6th International Symposium on ESR Dosimetry and Applications
Campos do Jordão, SP 12-16 outubro 2003

THERMALLY STIMULATED LUMINESCENCE AND EPR STUDIES ON TOPAZ

(electron spin resonance)

Divanizia N. Souza[1], José Fernandes de Lima[2], Mário Ernesto G. Valerio[2] and Linda V. E. Caldas[3]

[1]Universidade Federal de Sergipe, Depto. de Educação, CECH

49100-000, Aracaju, SE, Brazil

[2]Universidade Federal de Sergipe, Depto. de Física, CCET

49100-000, Aracaju, SE, Brazil

[3]Instituto de Pesquisas Energéticas Nucleares, CNEN

C. P. 11049, Pinheiros, 05508-000, São Paulo, SP, Brazil

- Corresponding author. Tel.: +55-79-212-6725. FAX:+55-79-212-6807. E-mail: dnsouza@fisica.ufs.br

10376

Abstract

In the present work the EPR spectra and TL emission of colorless natural topaz from Santo Antônio do Jacinto, MG, Brazil, was studied as a function of the thermal treatments and irradiation with gamma dose aiming the use of this material as a radiation dosimeter. EPR measurements in "as received" samples at room temperature presented signals in the region about 500 at 5000. The signal located around $g \cong 2$, frequently attributed to $(AlO_4)^0$, increased with additional gamma dose and disappeared after thermal treatment at 500°C for 1h. The irradiation after thermal treatment recovered this signal. The decay promoted by the isochronal thermal treatment shows that the $(AlO_4)^0$ defects is direct related with TL glows peaks. The variation of EPR spectrum with temperature of the annealing previous to the radiation shows that the variation of TL sensitivity is a consequence of the variation of $(AlO_4)^0$ population.

Keywords: Topaz, Thermoluminescence, EPR.

I. Introduction

Thermoluminescence (TL) has proved to be useful in measuring the radiation doses in a particular material. Part of the radiation energy gets absorbed inside the materials forming charge carrier trapped in localized energy levels in the band gaps. During the heating process, the detrapping and recombination of the charge carriers give rise to the typical TL emission of the material. The intensity of the emitted light is proportional to the amount of radiation, up to saturation. The colour of the emitted light and the temperature at which it occurs are related to the properties of the defects responsible for traps and the recombination centers.

TL of many different materials, including artificially grown and natural crystals, has been studied with the aim of developing new solid-state TL dosimeters (TLD). An advantage of artificially grown crystals is the possibility to control the composition of the starting materials. On the other hand, natural crystals can be cheaper and available in reasonable large quantities.

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 related to [OH]/[F] concentration ratio. The structure of topaz consist of SiO_4 groups linking octahedral chains of $Al[O_4(F,OH)_2]$ in a zigzag fashion parallel to the crystalline c-axis. Four of the six anions surrounding the Al^{3+} ion belong to SiO_4 tetrahedral and the remaining two are either a F^- a OH^- group. Topaz crystallizes in the orthorhombic system, space group Pbnm (Ribbe et al. 1971 and Northup et al. 1994) , and is normally found as well-developed prismatic crystals with pyramidal terminations. Topaz is contained in pegmatite dikes, particularly those carrying tin, and also as rolled pebbles in stream gravels.

The first report of TL in topaz was provided by Moss and McKlveen (1978). The saturation dose for their natural samples from the topaz Mountain in Utah, USA, was found to be 700Gy, and the TL signal intensity increased by 20% after 40 cycles. Azorin et al. (1982) studied TL properties of various minerals from Mexico and found topaz to be the most sensitive. They reported two main TL peaks on a typical topaz TL glow curve.

Lima et al (1986), on the other hand found four peaks in their studies of natural topaz from Governador Valadares, Brazil. They also reported that the number and positions of the peaks depend on the time between the irradiation and the TL measurements.

In previous works (Souza et al., 1995, 1997) we studied the TL emission of natural topaz samples from various parts of Brazil. We found that: (i) there are up to six TL peaks at 80, 140, 170, 230, 280, and 330°C in same samples, (ii) colourless samples are more sensitive to gamma radiation then colored ones, and (iii) UV light can promote filling of some TL traps. Also, we found that the 170°C TL peak of the natural samples displays an anomalous fading.

