



ELSEVIER

Nuclear Instruments and Methods in Physics Research B 166–167 (2000) 209–214

**NIM B**  
Beam Interactions  
with Materials & Atoms  
[www.elsevier.nl/locate/nimb](http://www.elsevier.nl/locate/nimb)

## Dosimetric properties of natural brazilian topaz: A thermally stimulated exoelectronic emission and thermoluminescence study

Divanízia N. Souza <sup>a</sup>, Mário Ernesto G. Valerio <sup>b,\*</sup>, José Fernandes de Lima <sup>b</sup>,  
Linda V.E. Caldas <sup>c</sup>

<sup>a</sup> Depto. de Educação-CECH, Universidade Federal de Sergipe, 49.100-000 São Cristóvão, SE, Brazil

<sup>b</sup> Depto. de Física-CCET, Universidade Federal de Sergipe, 49.100-000 São Cristóvão, SE, Brazil

<sup>c</sup> Instituto de Pesquisas Energéticas Nucleares-CNEN, Caixa Postal 11049, Pinheiros, 05542-970 São Paulo, Brazil

### Abstract

The dosimetric properties of natural colourless Brazilian topaz were studied via thermally stimulated exoelectronic emission (TSEE) and thermoluminescence (TL) techniques. The samples were prepared in three ways: (i) powdered samples with grain sizes from 0.75 to 0.150 mm, (ii) pellets prepared with powdered topaz mixed with Teflon in the 1/2 ratio (wt), and (iii) crystals sizing about  $5.0 \times 5.0 \times 3.0$  mm<sup>3</sup>. The TSEE curves displayed a peak at 190°C and the area under this peak increases sublinearly with the dose range from  $10^{-1}$  to  $10^2$  Gy, for irradiations with X-rays and  $\gamma$ -rays from a <sup>60</sup>Co source. The dependence of the TSEE with the energy of the X-rays indicates that the TSEE intensity increases as the energy of the photon increases. The TL emission curves of topaz samples both as pellets and powder were measured using a home made TL reader. The glow curves were composed by three main peaks at 100°C, 180°C and 210°C. The emission spectra were obtained from 300 to 580 nm in steps of 10 nm. All three peaks have the same spectra with main emissions centred at 390, 430 and 460 nm. The dose dependence of the TL curves up to 500 Gy of  $\gamma$ -rays from the <sup>60</sup>Co source indicates that all the TL peaks increases non-linearly as the dose increases. The results were compared with the well known CaSO<sub>4</sub>:Dy and LiF dosimeters and it was possible to conclude that the colourless natural Brazilian topaz is a suitable material for dosimetric applications. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 78.60.Kn; 73.50.Gr; 79.75.+g; 87.53.Dq

Keywords: Topaz; TSEE; TL; Dosimeters; Emission spectra

### 1. Introduction

The search for materials suitable for solid state radiation dosimeters has been the aim of

many researches after the discover of the thermoluminescence (TL). Different systems were studied so far including artificial grown crystals or natural materials. One advantages of the artificial materials is that it is possible to control the composition, and so, the purity, of the starting materials used to prepare the solid state dosimeters. On the other hand, natural materials

\* Corresponding author. Tel.: +55-79-212-6636; fax: +55-79-212-6684.

E-mail address: mvalerio@ufs.br (M.E.G. Valerio).

can be cheaper and available in reasonably large quantities.

The main property that decides which material is the best for the application in TL dosimetry is the TL sensitivity for low radiation doses ( $10^{-5}$  Gy) that should extend to some few hundreds of Gy before saturation of the signal is reached [1]. It is also important that the TL response has an energetic dependence that makes possible to distinguish the effective energy of the radiation. It is also desirable that, from the TL signal of the dosimeter, one should be able to identify the contribution of  $\alpha$ -,  $\beta$ - and  $\gamma$ - or X-rays to the total dose. These features, as far as we know, are not found yet in just one single solid state TL dosimeter, and the way of getting the information that is needed is using a combination of different dosimetric techniques.

Thermally stimulated exoelectron emission (TSEE) was also found to be a very useful technique to be applied in dosimetry. The TSEE is related to the emission of low energetic electrons mainly from the surface and the few layers of atoms close to the surface of many insulating materials [2]. Consequently, the TSEE is specially useful for detecting the radiation that does not penetrate deeply into the material, like low energy X-rays,  $\alpha$ -,  $\beta$ -rays, electrons etc. So, TSEE can be used as a complementary technique to the TL when it is necessary to separate the contribution of different kinds of radiation to the total dose with the advantage that it can be measured simultaneously in the same solid state dosimeter.

