe	13.7	0.1
Zn	11.08	0.07
K	10.4	0.4
Cu	2.38	0.04
Cr	0.75	0.08
Ni	0.32	0.04
Mn	0.19	0.06

3.2 Luminescence study

Samples in powder form were irradiated with crescent doses of beta particles, in an interval of 0.89 – 21.36 Gy and showed prominent TL peaks at approximately 110, and 240 °C (Fig.3a), the last peak supplied a linear tendency with the dose (Figs.3b and c). This TL curve is like that found by Rocha et al. 2003[8], which used Teflon pellets with amethyst, however the second peak has a lower temperature around 210 ^{o}C when the pellets were irradiated with 1 kGy of gamma radiation. TL results of amethyst from Turkey [5] irradiated with high doses showed several prominent peaks at 120, 170, 270, and 450 ^{o}C. Therefore, despite being of the same variety, they can exhibit different behaviors.

Figure 3: *a) TL glow curve were detected at VIS region, b) TL growth curve of 240 °C TL peak, low dose and c) high dose of beta particles***.**



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OSL response was verified with pellets (Figure 4), the pellets supplied an excellent OSL response, it can be observed a rapid decay of the signal in almost 5 seconds. OSL growth curve was fitted with a polynomial equation (Figure 5). No work was found in the literature addressing the results of amethyst-Teflon pellets. The supralinear behavior of OSL at low doses differs from the linear growth found in the TL results. This fact may be indicating that the emission kinetics related in TL is different from that responsible for OSL. It is worth mentioning that TL is being detected in the UV and Visible spectrum and OSL is only detected in the UV region, therefore, it is not expected that the centers or kinetics are similar.

Figure 4: *OSL decay curves of amethyst-Teflon pellets obtained with different doses of irradiations.*

