



# Influence of thermal treatment on the Raman, infrared and TL responses of natural topaz

Divanizia N. Souza <sup>a</sup>, José Fernandes de Lima <sup>b</sup>, Mário Ernesto G. Valerio <sup>b,\*</sup>,  
Cristiano Fantini <sup>c</sup>, Marcos A. Pimenta <sup>c</sup>, Roberto L. Moreira <sup>c</sup>,  
Linda V.E. Caldas <sup>d</sup>

<sup>a</sup> *Depto. de Educação, Universidade Federal de Sergipe, CECH 49100-000 São Cristóvão, SE, Brazil*

<sup>b</sup> *Depto. de Física, Universidade Federal de Sergipe, CCET 49100-000 São Cristóvão, SE, Brazil*

<sup>c</sup> *Depto. de Física, Universidade Federal de Minas Gerais, ICEx C.P. 702, 30123-970 Belo Horizonte, MG, Brazil*

<sup>d</sup> *Instituto de Pesquisas Energéticas Nucleares, CNEN, 05508-000, São Paulo, SP, Brazil*

## Abstract

Analyses of thermoluminescence (TL) and thermally stimulated exoelectron emission have proved that the natural Brazilian topaz is a promising material for dosimetry of ionizing radiation. Topaz is an aluminum fluorosilicate with a general composition of  $\text{Al}_2(\text{SiO}_4)(\text{F},\text{OH})_2$  whose main defect is the presence of  $\text{OH}^-$  groups substituting for the  $\text{F}^-$  ions. Analyses of topaz samples from Santo Antonio do Jacinto, MG, Brazil, showed that their TL responses are strongly affected by the temperature of pre-irradiation thermal treatment. This behavior was correlated to the changes observed in the infrared and Raman spectra and a model could be proposed for the charge trapping and recombination process in colourless topaz. © 2002 Published by Elsevier Science B.V.

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## 1. Introduction

Topaz is an aluminum fluorosilicate with a fairly constant chemical composition  $\text{Al}_2\text{SiO}_4(\text{OH},\text{F})$ . The only major variation found in different samples is related to the OH/F concentration ratio. The structure of topaz consists of  $\text{SiO}_4$  groups linking octahedral chains of  $\text{Al}[\text{O}_4(\text{F},\text{OH})_2]$  in a zigzag fashion parallel to the crystalline *c*-axis.

Four of the six anions surrounding the  $\text{Al}^{3+}$  ion belong to  $\text{SiO}_4$  tetrahedra and the remaining two either to  $\text{F}^-$  or  $\text{OH}^-$  group. Topaz crystallizes in the orthorhombic system, space group  $\text{Pbnm}$  [1–3] and is normally found as well-developed prismatic crystals with pyramidal terminations. Topaz is found in pegmatite dikes, particularly those carrying tin, and also as rolled pebbles in stream gravels [4].

In previous papers [5,6], investigations of natural topaz from different origins were done using thermoluminescence (TL) and thermally stimulated exoelectron emission showing that colourless samples displayed TL responses higher than the coloured ones. Colourless topaz pellets were

\* Corresponding author. Tel.: +55-79-212-6636; fax: +55-79-212-6807.

*E-mail addresses:* dnsouza@fisica.ufs.br (D.N. Souza), mvalerio@fisica.ufs.br (M.E.G. Valerio).

proved to be promising materials for dosimetric applications [7].

Infrared and Raman spectroscopies were used by a number of authors [2–4,8–10] to investigate the OH, SiO<sub>4</sub> and Al-related groups in topaz. In particular the modes associated with the SiO<sub>4</sub> groups are located around 935 cm<sup>-1</sup>, while the lines in the region from 3625 to 3675 cm<sup>-1</sup> are mainly due to different OH<sup>-</sup> vibration modes.

In the present work, TL was combined with the infrared and Raman spectroscopies to identify the charge carrier traps and the recombination centres aiming to understand the processes of light emission in natural colourless topaz.