Topaz is an aluminium fluorsilicate with a general composition of  $\text{Al}_2(\text{SiO}_4)(\text{F},\text{OH})_2$ . It crystallises in a rhombohedral structure, belonging to the space group Pbnm. Topaz is a very hard mineral, with a vitreous aspect normally being yellow, blue or colourless. Gandise et al. [3] studied natural topaz found in Minas Gerais, Brazil, and found that the average lattice parameters of the crystals are  $a = 4.64 \text{ \AA}$ ,  $b = 8.8 \text{ \AA}$  and  $c = 8.4 \text{ \AA}$ . It was also found in the coloured Brazilian topaz that the main impurities are V, Cr, Fe and Mn [3] and the authors pointed out that these impurities can be the source for the colour in topaz.

The main defect found in topaz is related to the  $\text{OH}^-$  group substituting for the  $\text{F}^-$  ion.

Rosemberg et al. [4] found that the concentration of the  $\text{OH}^-$  in their natural samples does not exceed 0.30, and that the refraction index as well as the density is directly related to the  $[\text{OH}^-]/[\text{F}^-]$  ratio. One third of the octahedral sites in topaz are occupied by an aluminium ion and 1/12 of the tetrahedral sites is filled with  $\text{Si}^{4+}$  ions. The oxygen atoms are co-ordinated by two  $\text{Al}^{3+}$  and one  $\text{Si}^{4+}$  ion and the  $\text{F}^-$  site is co-ordinated by two  $\text{Al}^{3+}$  ions [5]. All the F-sites in the topaz unit cell are equivalent thus generating an “intrinsic disorder” of the occupancy of the F-sites by the OH-groups.

The first results of the TL in topaz were reported by Moss and McKlveen [6]. They found that in their natural samples from the Topaz Mountain in Utah, USA, the saturation dose for topaz is 700 Gy and that, after 40 cycles of irradiation-TL measurements-thermal treatment, the intensity of TL signal was increased by 20%. Azorin and co-workers [7] studied different natural samples from Mexico, including topaz. The best sensitivity found was the topaz with TL signals 100 times higher than the TL signal of amethyst. They have pointed out the existence of two main TL peaks.

Lima et al. [8], on the other hand, found four TL peaks in their measurements of natural topaz from Goverdador Valadares, Minas Gerais, Brazil. They also observed that the number and position of TL peaks depends on the storage time between the irradiation of the samples and the TL measurement.

In previous works [9,10], we have studied the TL emission of natural topaz from different parts of Brazil and with different colours. We found that: (i) in some samples there are six TL peaks at  $80^\circ\text{C}$ ,  $140^\circ\text{C}$ ,  $170^\circ\text{C}$ ,  $230^\circ\text{C}$ ,  $280^\circ\text{C}$  and  $330^\circ\text{C}$ , (ii) colourless samples have better sensitivity to  $\gamma$  irradiation than coloured ones; (iii) UV light can promote the filling of some TL traps. We also determined the kinetic parameters of the peaks and we found that some of them follows a first-order model. Natural topaz also displays an anomalous fading of the peak at  $170^\circ\text{C}$ .

The aim of the present work is to investigate the possibility of using these properties of the TL emission of Brazilian natural topaz for dosimetric application. We are combining the results of TSEE

with TL in order to analyse the possibility of building a solid state dosimeter that can be used in both techniques simultaneously in order to detect contribution of different types of radiation.

## 2. Experimental

The TSEE signal was registered using a system with a  $2\pi$  windowless gas-flow proportional counter (the gas mixture is 90%Ar + 10%CH<sub>4</sub>). The temperature follows a linear heating program from 25°C to 300°C with a heating rate of 5.0°C/s. The irradiation of the samples with X-rays was performed in air, at 50 cm of the focus of the X-ray tube, with energies between 14 and 22 keV. The irradiation with  $\gamma$ -rays was done at a distance of 1 m from a <sup>60</sup>Co source. The sample was kept under a plate of Lucite of 3.5 mm thickness during the  $\gamma$  irradiation.