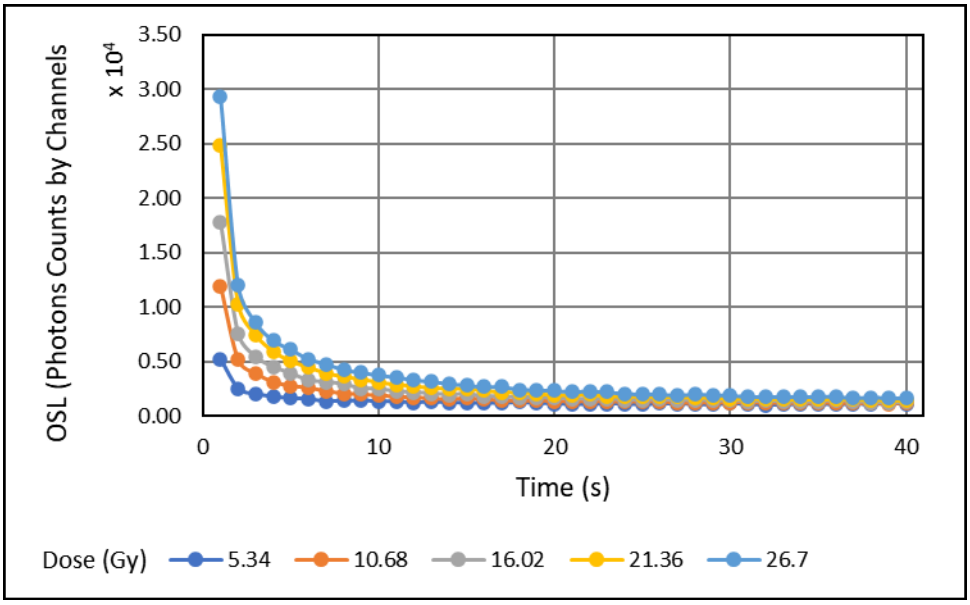

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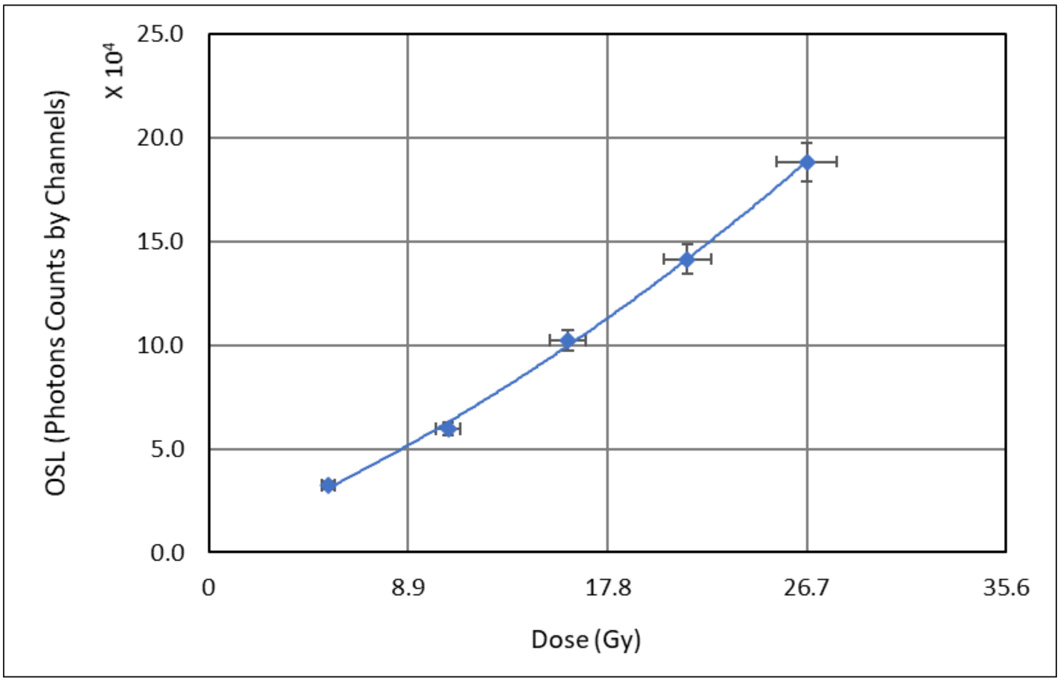
Figure 5: *OSL growth curve of amethyst-Teflon pellets.*



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The Computerized Glow Curve Deconvolution (CGCD) for CW-OSL was performed to verify existing components in the emission curve, according to general order kinetic model [9]:

$$I(t) = I_0\left(1 + (b-1)\frac{t}{\tau}\right)^{\left(\frac{b}{b-1}\right)} \qquad (1)$$

Where *I(t)* is the intensity signal as function of time, I_0 is the initial intensity, *b* is the kinetic order, and τ is de lifetime. To check the fitting precision Figure of Merit (FOM) value was used:

$$FOM = \sum_i \frac{|Y_{Exp} - Y_{Fit}|}{A} \qquad (2)$$

Where *A* is the area below the fit curve, Y_{Exp} are the experimental curve data, and Y_{Fit} are the fit curve values. Usually the FOM values lower than 5 % indicated a good quality of fit.

Figure 6 shows an example of an adjustment obtained for an OSL curve of an aliquot irradiated with a dose of 26.70 Gy. The curve was deconvolved and three components were determined, whose parameters are listed in Table 2. The first component decays more quickly with a life span of 0.5 s and has a kinetic order of 1.5; the second component with an average lifetime of 17 s and b = 1.2 and the third longest component with a lifetime of 100 s and b = 1.8. The value of the FOM was 5%.

Figure 6: *Computerized Glow Curve Deconvolution applied* to *OSL curve of amethyst-Teflon pellets showing experimental curve and theoretically deconvoluted components.*

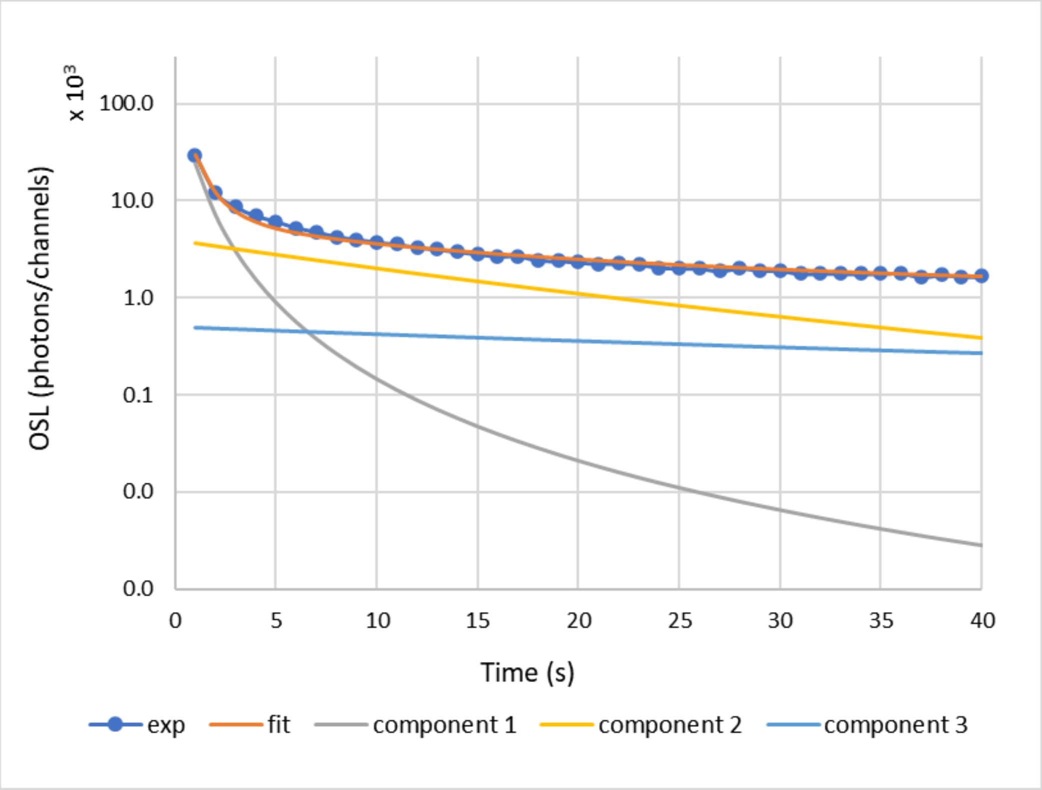

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Table 2: Fittings parameters determined with Computerized Glow Curve Deconvolution applied to OSL curve of amethyst-Teflon pellets. $I(t)$ is the intensity signal as function of time, I_0 is the initial intensity, b is the kinetic order, and τ is de lifetime

Parameters	Component 1	Component 2	Component 3
I_o ***(a.u.)***	195000	3960	500
b	1.5	1.2	1.8
τ ***(s)***	0.5	17	100

4 CONCLUSIONS

Our results indicate that the amethyst crystal studied has a hexagonal crystalline structure and axes of trigonal symmetry. Several impurities were found and could be responsible for the luminescence such as Cr, Mn and Ni. Its color probably comes from Fe. It exhibits two TL peaks at 110 and 240 ^{o}C, when irradiated with low doses up to 21.36 Gy. The 240 ^{o}C peak has a linear response with the dose.

The pellets made with amethyst and Teflon exhibit a high OSL emission and have a supralinear growth with the dose. Computerized Glow Curve Deconvolution applied to OSL curve showed that the curve is composed of three components with lifetime of 0.5, 17 and 100 s, and kinetic order of 1.5, 1.2 and 1.8 respectively, for a dose of 26.70 Gy

We can conclude that amethyst can be used for TL and OSL dosimetric applications even at low doses.

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