INFLUENCE OF THERMAL TREATMENT ON THE RAMAN, INFRARED AND TL RESPONSES OF NATURAL TOPAZ

Divanizia N. Souza[1], José Fernandes de Lima[2], Mário Ernesto G. Valerio[2], Cristiano Fantini[3], Marcos A. Pimenta[3], Roberto L. Moreira[3] and Linda V. E. Caldas[4]

[1]Universidade Federal de Sergipe, Depto. de Educação, CECH
49100-000, Aracaju, SE, Brazil – dnsouza@fisica.ufs.br

[2]Universidade Federal de Sergipe, Depto. de Física, CCET
49100-000, Aracaju, SE, Brazil

[3]Universidade Federal de Minas Gerais - Depto. de Física - ICEx
C.P. 702, 30123-970, Belo Horizonte, MG, Brazil

[4]Instituto de Pesquisas Energéticas Nucleares, CNEN
C. P. 11049, Pinheiros, 05542-970, São Paulo, SP, Brazil

ABSTRACT

Analyses of Thermoluminescence (TL) and Thermally Stimulated Exoelectron Emission (TSEE) 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 $Al_2(SiO_4)(F,OH)_2$ whose main defect is the presence of to the OH^- groups substituting for the F^- ion. 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 colorless topaz.

Key Words: topaz, TL, infrared spectroscopy, Raman.

I. INTRODUCTION

Topaz is an aluminum fluorosilicate with a fairly constant chemical composition $Al_2SiO_4(OH,F)$. The only major variation found in different samples is in the OH/F concentration ratio. The structure of topaz consists of SiO_4 groups linking octahedral chains of $Al[O_4(F,OH)_2]$ in a zigzag fashion parallel to the c-axis. Four of the six anions surrounding the Al^{3+} ion belong to SiO_4 tetrahedra and the remaining two anions are either F^- or OH^- group. Topaz crystallizes in the orthorhombic system, space group Pbnm [1, 2, 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 gravel [4].

In previous papers [5, 6], investigations of natural topaz from different origins using Thermoluminescence (TL) and Thermally Stimulated Exoelectron Emission (TSEE) showed that colorless samples displayed TL responses higher than the colored ones. Furthermore, in some samples, up to 6 TL peaks were found in the range from room temperature to $400°C$. Colorless topaz pellets were 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_4 and Al-related groups in topaz. In particular, the modes associated with the SiO_4 groups are located around 935 cm^{-1}, while the lines

in the region from 3625 to 3675 cm^{-1} are mainly due to different OH^{-} vibration modes.

In the present work TL was combined with the Infrared and Raman spectroscopies to identify the charge carrier traps and the recombination centers aiming to understand the processes of light emission in natural colorless topaz.

II. EXPERIMENTAL

Rolled pebble samples of natural colorless topaz from Santo Antonio do Jacinto, Minas Gerais, Brazil, were used in this work. For the thermoluminescence measurements, the samples were powdered with grain sizes form 0.75 to 0.150 mm. The grains were annealed during 1.0 h at temperatures between 300°C and 700°C. The Raman measurements were performed using a backscattering geometry, with the light polarization samples parallel to the c crystalline axis. For the infrared measurements, slices of about 2.0 mm thick were cut. These samples were thermally treated in the same conditions of the ones used for the TL measurements.

The TL readouts were performed from room temperature up to 350°C in a home-made TL reader. The doses used were 50 Gy from a ^{60}Co source. The Raman measurements were performed at room temperature using a Dilor XU triple monochromator equipped with and argon/kripton source (5145Å, 50mW), a confocal microscope and a CCD detector. The infrared measurements were also performed at room temperature from 500 to 4000 cm^{-1}, using a Bomen DA8 Fourier Transformer spectrometer equipped with a SiC source, a coated KBr beamsplitter and a MCT detector.

