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Thermally stimulated luminescence and EPR studies on topaz

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Abstract

In the present work, electron paramagnetic resonance (EPR) spectra and thermoluminescence (TL) emission of colourless natural topaz from Santo Antônio do Jacinto, Brazil, was studied as a function of thermal treatment and gamma irradiation dose, focussing on the use of this material as a radiation dosimeter. EPR measurements on "as-received" samples at room temperature provided signals in the region of about 500 at 5000 G. 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 1 h. Irradiation after thermal treatment recovered this signal. The decay promoted by isochronal thermal treatment showed the $(AlO_4)^0$ defects to be directly related to the TL glows peaks. The variation of EPR spectrum with annealing temperature prior to irradiation showed that the variation of TL sensitivity is a consequence of the variation of the $(AlO_4)^0$ population.

Keywords: Topaz; Thermoluminescence; EPR

1. Introduction

Thermoluminescence (TL) has proven to be useful in measuring the radiation dose in a particular material. A fraction of the radiation energy is absorbed by the material, 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 TL emission which is typical 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 that are responsible for traps and the recombination centres.

The 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 that this presents to control the composition of the starting materials. On the other hand, natural crystals can be cheaper and available in reasonably large quantities.

Topaz is an aluminium fluorosilicate with a fairly constant chemical composition Al_2SiO_4 (OH,F). The only major variation found in different samples is related to 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 crystalline *c*-axis. Four of the six anions surrounding the Al^{3+} ion belong to SiO_4 tetrahedral and the remaining two are both an F^- and OH^- group. Topaz crystallizes in the orthorhombic system, space group Pbnm (Ribbe and Gibbs, 1971; Northrup 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

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found to be 700 Gy, 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. On the other hand, Lima et al. (1986) 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 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) in the same samples there are up to six TL peaks, at 80, 140, 170, 230, 280, and 330 °C; (ii) colourless samples are more sensitive to gamma radiation then coloured ones; and (iii) UV light can promote filling of some TL traps. We also 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 other techniques such as electron paramagnetic resonance (EPR). Thus, the aim of the present work has been to combine TL and EPR to study the nature of traps and their 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.

2. Experimental

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

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 °C s^{-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).

3. Results and discussion

Typical TL glow curves for ‘‘as-received’’ natural samples and samples irradiated with supplementary dose are shown in Fig. 1. Also in Fig. 1 we show the glow curves of topaz samples pre-treated at 400, 500, 600, 700 and 800 °C for 1 h and irradiated with 100 Gy of γ-rays from the ^{60}Co source. While natural samples exhibit TL peaks in the range from 150 to 400 °C, the pre-annealed samples present four glow peaks at 100, 180, 210, and 300 °C. The

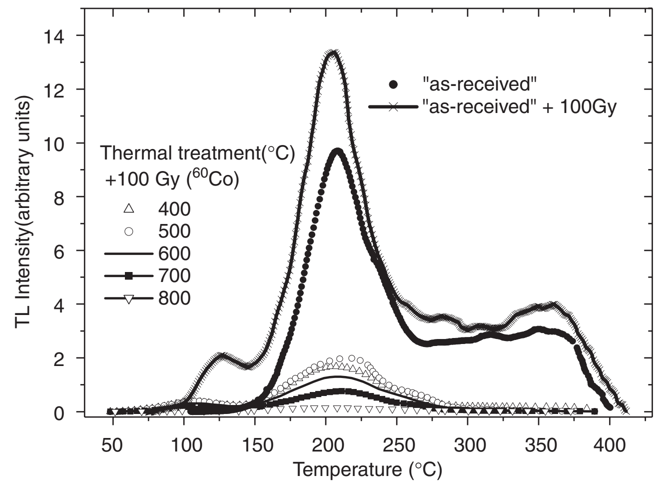

Fig. 1. TL glow curve of samples thermally treated at different temperatures, from 400 to 800 °C for 1 h previous to irradiation with a 100 Gy dose from a ^{60}Co source. The ‘‘as-received’’ and the ‘‘as-received, with additional dose’’ glow curves are also shown for comparison.

‘‘as-received’’ sample presented relatively 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 on the low-temperature side of the TL curve since the low-temperature peaks decay more rapidly at room temperature than the high-temperature ones. The thermally treated samples presented similar glow curves to the untreated ones, the main difference being 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 were treated.