The TL equipment was described in a previous paper [10]. It can operate from room temperature up to 400°C following a linear heating program. For the measurement of the TL emission spectra, a monochromator was attached between the photomultiplier tube and the sample holder. A monochromatic TL curve was taken every 10 nm from 300 to 700 nm and the 3D TL emission spectra or the contour plots were composed via software.

Natural colourless topaz samples from Santo Antonio do Jacinto, Minas Gerais, Brazil, were used in this work. They were prepared in three ways: (i) powdered samples with grain sizes from 0.75 to 0.150 mm, (ii) pellets prepared with powdered topaz mixed with Teflon and (iii) crystals sizing about 5.0 × 5.0 × 3.0 mm<sup>3</sup>. For the pellets, the crystals were powdered and the grains between 0.075 and 0.150 mm were thermally treated at 300°C for 30 min followed by another thermal treatment at 400°C for 1.5 h. These are the same treatments that are used for the CaSO<sub>4</sub>:Dy dosimeters produced by IPEN/CNEN/SP, Brazil. The thermally treated topaz powder was mixed with Teflon in the 1:2 ratio (wt) and pressed producing pellets with sizes of 6 mm diameter × 1 mm thickness. The TSEE measurements were per-

formed in the crystals while the TL measurements were done in all three kinds of samples.

## 3. Results and discussion

The TSEE curves of thermally treated (300°C/1 h) crystals of topaz irradiated with either  $\gamma$ - or X-rays display only one main peak at about 190°C, if a heating rate of 5°C/s is used. Fig. 1 displays the TSEE peak area as a function of  $\gamma$ - and X-ray doses. We can see that the area increases with the dose obeying the following equation:

$$A_{\text{TSEE}} = aD^b, \quad (1)$$

where  $A_{\text{TSEE}}$  is the TSEE area of the peak and D is the dose. For both the X- and  $\gamma$ -rays, in the dose range investigated here, the dependence is sublinear and the coefficient b is 0.55 and 0.70, respectively.

In Fig. 2 we present the dependence of the area of the TSEE peak with the energy of the X-rays at a constant dose. We can see a strong energetic dependence with the total emitted charge increasing with the energy of the photons.

In Fig. 3 we can see the 3D TL curve of a powdered sample of natural topaz from 300 to 580 nm and from room temperature up to 350°C, ob-

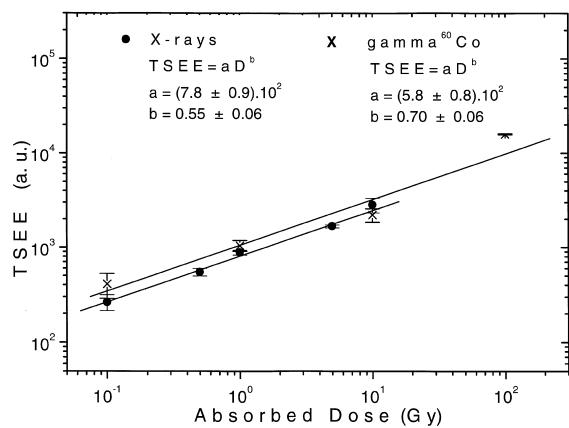


Fig. 1. Area of the TSEE peak at 190°C as a function of the dose for  $\gamma$ - and X-rays of 21.2 keV. The data points were fitted to Eq. (1). The obtained parameters are  $a = (5.8 \pm 0.8) \times 10^2 \mu\text{A/Gy}$  and  $b = 0.70 \pm 0.03$ , for  $\gamma$  irradiation, and are  $a = (7.8 \pm 0.9) \times 10^2 \mu\text{A/Gy}$  and  $b = 0.55 \pm 0.06$ , for X-rays.

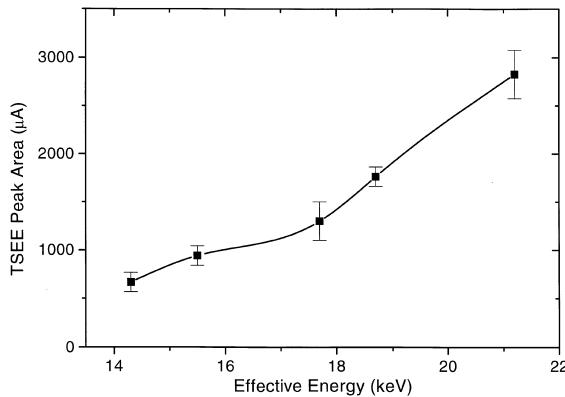


Fig. 2. Area of the TSEE peak as a function of the energy of the X-rays for a fixed dose of 10 Gy.