The TL emission studies in minerals can be usefully employed in elucidating the nature of the intrinsic and radiation induced defects by establishing correlations with others techniques such electron paramagnetic resonance (EPR).

The aim of the present work is to combine TL and EPR to study the nature of traps and its correlation with luminescence in topaz, establishing a model that can explain the whole microscopic process involved in the charge trapping during irradiation and the release and recombination process upon heating.

II. Experimental

Natural colorless topaz from Santo Antônio do Jacinto, Minas Gerais, Brazil, were used in this work. They were carefully ground into powders sizing between 0.075 and 0.150 mm. Gamma irradiation was carried out at room temperature from a ^{60}Co source with a dose rate of 10 $kGy.h^{-1}$.

The TL measurements were made using a home made TL reader equipped with a photomultiplier THORM EMI 9789QB and the measurements were recorded from room temperature up to 400°C, with a heating rate of $5°Cs^{-1}$.

EPR measurements were performed using 200 mg of topaz grains contained in a quartz tub carried out in a BRUKER EMX spectrometer with a standard rectangular cavity (ER4102ST).

III- Results and discussion

Typical TL glow curves of "as-received" natural samples and samples irradiated with supplementary dose are shown in Figure 1. Also in Figure 1 we show the glow curves of topaz samples pre-treated at 400, 500, 600, 700 and 800°C for 1h and irradiated with 100Gy of γ-ray from ^{60}Co source. While natural samples exhibit TL peaks in the range from 150 and 400°C, the pre-annealed samples presents four glow peaks at 100, 180, 210, and 300°C. The "as received" sample presented a quite strong TL emission due to the natural dose. When a 100 Gy is added to that natural dose the change in the overall emission is increased mainly for the low temperature side of the TL curve since the low temperature peaks decay fast at room temperature than the high temperature ones. The thermally treated samples presented similar glow curves to the untreated ones and the main

difference is in the intensity of the peaks. The 500°C treated sample is the one that displayed the higher TL curve, considering only the samples that was treated.

The emission of the four TL peaks observed in the glow curves are mainly composed by a broad emission band centered at 420nm to 500nm and this emission can be identified to the $[AlO4]^0$ defect, a center created when a Al impurity substitute for the Si with an extra hole. This center was proposed by McKeever et al. (1991) to explain the emission spectra of natural quartz. In Figure 2 the emission spectra of the TL peak at 180°C of samples pre-annealed at different temperatures are shown. As it is easily seen, the pre-irradiation thermal treatments did not change the emission centers but mainly changed the intensity of the overall emission. It means that the thermal treatments do not create different kinds of emission centers.

In a previous paper (Souza et al., accepted to publication) we have showed that the changes observed in the TL intensity of the topaz natural samples due to the thermal treatments are correlated to the changes in the amount of OH^- in the sample. Samples from differing origins also displayed the similar correlation between the OH^- concentration and the intensity of the TL peaks and it was possible to conclude that the TL traps must be connected to the OH^- species available in the sample. This conclusion is also compatible to the observation displayed in figure 2 that no appreciable change is observed in the existing kinds of emission centers and the change in the relative TL intensity can be interpreted in the changes induced by the thermal treatments in the amount of OH^-, the main trapping centers.

Figure 3 presents the EPR spectra of natural samples and of samples irradiated with different supplementary doses. These spectra were obtained at room temperature with a microwave power of 50.655 mW, below saturation. The main radiation induced defects in topaz have been observed by Yukiara at al (2002). The most intense line occurs at g=2.012

(3454G) and was identified as a hole localized at a substitutional Al^{3+} ion at a Si^{4+} site, the site proposed by McKeever et al (1991).The intense line at g=1.966 (3534G) was attributed by Petrov (1983) to a Ti^{3+} impurity at Al^{3+} site, a neutral defect formed when a substitutional Ti^{4+} captures one electron.

It is possible to see that some of the EPR lines presented in figure 3 changed the intensity when the radiation dose increased. The insert in figure 3 shows the normalized EPR line intensities plotted as a function of gamma dose. While the line at g=2.02 (3434 G), to the $[AlO4]^0$ center, increases as the dose increases, the other lines does not change appreciably. The thermal treatment almost completely removes this line and the radiation after the thermal treatment recovers the signal, as can be seen in figure 4. It is also clear from the figure that apart forms the $[AlO4]^0$ lines; the other signals almost did not change intensity. These results combined to the results presented in figure 3, indicates that the $[AlO4]^0$ must be connected to the TL emission in topaz. In addition, if we consider the spectra of the TL emission of topaz, as discussed in above and in details in refs (Souza et al., 2000 and 2002) we can conclude that the $[AlO4]^0$ must be strongly correlated to the luminescence center.