III. RESULTS AND DISCUSSIONS

A typical 3D TL spectra of a sample irradiated with 50 Gy is shown in Figure 1. The TL glow curve is composed by 4 main peaks at 100, 180, 210, 300°C, while the emission is mainly composed by a broad emission centered at 420nm, which spreads from 330 to 500nm (Figure 2). This emission is similar to that observed in thermally treated quartz, being attributed to $(AlO_4)^0$ and $(H_3O_4)^0$ centers. The former leads to an emission centered at 460nm while the latter gives the emission at 380nm [11]. These defects are formed when Al^{3+} or $3H^+$ ions substitute for the Si^{4+} site

and the resulting dangling bond is neutralized by a trapped hole, forming a neutral defect. Owing to the similarities of the spectra, the proposal of this work is that these are also the main emission centers in topaz.
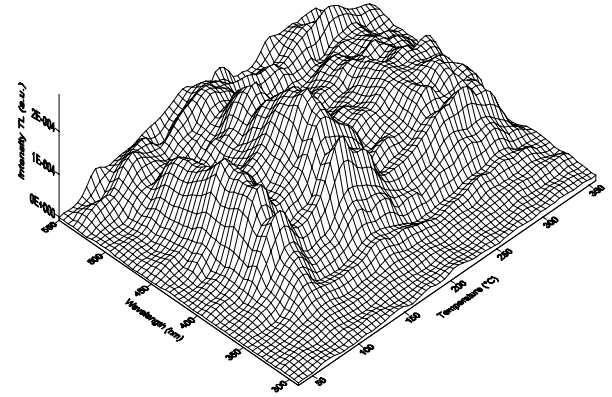

Figure 1. 3D TL curve of powdered colorless topaz thermally treated at 300°C/1h.
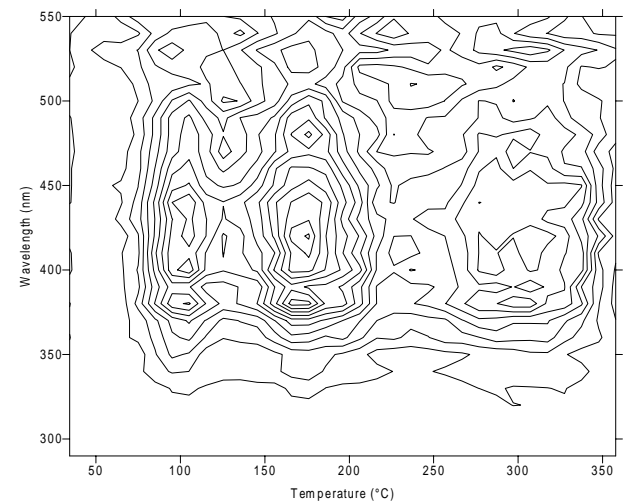

Figure 2. Contour plot of the TL emission of colorless topaz thermally treated at 300°C/1h.

Thermal treatments, prior to the irradiation, can induce changes in the TL peaks. In figure 3 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, as can be seen in Figure 4. The peaks at 180 and 210°C have quite the same behavior. 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 centers.
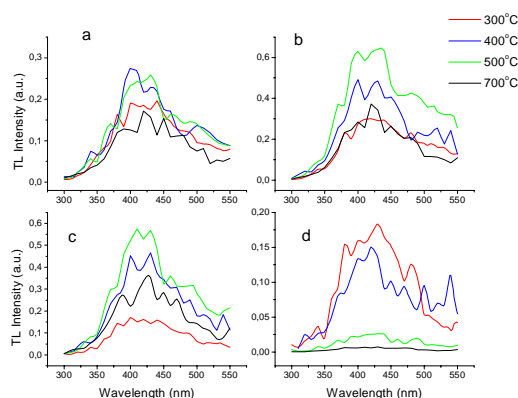

Figure 3. TL emission spectra, at the peak temperatures, as a function of the temperature of the thermal treatment.
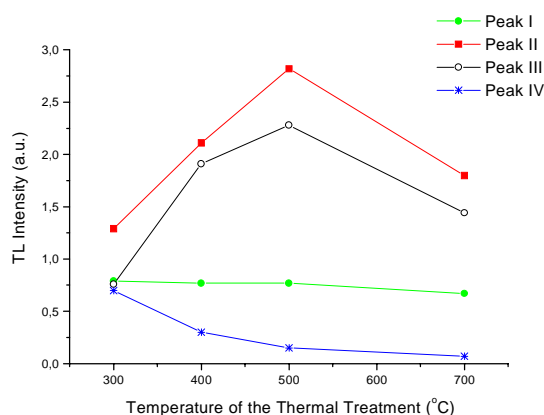

Figure 4. TL peak intensities at 100 (peak I), 180 (peak II), 210 (peak III), 300°C (peak IV) as a function of the temperature of the thermal treatment.