## 2. Experimental

Rolled pebble samples of natural colourless topaz from Santo Antonio do Jacinto, Minas Gerais, Brazil, were used in this work. For the TL measurements, the samples were powdered in grains of sizes from 0.75 to 0.150 mm. The grains were annealed during 1.0 h at temperatures between 300 and 1000 °C. The TL readouts were performed from room temperature up to 350 °C in a home-made TL reader. The doses were 50 Gy

from a <sup>60</sup>Co source. The Raman measurements were performed using a backscattering geometry, with the light polarisation samples parallel to the *c* crystalline axis. For the infrared measurements, slices of about 2.0 mm thick were cut. These samples were thermal treated in the same conditions as those used for TL measurements. The Raman measurements were performed at room temperature using a Dilor XU triple monochromator equipped with an argon/krypton source (5145 Å, 50 mW), a confocal microscope and a CCD detector. The infrared measurements were also performed at room temperature in the range from 500 to 4000 cm<sup>-1</sup>, using a Bomem DA8 Fourier Transformer spectrometer equipped with a SiC source, a coated KBr beamsplitter and a MCT detector.

## 3. Results and discussions

A typical 3D TL spectra of a sample thermally treated at 500 °C and irradiated with 50 Gy is shown in Fig. 1. The TL glow curve is composed by four main peaks at 100, 180, 210 and 300 °C, while the emission is mainly composed by a broad emission centred at 420 nm, which spreads from

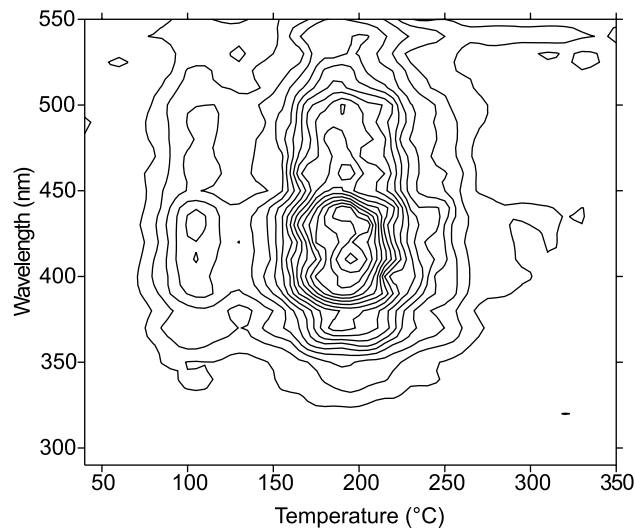


Fig. 1. Contour plot of TL curves of powdered colourless topaz, thermally treated at 500 °C/1 h and irradiated with 50 Gy from a <sup>60</sup>Co source.

330 to 500 nm. This emission is similar to that observed in thermally treated quartz being attributed to  $(\text{AlO}_4)^0$  and  $(\text{H}_3\text{O}_4)^0$  centres. The former leads to an emission centred at 460 nm while the latter gives the emission at 380 nm [11]. These defects are formed when an  $\text{Al}^{3+}$  or  $3\text{H}^+$  ions substitute for the  $\text{Si}^{4+}$  site and the resulting dangling bond is neutralised by a trapped hole forming a neutral defect. Owing to the similarities of the spectra, the proposal of this work is that these two centres are also the main emission centres in topaz.

Thermal treatments, prior to the irradiation, can induce changes in the TL peaks. In Fig. 2 the intensities of the emission spectra, at the peak temperatures, are shown as a function of the temperature of the thermal treatments. The main effect of the pre-irradiation thermal treatment is the reduction of the overall emission. On the other hand, the thermal treatment induces different

changes in the intensities of each individual TL peak. The peaks at 180 and 210 °C have quite the same behaviour. They both increase as the temperature of the thermal treatment increases reaching the maximum intensities at 500 °C. Further increase in the temperature decreases the peaks. These effects indicate that the thermal treatment is probably changing the amount of charge traps responsible for each TL peak, rather than changing the distribution of recombination and/or luminescent centres.