The emission of the four TL peaks observed in the glow curves is mainly composed of a broad emission band centred at 420–500 nm and this emission can be traced to the $[AlO_4]^0$ defect, a centre created when an Al impurity substitutes for the Si with an extra hole. This centre was proposed by Mckeever (1991) to explain the emission spectra of natural quartz. In Fig. 2, the emission spectra of the TL peak at 180 °C for samples pre-annealed at different temperatures are shown. As it can easily be seen, the pre-irradiation thermal treatments did not cause change in the emission centres but mainly changed the intensity of the overall emission. This infers that the thermal treatments do not create different kinds of emission centre.

In a previous paper (Souza et al., 2004), we have shown that changes observed in the TL intensity of natural topaz samples due to thermal treatment are correlated with change in the amount of OH^- in the sample. Samples from differing origins also displayed 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 with the observation displayed in Fig. 2 that no appreciable change is observed in the existing kinds of emission centres and the change in relative TL intensity can be interpreted in terms of changes

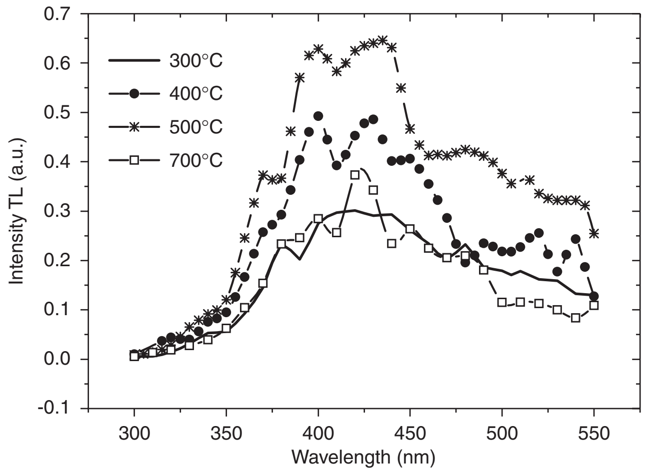

Fig. 2. TL spectra associated with the 180 °C peak of samples thermally treated at different temperatures for 1 h followed by irradiation at 100 Gy from the ^{60}Co source.

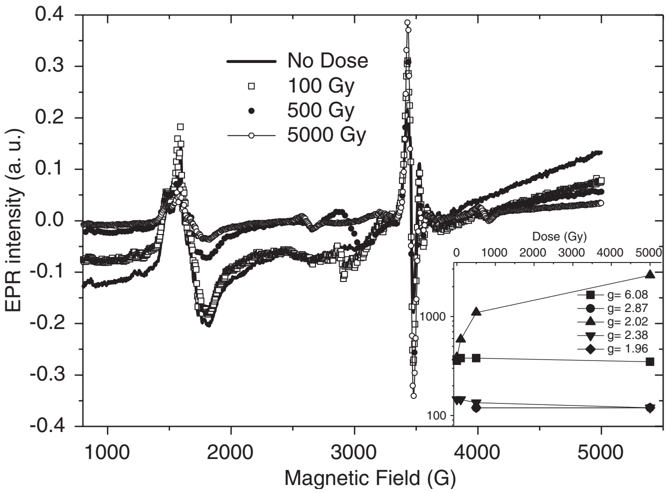

Fig. 3. EPR spectra of natural samples and of samples irradiated with different supplementary doses.

induced by the thermal treatments in the amount of OH^-, the main trapping centres.

Fig. 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, being below saturation. The main radiation-induced defects in topaz have been observed by Yukihara et al. (2002). The most intense line occurs at $g = 2.012$ (3454 G), where g is the gyromagnetic ratio of the electron, and was identified as a hole localized at a substitutional Al^{3+} ion at a Si^{4+} site, the site proposed by Mckeever (1991). The intense line at $g = 1.966$ (3534 G) was attributed by Petrov (1983) to a Ti^{3+} impurity at the Al^{3+} site, a neutral defect formed when a substitutional Ti^{4+} captures one electron.

It is possible to observe that some of the EPR lines presented in Fig. 3 changed the intensity when the radiation dose was increased. The inset in Fig. 3 shows the normalized EPR line intensities plotted as a function of gamma dose. While the line at $g = 2.02$ (3434 G), for the $[AlO_4]^0$ centre, increases in intensity as dose increases, the intensity of other lines do 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 Fig. 4. It is also clear from the figure that apart from the $[AlO_4]^0$ lines, the other line intensities showed little or no change. These results, combined with the results presented in Fig. 3, indicate that the $[AlO_4]^0$ must be connected to the TL emission in topaz. In addition, if we consider the spectra of the TL emission of topaz, as discussed above and in detail in references (Souza et al., 2000, 2002), we can conclude that the $[AlO_4]^0$ must be strongly correlated to the luminescence centre.