The Raman spectra of the colorless topaz from Santo Antonio do Jacinto, Minas Gerais, Brazil analyzed in this work are comparable to those found in the literature [4-6]. The natural samples or the samples thermally treated at 400, 500 and 700°C display very similar spectra (see Figure 5). The bands at 646, 847, 934, 983 and 1163 cm^{-1} are related to the SiO$_4$ [4, 8, 9]. The two OH-stretching bands around 3640 and 3650 cm^{-1} present a faint evolution with the thermal treatment (Figure 6): the shoulder at lower frequencies tends to increase as the temperature of the thermal treatment increases.
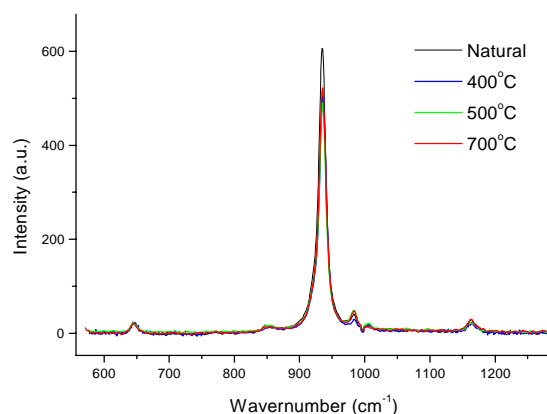

Figure 5. Raman spectra of the colorless topaz for different temperatures of the thermal treatment.
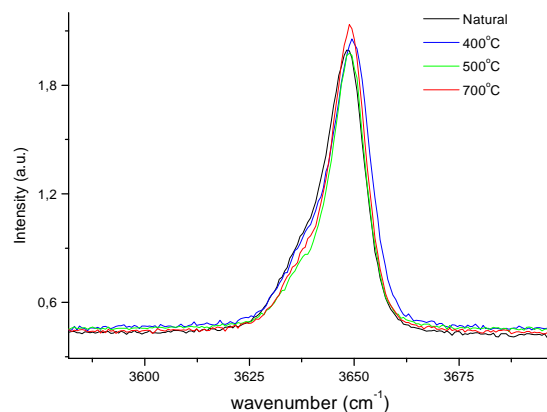

Figure 6. Raman spectra of the bands related to the OH$^-$ of the colourless topaz.

The infrared spectra of the treated samples, however, show remarkable changes, mainly in the 3400 to 3700 cm^{-1} region, as can be seen in Figure 7. In Figure 8 the intensities of the bands in this region are plotted as functions of the thermal treatment temperature. The bands in this region are attributed to various OH$^-$ vibrational modes [3-5, 9-13]. We can see that, while the bands at 3423 and 3486cm^{-1} decrease, the bands at 3585, 3625 and 3650 cm^{-1} increase as the temperature of the thermal treatment increases. The other bands in the whole spectra (not showed here), including the SiO$_4$ bands at 935 cm^{-1}[3, 4], did not show any appreciable differences. The bands at 3625 and 3650 cm^{-1} are due to crystallographically "normal" hydroxyl site [4, 12], while the others are normally attributed to OH$^-$ associated with different defects [12]. Thus, the main effect of the thermal treatment seen in the IR spectra is the improvement of ordering in the sample (enhancing of the intensities

of the "normal" OH⁻ bands weakness of those corresponding to off site OH⁻ ions with increasing temperature).
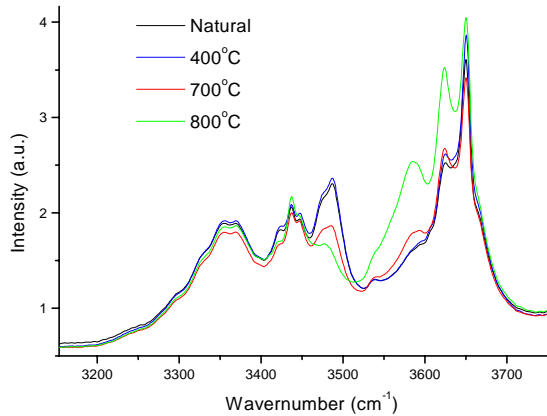