The Raman spectra of the colourless topaz from Santo Antonio do Jacinto, Minas Gerais, Brazil, analysed in this work are comparable to those found in the literature [4–6]. The natural samples or the samples thermally treated display similar spectra (see Fig. 3). The bands at 646, 847, 934, 983 and 1163  $\text{cm}^{-1}$  are related to  $\text{SiO}_4$  [4,8,9]. The two OH-stretching bands around 3640 and 3650  $\text{cm}^{-1}$  present a faint evolution with the

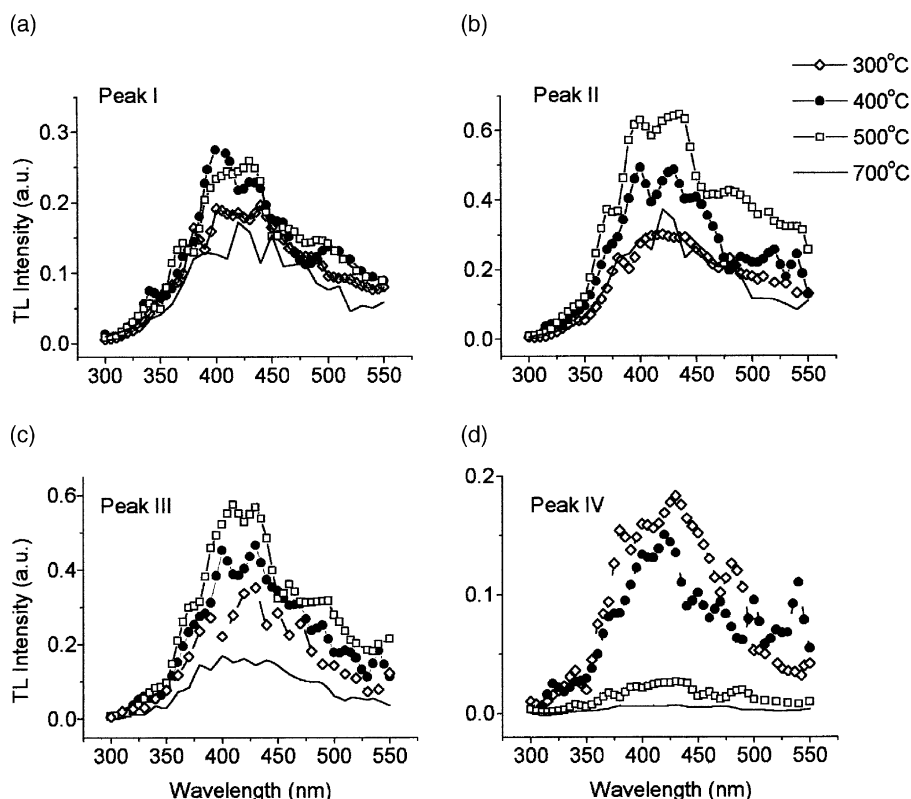


Fig. 2. TL emission spectra, at the peak temperatures, as function of the thermal treatment temperature.

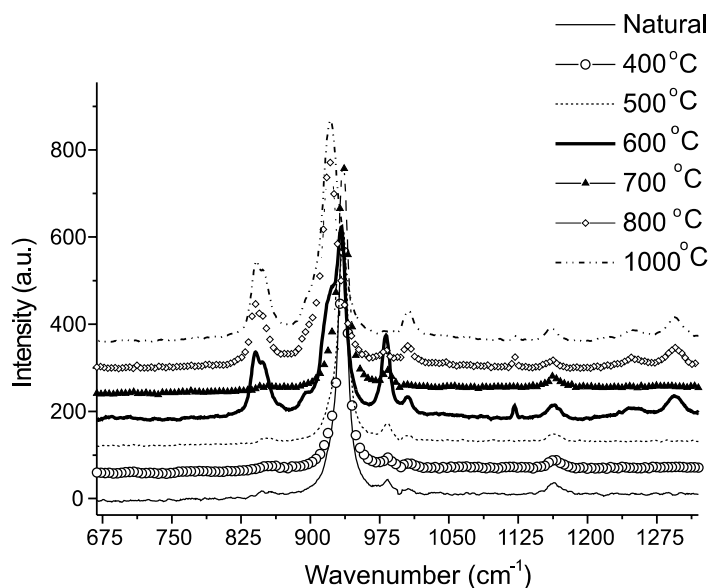


Fig. 3. Raman spectra of the colourless topaz, as function of the thermal treatment temperature.