In order to confirm this, a series of isochronal annealings were performed at different temperatures, in samples that were thermally treated at 400 °C for 1 h and then irradiated with 100 Gy of gamma rays. The isochronal annealing was

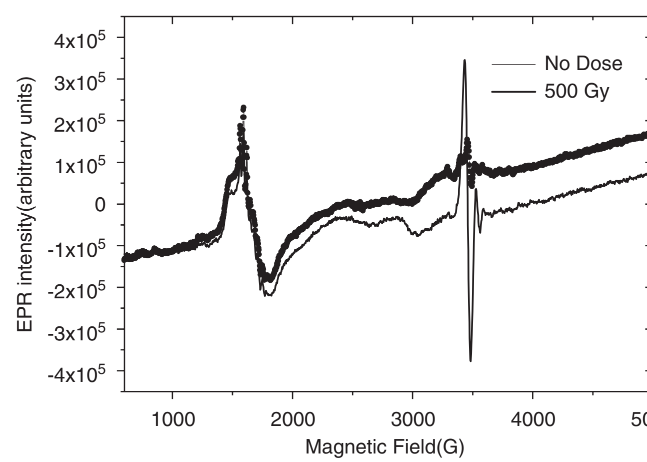

Fig. 4. EPR spectra of the sample thermally treated at 500 °C/1 h, with and without any irradiation after the thermal treatment.

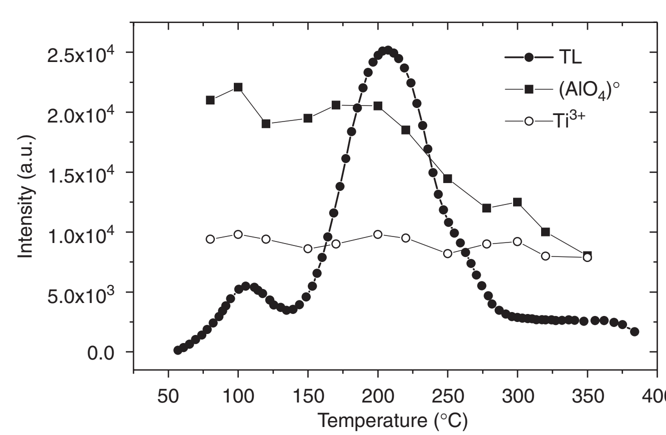

Fig. 5. Intensity of the $[AlO_4]^0$ and Ti^{3+} EPR lines as functions of the isochronal annealing temperature for the samples previously treated at 400 °C/1 h and irradiated with 100 Gy. A typical TL glow curve of the topaz samples prepared in the same way is shown for comparison.

done from 70 up to 350 °C for 10 min, and after each annealing an EPR measurement was performed under the same conditions as before. In Fig. 5, the intensity of the $[AlO_4]^0$ and Ti^{3+} lines are plotted as functions of the temperature of the isochronal annealing. A typical TL glow curve for a sample thermally treated at 400 °C for 1 h and irradiated with 100 Gy is also shown. We can clearly see that, while the $[AlO_4]^0$ EPR line decreases in steps, approximately following the TL peaks, the Ti^{3+} line is quite insensitive to the isochronal annealing. This correlation confirms that the $[AlO_4]^0$ is the main recombination and luminescence centre in topaz.

4. Conclusions

In the present paper, we have examined the combination of TL and EPR signals in an effort to understand charge trapping and the recombination process in topaz. The results point to unambiguous identification of the centres and thus it is possible to conclude that $[AlO_4]^0$ is the main recombination and luminescent centre and also that the OH^--related centres are responsible for the charge trapping process. Upon irradiation, charges are transferred from one centre to the other, while during heating the charges recombine in the $[AlO_4]^0$ centres decaying from the excited state emitting light centred at typically 420 nm.

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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. Nucl. Tracks Radiat. Meas. 18, 5.

Moss, A.L., McKlveen, J.W., 1978. Thermoluminescent 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. Fortschr. 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. Radiat. Eff. Defects Solids 135, 109.

Souza, D.N., Lima, J.F., Valerio, M.E.G., 1997. Thermoluminescence of natural topaz crystals of differing genesis. Mater. 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. Instrum. Methods 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., 2002. Influence of thermal treatment on the Raman, infrared and TL responses of natural topaz. Nucl. Instrum. Methods B 191, 230.

Souza, D.N., Lima, J.F., Valerio, M.E.G., Sasaki, J.M., Caldas, L.V.E., 2004. Radiation-induced charge trapping recombination process in natural topaz studied by TL, EPR and XRD. Nucl. Instrum Methods B 218, 123.

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