TL and EPR correlations in a quartz-like silicate mineral

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Abstract. A sample of silicate mineral considered as being jadeite but revealed to be more quartz-like, therefore named JQ2 has been studied concerning its TL and EPR properties. This study revealed a full correlation between the 210 °C TL peak and the g=2.0025 EPR signal. In both cases, the centers disappear at the same temperature and are restored after gamma irradiation. The TL peak at 210 °C may be related to the $E'_1$ centers formed on irradiation. JQ2 responds to very high $\gamma$-dose and can be used as a high-dose dosimeter using TL and/or EPR techniques.

1. Introduction
Synthetic as well as naturally available materials with luminescent properties have many applications such as radiation dosimetry and archaeological and geological dating [1-3]. The defect centers created by ionizing radiation are responsible for their TL properties [3]. The identification and characterization of these centers constitutes an essential step in understanding the mechanism of thermoluminescence (TL). In this context, electron paramagnetic resonance (EPR) provides a convenient and sensitive technique and it helps in providing support and further identification of the species detected by TL technique. The EPR technique has been extensively used in the identification of the main paramagnetic defects in the mineral silicates [2,3].

The dosimetric properties of these materials have already been studied using the TL and EPR techniques and it was suggested that they show potential for use in high-dose dosimetry [4,5]. Rocha et al. [6] studied the natural jade using the thermally stimulated exoelectron emission technique. Arslanlar et al. [7] investigated some physical properties dependent on point defects of natural crystals of jade from Turkey using the cathodoluminescence, radioluminescence and TL techniques; but there is no evidence in the literature describing the defects responsible for the TL properties in quartz-like and the correlation between TL and EPR measurements. In the present work, green samples acquired as jadeite, have been investigated concerning the EPR and TL properties and also the effects of the ionizing radiation and the thermal treatments at high temperatures of the samples, elucidating the defect center responsible for production of 210 °C TL peak in natural quartz-like.
2. Materials and experimental

The sample studied here was acquired from LEGEP Minerals Ltd. in São Paulo. It presents a green color. About 30 grams of the sample were pulverized and sieved to retain grains sizes between 0.080 and 0.180 mm for TL and EPR measurements. Those with size smaller than 0.080 mm have been used for X-ray fluorescence (XRF) measurement.

The TL measurements have been carried out on Harshaw model 4500 TL reader (temperature range: 50 °C up to 400 °C and heating rate: 4 °C/s). The EPR measurements were performed using a Bruker EMX spectrometer using a rectangular cavity (ST ER4102) with a microwave frequency of 9.767 GHz.

For irradiation, IPEN/CNEN/SP - Institute for Energy and Nuclear Researches Radiation Center’s 60Co source was used. The XRF measurement was carried out at Department of Mine and Petroleum, University of Sao Paulo.

3. Results and discussion

An analysis of the main components of the quartz-like (JQ2) sample was obtained by XRF. Results are presented in Table 1. This analysis was performed to identify the chemical elements in the sample, and for future studies about which of these elements are responsible for the TL signal. Although the XRF results have shown that has the same compound that the quartz crystal, the TL glow curve of α-quartz is different, when compared with the TL glow curves of JQ2 sample which is described by Barbosa et al.[8].

| Sample | Compound (w. %) |
|--------|----------------|
| JQ2   | SiO₂ 87.2 Al₂O₃ 4.55 Fe₂O₃ 0.14 Cr₂O₃ 0.40 MgO 0.37 CaO 0.16 Na₂O 0.19 K₂O 1.48 TiO₂ 0.01 P₂O₅ 0.04 |

The TL glow curves of this sample as function of high dose gamma irradiation have been reported by Barbosa et al. [8]. Here, we studied the correlation between the TL glow curves of each peak and the EPR signals.

![Figure 1. TL glow curve from natural JQ2 pre-annealed at 500 °C/30min. and subsequently receiving a γ-ray dose of 10 kGy. A good fit between the experimental glow curve (circles) and the simulated glow curve (full line) can be achieved by assuming the presence of four peaks.](image-url)
In this work, EPR studies were carried out mainly to identify the defect centers responsible for the observed TL peaks in JQ2. Fig. 2 shows the EPR spectrum for JQ2 sample without irradiation. It shows $g=4.3$ signal due Fe$^{3+}$ ion and an intense signal extending from about 2200 to 5000 G due to spin-spin interaction of Fe$^{3+}$ ions. In the inset, the EPR signal with $g$ between 2.00 and 2.02 are shown. We then irradiated JQ2 sample with gamma rays with dose varying from 100 Gy and 70 kGy. The EPR results are shown in Fig. 3 for $g$-values from 1.96 and 2.08.

Analysing Fig. 3, we can see two EPR signals at $g = 2.0025$ and at $g = 2.0068$. They are found to increase with irradiation dose. To see whether there is any correlation between EPR signals and the TL peaks behaviour, we compared EPR results with TL intensity behavior of TL peaks obtained by Barbosa et al. [8]. Fig. 4 shows such comparison.