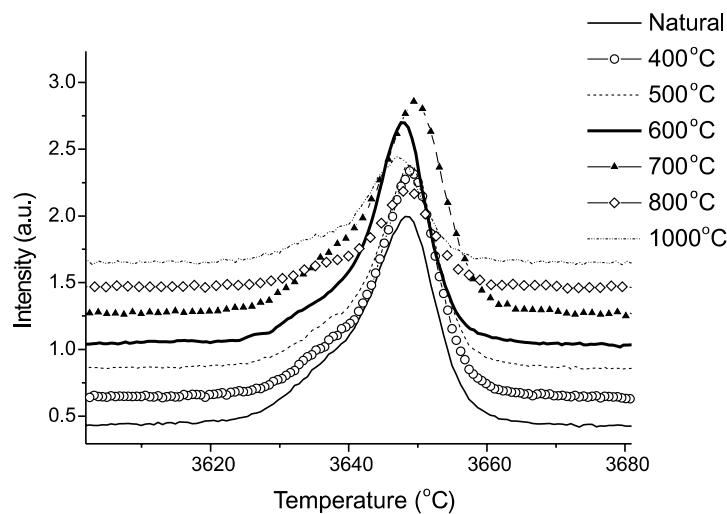


Fig. 4. Raman spectra of the bands related to the  $\text{OH}^-$  of the colourless topaz.

thermal treatments (Fig. 4): the shoulder at lower frequencies tends to increase as the temperature of the thermal treatments increases.

The infrared spectra of the treated samples, however, show remarkable changes, mainly in the  $3400\text{--}3700\text{ cm}^{-1}$  region, as can be seen in Fig. 5. In Fig. 6 the intensities of the bands in this region are

plotted as function of the thermal treatment temperature. The bands in this region are attributed to various  $\text{OH}^-$  vibrational modes [3–5,9–13]. We can see that, while the bands at  $3423$  and  $3486\text{ cm}^{-1}$  decrease, the bands at  $3585$ ,  $3625$  and  $3650\text{ cm}^{-1}$  increase as the temperature of the thermal treatment increases; the other bands in the whole

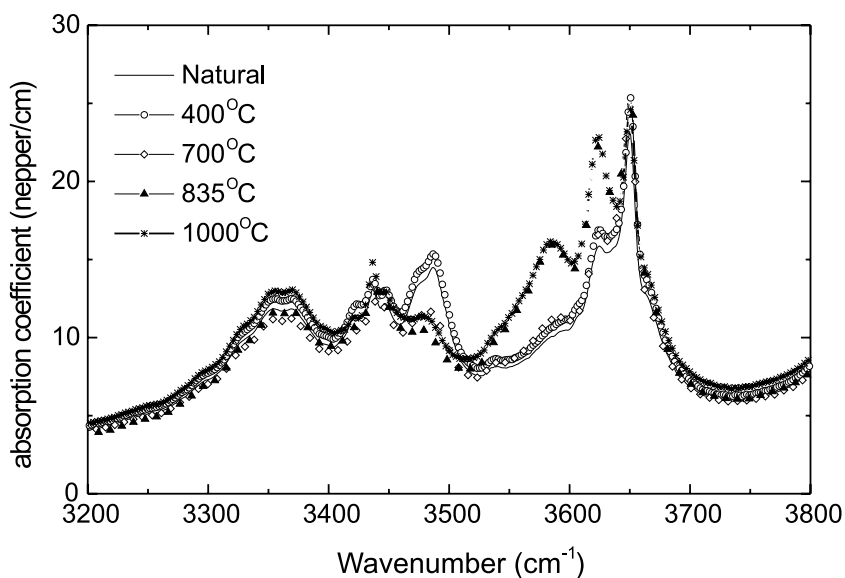


Fig. 5. Infrared spectra of the thermally treated samples.