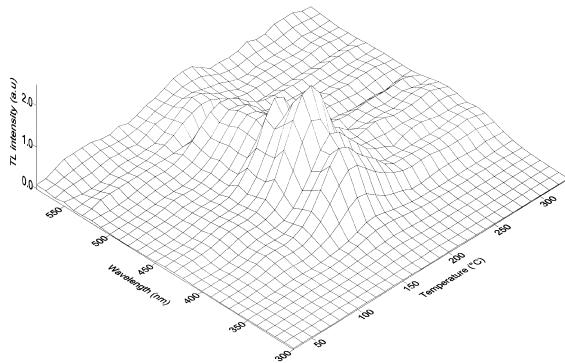


Fig. 3. 3D TL curve of powdered samples of natural colourless topaz. Each monochromatic glow curve were recorded with a heating rate of 4°C/s and the spectral response of the detection system (photomultiplier + monochromator) was taken into account.

tained using a heating rate of 4°C/s. The main TL peaks are located at 110°C, 170°C and 250°C. It is also possible to see that the spectra of these TL peaks are quite the same and are mainly composed by emissions centred at 380, 420, 460 and 480 nm.

The 3D TL curve of the pellets produced with topaz is displayed in Fig. 4. As we can see, the main peaks are at 130°C and 230°C. It is also possible to see a shoulder at about 270°C. The main difference between the TL of the natural samples and the pellets is the overall intensity of the emission, that is smaller in the case of the pellets. It was also observed that the relative

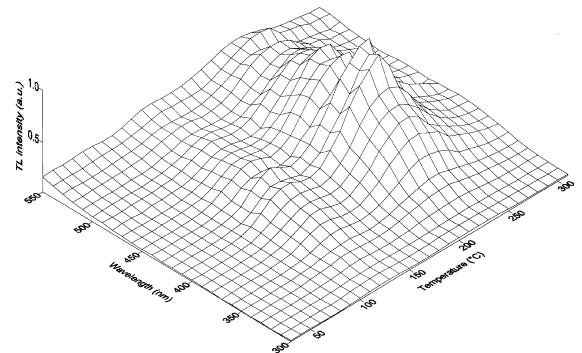


Fig. 4. 3D TL curve of topaz pellets. Each monochromatic glow curve were recorded with a heating rate of 4°C/s and the spectral response of the detection system (photomultiplier + monochromator) was taken into account.

intensity of the TL peaks are different. In the natural samples irradiated with an extra dose of 50 Gy, the peak at 170°C is the most intense one, while in the pellets, where the topaz powder was thermally treated, the peak at 230°C is the most intense one. In a previous paper [10], we showed that there are at least six TL peaks in the colourless natural topaz within this temperature range. It was also found that thermal treatments can change the intensities of the TL peaks. The maximum temperatures of these peaks are very close and in some cases two or more peaks can be superimposed generating "extra" TL peaks. As a result, these "extra" peaks can shift the position after thermal treatments since these treatments change the intensity of the six original peaks. This result can explain why the TL peaks seem to be different when we compare the TL emission of treated and untreated samples of topaz.

If the relative intensity of the different peaks changes, producing apparently different TL peaks, this means that the distribution of the charge traps in topaz are changing when the samples are submitted to thermal treatment. This feature was also observed in many other silicates [11,12].

Another important feature that we can observe when comparing Figs. 3 and 4 is that the spectral composition of the peaks does not change indicating that the recombination and emission centres remain unchanged after the thermal treatment that pellets of topaz are submitted to.

We also measured in the same experimental conditions the 3D TL curves of the LiF dosimeters (TLD-100) and the CaSO<sub>4</sub>:Dy dosimeters produced at IPEN/CNEN/SP, Brazil. In Table 1 we summarised the main results obtained for these dosimeters comparing them to the values obtained in the present work for the pellets of colourless topaz. We can see that the intensity of the main TL peaks at the maximum wavelengths for the CaSO<sub>4</sub> dosimeters are higher than the values obtained for the other systems. But our samples displayed higher intensities than those obtained for the commercial LiF TLD-100 dosimeters.