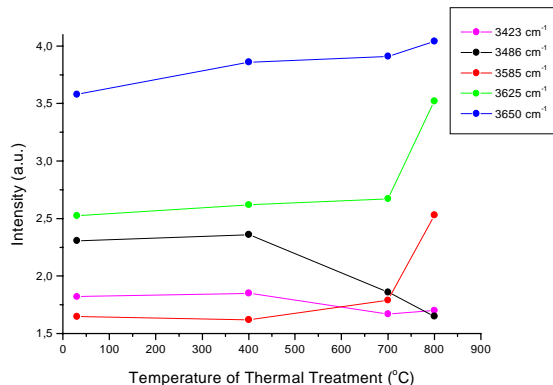Figure 7 : Infrared spectra of the thermally treated samples.

Figure 8: Intensities of the IR bands as a function of the temperature of the thermal treatments.

IV. CONCLUSIONS

Three main conclusions can be drawn from the results: i- the TL spectra show that the main emission centers in topaz are related to the $(AlO_4)^0$ and $(H_3O_4)^0$ defects; ii- the vibrational spectra suggest that the charge trapping centers are probably related to various OH-related defect centers; iii- the thermal treatments are mainly changing the distribution of the traps, rather than modifying the amount of recombination centers, enhancing the crystallographically "normal" hydroxyl ions.

REFERENCES

[1] Northrup, P.A.; Leinenweber, K.; Parise, J.B. The location of H in the high-pressure synthetic $Al_2SiO_4(OH)_2$ topaz analogue. Am. Mineral. 79, 401-404, 1994.

[2] Ivanov, Y.V.; Belokoneva, E.L.; Protas, J.; Hansen, N.K.; Tsirelson, V. G.; Multipole Analysis of the Electron Density in Topaz Using X-ray Diffraction Data, Acta Crystallographica. B, 54, 774-780, 1998.

[3] Wunder B.; Rubie, D.C.; Ross II, C.R. Medenbach, O.; Seifert, F.; Schreyer, W. Synthesis, stability, and properties of $Al_2SiO_4(OH)_2$: A fully hydrated analogue of topaz. Am. Mineral., 78, 285-297, 1993.

[4] Kloprogge, J.T.; Frost, R.L. Raman microscopic study at 300 and 77 K of some pegmatite minerals from the Iveland-Evje area, Aust-Agder, Southern Norway. Spectroch. Acta A, 56, 501-513, 2000.

[5] Souza, D.N.; Lima, J.F.; Valerio, M.E.G. Thermoluminescence of Brazilian topaz. Rad. Eff. Def. Sol., 135, 109-113, 1995.

[6] Souza, D.N.; Lima, J.F.; Valerio, M.E.G. Thermoluminescence of natural topaz crystals of differing genesis. Materials Science Forum, 239-241, 765-768, 1997.

[7] Souza, D.N.; Lima, J.F.; Valerio, M.E.G.; Caldas, L.E.V. Dosimetric properties of natural Brazilian topaz: A thermally stimulated exoeletronic emission and thermoluminescence study. Nuc. Instrum. and Meth. in Phys. Res. B, 166-167, 209-214, 2000.

[8] Krishnan, R.S. The Raman effect in Topaz and its relation to the luminescence spectrum.

Proceedings of The Indian Academy of Sciences, Section A, XXVI, 460-469, 1948.

[9] Xiong, G.; Yu, Y.; Feng, Z.; Xin, Q.; Xiao, F.; Li, C. UV Raman spectroscopic study on the synthesis mechanism of zeolite X. Microp. and Mesop. Materials, 42 – 317-323, 2001.

[10] Londos, C. A.; Vassilicokou-Dova, A.; Georgiou, G.; Fytros, L. Infrared Studies of Natural Topaz. Physica Status Solidi (a), 39, 473-479, 1992.

[11] Yang, X.H.; Mckeever, S.W.S. The pre-dose effect in crystalline quartz. J. Phys. D: Appl. Phys. 23, 237-244, 1990.

[12] Bahadur, B. Hydroxyl defects in germanium-doped quartz: Defect dynamics and radiation effects. Physical Review B, 52 – 7065-7075, 1995.

[13] Aines, R. D.; Rossman, G. R. The high temperature behaviour of trace hydrous components in silicate minerals. Am. Mineral., 70, 1169-1179, 1985.