In order to confirm that, a series of isochronal annealing at different temperatures were performed in samples that was thermally treated at 400°C/1h and irradiated with 100 Gy of gamma rays. The isochronal annealing were done from 70 up to 350° C for 10 min. and after each annealing an EPR measurement was performed in the same conditions as before. In figure 5 the intensity of the $[AlO4]^0$ and Ti^{3+} lines are plotted as functions of the temperature of the isochronal annealing. A typical TL glow curve of the sample thermally treated at 400°C/1h and irradiated with 100Gy is also shown. We can clearly se that, while the $[AlO4]^0$ EPR line decreased in steps approximately following the TL peaks, the Ti3+

line is quite insensitive to the isochronal annealing. This correlation confirms that the $[AlO4]^0$ is the main recombination and luminescence center in topaz.

Conclusions:

In the present paper we presented a combination of TL and EPR in order to understand the charge trapping and recombination process in topaz. The results pointed out to an ambiguously identification of the centers and it is possible to conclude that the $[AlO4]^0$ is the main recombination and luminescent center and the OH^- related centers are responsible for the charge trapping process. Upon irradiation, charges are transferred from one center to the other and during heating the charge recombine in the $[AlO4]^0$ centers that decays from the excited state emitting light centered at the typical 420nm.

Acknowledgments:

The authors are grateful to the CAPES/PROCAD program, CNPq and FINEP for the financial support.

References

Azorin, J., Salvi, R. Gutiérrez, P. C. A., 1982. Some minerals as TL dosimeters. Health Phys. 43, 590.

Lima, C. A. F., Rosa, L. A. R., Cunha, P . G., 1986. The thermolumiscence properties of Brazilian topaz. Appl. Radiat. Isot. 37 (2), 135.

Mckeever, S. W. S., 1991. Mechanisms of Thermoluminescence Production - Some Problems and A Few Answers. Nuc. Tracks Radiat. Meas. 18, 5.

Moss, A. L., McKlveen, J. W., 1978. Thermo luminescent Properties of Topaz. Health Phys. 34, 137.

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

Petrov I., 1983. Correlation of electron-paramagnetic-res and optic absorption-spectra of natural topaz, Fortsch. Mineral. 61, 171.

Ribbe, P.H.; Gibbs, G.V., 1971. The crystal structure of topaz and its relation to physical properties. Am. Mineral. 56, 24.

Souza, D. N., Lima, J. F., Valerio, M. E. G., 1995. Thermolumiscence of Brazilian topaz. Rad. Eff. Def. Sol. 135, 109.

Souza, D.N.; Lima, J.F.; Valerio, M.E.G., 1997. Thermoluminescence of natural topaz crystals of differing genesis. Mat. Sci. Forum. 239-241, 765.

Souza, D.N., Lima, J.F., Valerio, M.E.G., Caldas, L. V. E., 2000. Dosimetric properties of natural Brazilian topaz: a thermally stimulated exoeletronic emission and thermoluminescence study. Nucl. Inst. Met. B. 166-167, 209.

Souza, D.N., Lima, J.F., Valerio, M.E.G., Fantini, C., Pimenta, M. A., Moreira, R. L., Caldas, L. V. E., 1997. Influence of thermal treatment on the Raman, infrared and TL responses of natural topaz . Nucl. Inst. Met. B. 191, 230.

Yukihara, E. G, Yoshimura, E. M., Okuno E., 2002. Paramagnetic radiation-induced defects in gamma-irradiated natural topazes, Nucl. Inst. Met. B. 191, 266.

Figure Captions

Figure 1: TL glow curve of the samples thermally treated at different temperatures from 400 to 800°C for 1 h previously to the irradiation with a 100Gy dose from a ^{60}Co source. The "as-received" and the "as-received" with additional dose glow curves are also shown for comparison.

Figure 2: TL spectra of the 180° C peak of the samples thermally treated at different temperature for 1h followed by irradiated with 100Gy form ^{60}Co source.

Figure 3: EPR spectra of natural samples and of samples irradiated with different supplementary doses

Figure 4: EPR spectra of the sample thermally treated at 500° C/ 1h with and without any irradiation after the thermal treatment.