**Figure 2.** EPR spectrum of non-irradiated JQ2. In the inset of the figure, detail of the EPR spectra in the region of the E$^+$ center.

**Figure 3.** EPR spectrum of JQ2 irradiated with different gamma doses.

**Figure 4.** Correlation between the EPR signal at $g=2.0025$ and the 210 °C TL peak behavior under gamma dose irradiation. In inset of the figure, the linear dependence between the E$^+$ center and 210 °C TL peak.

**Figure 5.** Decay of the 210 °C TL peak and the $g=2.0025$ EPR signal of the JQ2 samples submitted to different thermal treatments.
Fig. 4 shows a clear correlation between the EPR and TL results, i.e., the EPR signals increase parallel to 210 °C TL peak intensity with irradiation dose. In the inset of Fig. 4 presents the linear dependence between TL and EPR results indicates that the growths of both the 210 °C TL peak and EPR center with gamma-dose are similar. It leads us to say that the center responsible for the EPR signal at g=2.0025 is the same as the one that produce 210 °C peak, since both signals increase in the same way with dose. Therefore, it may be concluded that the center responsible for the EPR signal at g=2.0025 is the same as the center that produces the 210 °C TL peak. The EPR signal observed at g=2.0025 has been assigned to E₁⁻type centers. This center grows with radiation dose. Some other silicates, as petalite [9], kaolinite [10] and diopside [11], have shown the formation of E₁⁻ centers on irradiation. The isochronal thermal decrease of EPR signals of the JQ2 sample were performed after sample irradiation with gamma-ray dose of 5 kGy and annealed from 100 up to 400 °C. The EPR signal at g~2.017 do not change, while g=2.0068 and g=2.0025 signals decrease with increasing annealing temperature. The 210 °C TL peak behavior was examined under similar annealing and irradiation conditions. Fig. 5 shows a comparison of these results and it is observed that the EPR signal due to E₁⁻center and TL peak at 210 °C behave in a very similar manner. The observed similarity among TL and EPR results indicates their clear correlation. The centers disappear at the same temperature and the gamma irradiation restores the centers simultaneously in the same way. Hence this glow peak may be attributed to the recombination of electrons that are liberated from electron traps with the hole centers.

4. Conclusions

The EPR results of JQ2 presented the typical g≈4.5 Fe³⁺ signal around 1500 G, and besides, an EPR signal around g≈2.0 which also due to Fe³⁺ ion. The signals around g=2.0025 and g=2.0068 are assigned to E₁⁻center and peroxy center, respectively. These signals grow with radiation dose and the signal due to E₁⁻center decrease with temperature. Data correlation analysis of EPR and TL results showed that the EPR signal at g=2.0025 and the TL peak at 210 °C can be attributed to the same defect. In both cases, the centers disappear at the same temperature and are restored after gamma irradiation. Even though the presence of Fe impurity ions was identified in the matrix of JQ2 crystals through XRF and EPR studies, they do not take part in the TL emission process directly. They induce the formation of native lattice defects that act as donors and acceptors. One needs further data to present a complete model about these defect centers for the TL glow curve of JQ2.

Acknowledgments

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References

[1] Ayta WEF, Silva VA, Cano NF, Silva MAP and Dantas NO 2011 J. Lumin. 131 1002
[2] Cano NF, Yauri JM, Watanabe S, Mittani JCR and Blak AR 2008 J. Lumin. 128 1185
[3] Cano NF, Turbiani-Filho IT, Gennari RF, Munita CS, Souza MC, Ângulo RJ and Watanabe S 2013 Quatern. Int. 306 137
[4] Melo AP, Valerio MEG and Caldas LVE 2004 Nucl. Instrum. Meth. B 218 198
[5] Teixeira MI, Melo AP, Ferraz GM and Caldas LVE 2010 Appl. Radiat. Isotopes 68 582
[6] Rocha FDG, Cecatti SGP and Caldas LVE 2002 Radiat. Prot. Dosim. 100 417
[7] Arslanlar YT, Garcia-Guinea J, Kibar R, Çetin A, Ayvacıklı M and Can N 2011 Appl. Radiat. Isotopes 69 1299
[8] Barbosa RF, Reichmann F, Cano NF, Rocca RR and Watanabe S 2013 Phys. Status Solidi C 10 242
[9] Souza SO, Chubaci JFD, Selvin PC, Sastry MD and Watanabe S 2002 J. Phys. D Appl. Phys. 35 1562
[10] Ildefonse P, Muller JP, Clozel B, Calas G 1991 Mater. Res. Soc. 212 749
[11] Cano NF, Yauri JM, Watanabe S, Mittani JCR and Blak AR 2008 J. Lumin. 128 1185