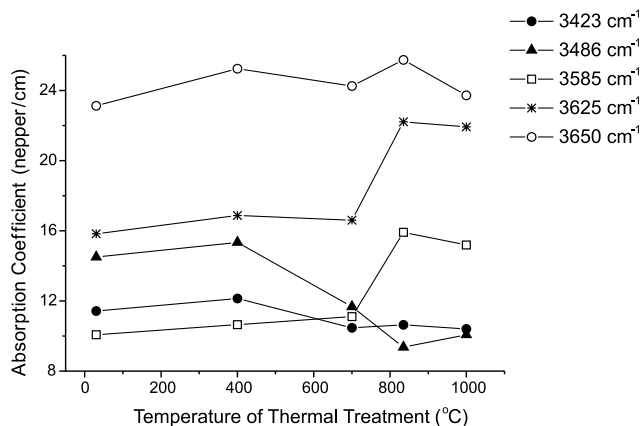


Fig. 6. Intensities of the IR bands, as function of the thermal treatment temperature.

spectra (not shown here), including the  $\text{SiO}_4$  bands at  $935\text{ cm}^{-1}$  [3,4], did not show any appreciable differences. The bands at  $3625$  and  $3650\text{ cm}^{-1}$  are due to crystallographically “normal” hydroxyl site [4,12] while the others are normally attributed to  $\text{OH}^-$  associated with different defects [12]. Thus the main effect of the thermal treatment, seen in the IR spectra, is improving the ordering in the sample (enhancing of the intensities of the

“normal”  $\text{OH}^-$  bands and weakness of those corresponding to the “defective”  $\text{OH}^-$  ions, as the temperature increases).

#### 4. Conclusions

Three main conclusions can be drawn from the results: (i) the TL spectra show that the main

emission centres in topaz are related to the  $(\text{AlO}_4)^0$  and  $(\text{H}_3\text{O}_4)^0$  defects; (ii) the vibrational spectra suggest that the charge trapping centres are probably related to various  $\text{OH}^-$  related defect centres; (iii) the thermal treatments are mainly changing the distribution of the traps, rather than modifying the amount of recombination centres, enhancing the crystallographically “normal” hydroxyl ions.

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### References

- [1] P.A. Northrup, K. Leinenweber, J.B. Parise, *Am. Mineral.* 79 (1994) 401.
- [2] Y.V. Ivanov, E.L. Belokoneva, J. Protas, N.K. Hansen, V.G. Tsirelson, *Acta Crystallographica. B* 54 (1998) 774.
- [3] B. Wunder, D.C. Rubie, C.R. Ross II, O. Medenbach, F. Seifert, W. Schreyer, *Am. Mineral.* 78 (1993) 285.
- [4] J.T. Klopogge, R.L. Frost, *Spectroch. Acta A* 56(2000) 501.
- [5] D.N. Souza, J.F. Lima, M.E.G. Valerio, *Rad. Eff. Def. Sol.* 135 (1995) 109.
- [6] D.N. Souza, J.F. Lima, M.E.G. Valerio, *Mater. Sci. Forum* 239–241 (1997) 765.
- [7] D.N. Souza, J.F. Lima, M.E.G. Valerio, L.V.E. Caldas, *Nucl. Instr. and Meth. B* 166–167 (2000) 209.
- [8] R.S. Krishnan, in: *Proceedings of The Indian Academy of Sciences, Section A*, XXVI, 1948, p. 460.
- [9] G. Xiong, Y. Yu, Z. Feng, Q. Xin, F. Xiao, C. Li, *Microp. Mesop. Mater.* 42 (2001) 317.
- [10] C.A. Londos, A. Vassilickou-Dova, G. Georgiou, L. Fytros, *Phys. Status Solidi A* 39 (1992) 473.
- [11] X.H. Yang, S.W.S. McKeever, *J. Phys. D: Appl. Phys.* 23 (1990) 237.
- [12] B. Bahadur, *Phys. Rev. B* 52 (1995) 7065.
- [13] R.D. Aines, G.R. Rossman, *Am. Mineral.* 70 (1985) 1169.