Figure 5: Intensity of the $[AlO4]^0$ and Ti^{3+} EPR lines as functions of the isochronal annealing temperature for the samples previously treated at 400°C/1h and irradiated with 100Gy. A typical TL glow curve of the topaz samples prepared in the same way is shown for comparison.

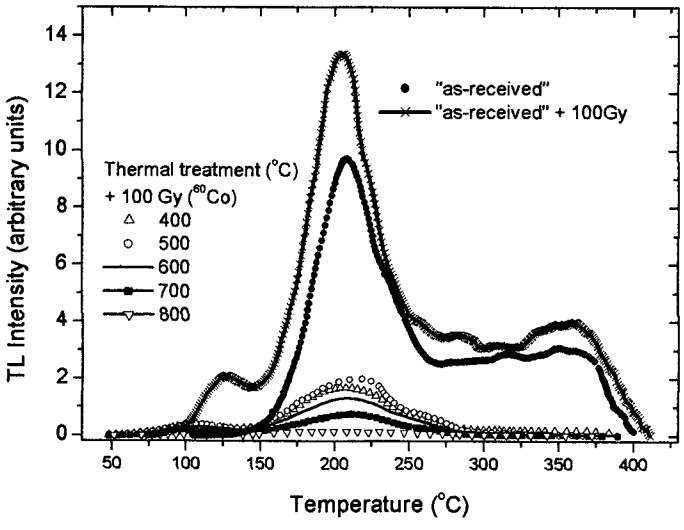
TL Intensity (arbitrary units)
Temperature (°C)
"as-received"
"as-received" + 100Gy
Thermal treatment (°C)
+ 100 Gy (60Co)
400
500
600
700
800

Figure 1

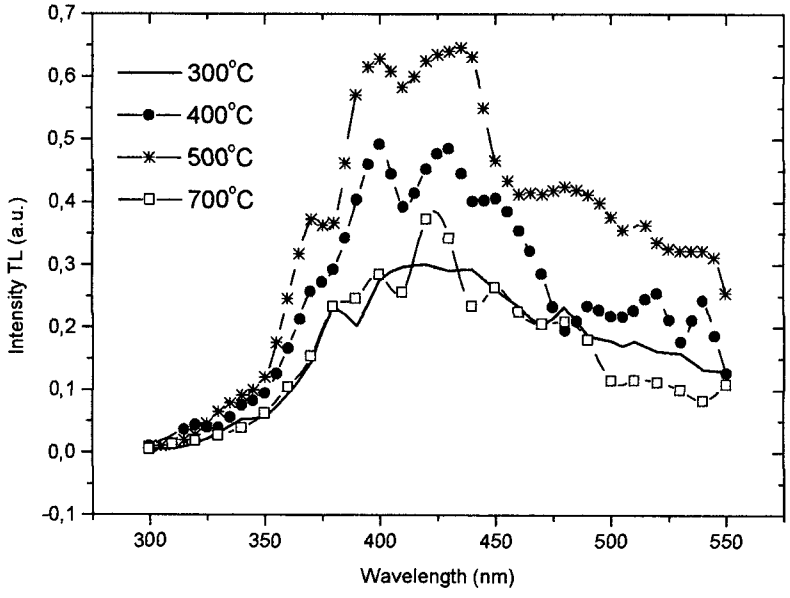
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
-0,1
Intensity TL (a.u.)
300°C
400°C
500°C
700°C
300
350
400
450
500
550
Wavelength (nm)