In Fig. 5 we plot the intensity of the main TL peaks as a function of the dose for irradiation with  $\gamma$ -rays obtained with topaz samples thermally treated at 400°C by 1 h. We can see that the intensity of the peaks increases with the dose without displaying any saturation until 400 Gy.

This result combined with the results presented in Fig. 1 and in Table 1, indicates that the colourless topaz from Minas Gerais, Brazil is a promising material for dosimetric application and it can be useful for personal dosimetry, in monitoring the radiation sources usually employed in radiotherapy, and in the dosimetry of nuclear accident, where sometimes we want to know which kind of material can be used to measure the radiation dose in the region of the accident during or after the accident.

Table 1

Maximum temperature, maximum wavelength and TL peak height at different maximum wavelengths for LiF TLD-100 dosimeter, CaSO<sub>4</sub>:Dy dosimeters produced by IPEN/CNEN/SP, Brazil, and pellets of topaz

Material	$T_{\max}$ (°C)	Wave-length (nm)	TL intensity (a.u.)
LiF	206	380	0.20
	206	420	0.19
	206	450	0.18
CaSO <sub>4</sub> :Dy	200	480	21.15
	200	570	49.00
	200	660	6.09
Topaz pellets	229	410	1.00
	230	450	0.76
	230	470	0.72

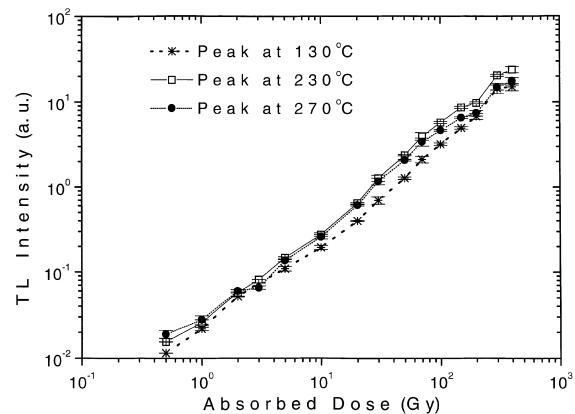


Fig. 5. TL peak heights of the main three peaks of colourless topaz as a function of the dose of  $\gamma$ -rays from a  $^{60}\text{Co}$  source. The dose response was taken using powdered samples thermally treated at 400°C/1 h.

### Acknowledgements

The authors wish to thanks the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, a Federal Brazilian Governmental agency for research funding) and the Secretaria de Estado do Planejamento Ciência e Tecnologia de Sergipe (Sergipe State Government Council for Science and Technology) for financial supports.

### References

- [1] Y.S. Horowitz, Thermoluminescence and Thermoluminescent Dosimetry, CRC Press, FL, USA, 1984.
- [2] F.D.G. Rocha, Desenvolvimento de um Sistema de Emissão Exoeletrolétrica Termicamente Estimulada para Aplicação em Dosimetria, PhD thesis, Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil, 1997.
- [3] A.L. Gandini, R.M.S. Bello, K. Fuzikawa, J.C. Gaspar, N.F. Botelho, S.V. Coelho, V.R. Marciano, A.M. Pimenta, D.P. Sviero, in: Proceedings of the IX Semana de Geoquímica-II Congresso de Geoquímica dos Países de Língua Portuguesa, Porto, Portugal, 1993, p. 233.
- [4] R.N. Abbott Jr, Canadian Mineralogist 28 (1990) 827.
- [5] P.H. Ribbe, G.V. Gibbs, The American Mineralogist 56 (1971) 30.
- [6] A.L. Moss, J.W. McKlveen, Health Phys. 34 (1978) 137.
- [7] J. Azorin, R.P.C. Salvi, A. Gutiérrez, Health Phys. 43 (1982) 590.
- [8] C.A.F. Lima, L.A.R. Rosa, P.G. Cunha, Appl. Radiat. Isot. 37 (1986) 135.

- [9] D.N. Souza, J.F. de Lima, M.E.G. Valerio, Rad. Eff. Def. Sol. 135 (1995) 109.
- [10] D.N. Souza, J.F. de Lima, M.E.G. Valerio, Mater. Sci. Forum. 239–241 (1997) 765.
- [11] D.J. McDougall, Thermoluminescence of Geological Materials, Academic Press, New York, 1968.
- [12] H.M. Rendell, P.D. Townsend, R.A. Wood, B.J. Luff, Radiat. Meas. 23 (1994) 441.