Figure 2

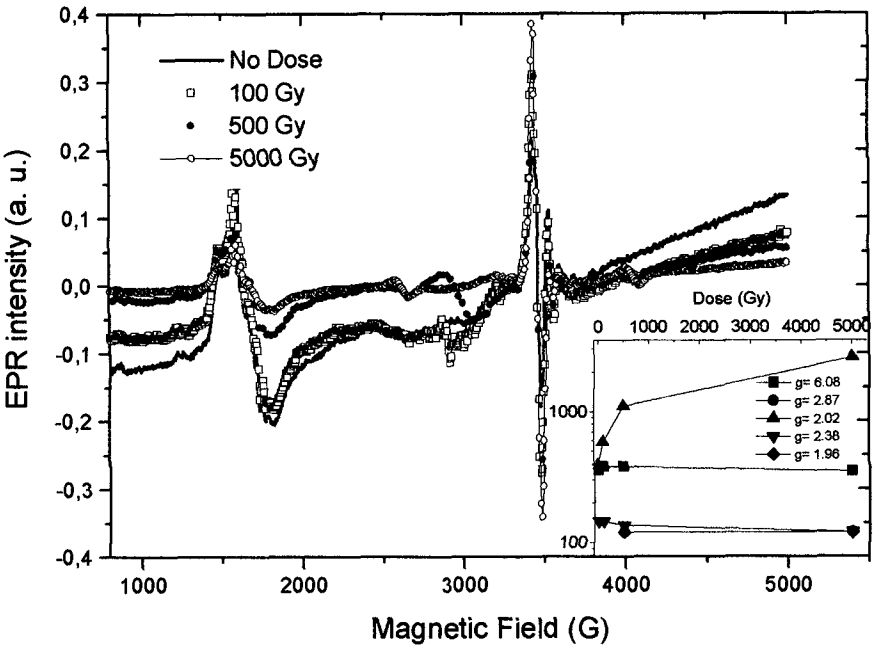
No Dose
100 Gy
500 Gy
5000 Gy
EPR intensity (a. u.)
Magnetic Field (G)
Dose (Gy)
g= 6.08
g= 2.87
g= 2.02
g= 2.38
g= 1.96

Figure 3

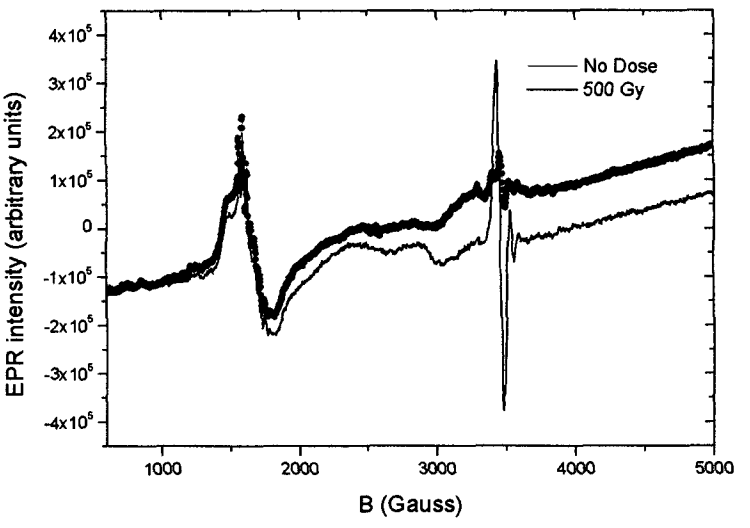
No Dose
500 Gy
EPR intensity (arbitrary units)
B (Gauss)
4x10^5
3x10^5
2x10^5
1x10^5
0
-1x10^5
-2x10^5
-3x10^5
-4x10^5
1000
2000
3000
4000
5000

Figure 4

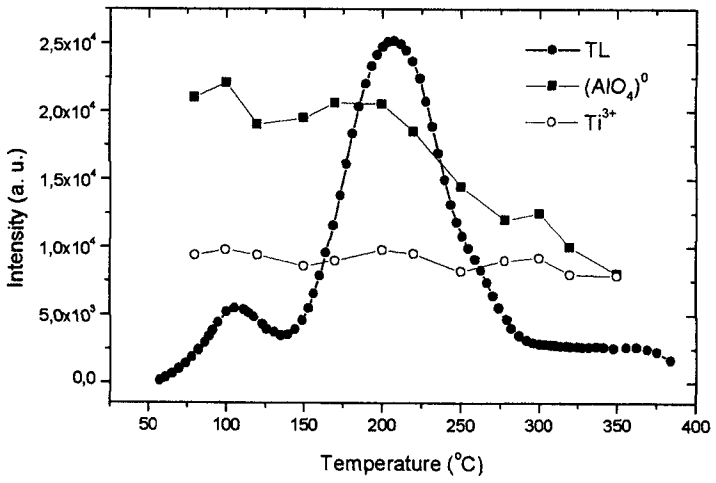
2,5x10⁴
2,0x10⁴
1,5x10⁴
1,0x10⁴
5,0x10³
0,0
Intensity (a. u.)
50
100
150
200
250
300
350
400
Temperature (°C)
TL
(AlO4)0
Ti3+

Figure 5: