TL in green tourmaline: Study of the centers responsible for the TL emission by EPR analysis

Nilo F. Cano⁎, T.K. Gundu Rao, Jorge S. Ayala-Arenas, Carlos D. Gonzales-Lorenzo, Letícia M. Oliveira, Shigueo Watanabe⁎⁎

⁎ Instituto do Mar, Universidade Federal de São Paulo, Rua Doutor Carvalho de Mendonça, 144, CEP 11070-100 Santos, SP, Brazil
⁎⁎ Instituto de Física, Universidade de São Paulo, Rua do Matão, Travessa R, 187, CEP 05508-090 São Paulo, SP, Brazil
⁎⁎ E-mail addresses: nilocano@if.usp.br, nilo.cano@unifesp.br (N.F. Cano), jayala@unsa.edu.pe (J.S. Ayala-Arenas), watanabe@if.usp.br (S. Watanabe).

A R T I C L E   I N F O
Keywords: TL, EPR, Radiation dosimetry, Silicate, Tourmaline

A B S T R A C T
Electron paramagnetic resonance (EPR) studies have been carried out to identify the defect centers responsible for the thermoluminescence (TL) peaks in the mineral tourmaline. The mineral exhibits three TL peaks approximately at 170, 250 and 310 °C. The EPR spectrum of the green tourmaline sample pre-heated to 500 °C presented a large signal around g = 4.3 due to Fe3+ ion. Room temperature EPR spectrum of irradiated green tourmaline shows the formation of two defect centers in the region of g = 2.0. One of the centers (center II) with a g factor equal to 1.96 is identified as an F−-center and is related to the observed high temperature 250 and 310 °C TL peaks. Center I exhibiting a doublet is due to hydrogen atoms (H0), stable in the crystal lattice at room temperature and this center correlates with the TL peak at 170 °C of the green tourmaline. An optical absorption measurement also was carried out. Bands at around 430, 730 and 1100 nm have been observed.

1. Introduction

The silicate minerals are, in general, excellent thermoluminescent materials, some of them with high sensitivity to low as well as high radiation doses [1–7]. Hence, they are candidates for radiation dosimetry.

There is one group of silicates called ring silicates or cyclosilicate to which belong beryl, cordierite and tourmaline. The tourmaline structure is typically rhombohedral with space-group R3m [8–10], although some studies report lower symmetry such as orthorhombic, monoclinic or triclinic [11–13]. The structure is characterized by groups of XO₆, YO₆, TO₆ and BO₃ polyhedra connected to each other through ZO₆ octahedra. The latter are arranged in a 3-D framework and are linked to the YO₆ octahedron through the O3–O6 edge. The tourmaline has a complex formula, XY₂Z₃(T₁O₁₃)(BO₃)₃V₄W, where X, Y and Z sites can be occupied by different ions [8–10]. Therefore, about 12 varieties of tourmaline are formed in nature. According to several authors [14–17], the following ions fit into the following structural sites: X = Na, Ca, o (= vacancy), K; Y = Al, Fe³⁺, Cr³⁺, V³⁺, Mg, Fe²⁺, Mn²⁺, Cu²⁺, Zn, Li, Ti⁴⁺, o; Z = Al, Fe³⁺, Cr³⁺, V³⁺, Mg, Fe²⁺; T = Si, Al, B, Be; B = B, o; W(O1) = OH, F, O; V(O3) = OH, O.

Tourmaline is a well known silicate mineral because some of its varieties have high gemological value [18,19].

The tourmaline crystal has been widely investigated by many authors through spectroscopic methods such as Mössbauer spectroscopy, UV–Vis spectroscopy, Raman spectroscopy and other spectroscopic techniques due to its color and gemological value [20–36].

Several authors [37–42] measured the effects of thermal treatments and irradiation on optical absorption spectra of natural tourmaline of different color and discussed the crystal field effect on the energy levels of transition ions, mostly Mn²⁺, Mn³⁺, Fe²⁺, Fe³⁺ and Ti⁴⁺, usually responsible for the coloration of the crystal. In contrast, studies on luminescence properties and the identification of the defects responsible for emission of the TL peaks of the tourmalines crystal so far are few.

The process of irradiation and thermal treatment can change some physico properties of the mineral that are dependent on point defects, such as luminescence and electron paramagnetic resonance. These properties make tourmaline crystal an interesting material for some applications like dosimetry. However, although it has been a subject of some experimental studies, an investigation of defect centers created by ionizing radiation responsible for TL properties of tourmaline is still lacking. The identification and characterization of these centers form an essential step in understanding the mechanisms of TL emission. In this context, EPR provides a convenient and sensitive technique for such a
study, as it helps in providing support and further identification of the paramagnetic species by EPR technique.

In the present work a green tourmaline sample was studied using the TL and EPR techniques to investigate the centers responsible for their TL properties and possible applications in gamma radiation dosimetry. No published papers in the literature were found related to study here carried out. Optical absorption measurements also have been carried out.

2. Material and experimental

A natural green tourmaline crystal from Teofilo Otoni, state of Minas Gerais, Brazil, was investigated in this work. The sample was crushed and sieved retaining grains with 0.080–0.180 mm diameters for TL and EPR analysis. Powder with diameter smaller than 0.080 mm were used for an analysis by X-ray Fluorescence (XRF) and X-ray diffraction (XRD) in order to determine the composition and to perform the structural analysis of the samples acquired as tourmaline.

XRF analysis was carried out in the Laboratory of Technological Characterization from the Polytechnic School of the University of São Paulo. The values presented were determined in a sample fused with anhydrous lithium tetraborate in the calibration ROC-1 (Rocks), relative to the quantitative analysis comparing them with certified reference materials in an XRF spectrometer, PANalytical, Zetium model. The major oxides are expressed as percentage by weight (wt%) and the estimated error is < 5%.

The crystalline phases of the green tourmaline was investigated by XRD using the MiniFlex 300 from Rigaku, with Cu Kα radiation (λ = 1.5418 Å), and the data collected by scanning 2θ from 10° to 90° at room temperature. Sieved samples as described above were each divided into several portions to be irradiated to several γ-rays doses.

For irradiation, Institute for Energy and Nuclear Researches Radiation Center's 60Co source was used for γ-doses below 1 kGy. The TL measurements were carried out in a Harshaw TL Reader, model 4500, equipped with a bialkali photomultiplier (PMT) for light detection. The applied heating rate was 4 °C/s in nitrogen atmosphere.

A Miniscope EPR spectrometer operating at X-band frequency with 100 kHz modulation frequency was utilized for the EPR experiments. Diphenyl Picryl Hydrazyl (DPPH) was used for calibrating the g-values. A 1 kGy. Whereas peak at 170 °C is supra-linear for doses between 10 and 100 Gy and then is linear. For low doses less than 10 Gy the sample is behavior as the curve slope equals to 45° in the dose range of 10 Gy to 1 kGy. Whereas peak at 170 °C is super-linear for doses between 10 and 100 Gy and then is linear. For low doses less than 10 Gy the sample is not very sensitive. This result shows that the peaks at 250 and 310 °C can be used in dosimetry for dose above of 10 Gy.

The emission curve of the green tourmaline sample was analyzed by the Glow Curve Deconvolution Function (GCDF) method to determine kinetic TL parameters using a second order (symmetrical) equation from Kitis et al. [44]. Mathcad software was used to create the deconvolution program. The program is based on chi-square minimization. Quality of fit was tested with the Figure of Merit (FOM) [45]. The TL parameter results determined by GCDF method are shown in Table 2. FOM = 1.25% shows that data fit is satisfactory.

The high content of Fe2O3 is a main indication. We assume that the structure of our tourmaline sample is similar to that of magnesium tourmaline. In the place of Mg we have Fe3+ [43]. The diffractogram of the green tourmaline natural sample is shown in Fig. 1. Comparing the powder XRD pattern to the JCPDS files, all the peaks of the crystal are identified as belonging to tourmaline variety with present of Fe denominate Schorl (NaFe3+3Al19Si19O63(OH)4) (JCPDS card, No. 43-1464). This result confirms the identification of the tourmaline variety by chemical XRF analysis.

Table 1 shows the composition in weight % of the oxide components of the tourmaline samples using the XRF analysis; several oxide components were not listed (with less than 0.01%) in the table and some oxide components were not detected due to limitations of the XRF technique. This analysis was performed to identify which are the chemical elements in the samples, and for future studies about which of these elements are responsible for the TL and EPR signals. Besides basic oxide components SiO2 and Al2O3, oxides such as Na2O, Fe2O3, K2O, ZnO, CaO, Na2O and others in smaller concentration are found.

There are many types of tourmaline [8], but from XRF analysis shown in Table 1 it seems that the sample here discussed can be Schorl.

3. Results and discussions

Table 1 shows the composition in weight % of the oxide components of the tourmaline samples using the XRF analysis; several oxide components were not listed (with less than 0.01%) in the table and some oxide components were not detected due to limitations of the XRF technique. This analysis was performed to identify which are the chemical elements in the samples, and for future studies about which of these elements are responsible for the TL and EPR signals. Besides basic oxide components SiO2 and Al2O3, oxides such as Na2O, Fe2O3, K2O, ZnO, CaO, Na2O and others in smaller concentration are found.

![Fig. 1. X-ray diffraction of the green tourmaline crystal compared with XRD pattern from JCPDS card, No. 43-1464 (Schorl).](image-url)
signal does not change with gamma irradiation. On gamma irradiation, the EPR spectrum recorded at room temperature is shown in Fig. 5. A single EPR line is seen near the free-electron region as well as a clear doublet separated by 513 G. Thermal annealing experiments indicate that the observed spectrum has contributions from two defect centers. These two centers are labelled in Fig. 5. The measured g-value of center I is 2.0146. The doublet spectrum closely resembles the doublet spectrum observed in gamma irradiated calcium phosphate [46,47] and acidic glasses [48,49].

The separation of the doublet, for example, is 503 G in irradiated Bayerite [50,51]. The doublet spectrum has been assigned to hydrogen atom radicals and arises from the hyperfine coupling of the electron spin of H to the nuclear magnetic moment of hydrogen nuclei. A relatively recent observation of H atoms in a mineral system is in beryl [52].

Based on these observations, center I in tourmaline is assigned to H atom. The EPR spectra obtained after a thermal treatment at 500 °C for 30 min followed by irradiation with different gamma doses are shown in Fig. 6. The thermal annealing results of center I is shown in Fig. 7. The EPR line intensity was determined by measuring the peak-to-peak height of the EPR lines. It is observed that the center becomes unstable...
around 100 °C and its intensity is found to decrease in the temperature range extending from 100 °C to 220 °C. This decrease in EPR intensity relates with the TL peak at 170 °C.

Divalent ions like Ca$^{2+}$, Mg$^{2+}$ and Zn$^{2+}$ are present in the lattice of tourmaline. Tourmaline also contains trivalent (Al$^{3+}$) and tetravalent (Si$^{4+}$) ions. A partial substitution of trivalent and tetravalent ions by divalent ions is possible due to anti-site cation exchange. These exchanges are point defects in crystals and are called as cation exchange disorder. Due to cation exchange, oxygen vacancies will be present in tourmaline. Center II shown in Fig. 5 is characterized by an isotropic g-value equal to 1.9976 and a linewidth of 36 G. On gamma irradiation, electrons can get trapped at oxygen vacancies to form F$^+$-centers (an electron trapped at an anion vacancy). F$^+$-centers have g-values close to free-electron value ($g \sim 2.0$) with a g-shift which may be negative or positive. Linewidth of F$^+$-centers are decided by the amount of delocalization of the unpaired electron and also on the relative abundance and magnetic moments of the ions present in the lattice. In alkali halides large linewidths are observed as the electron is considerably delocalized. In systems like MgO and CaO, smaller linewidths are observed. Center II in tourmaline has a relatively large linewidth of 36 G and the g-value is close to the free-electron value. On the basis of these observations, center II is tentatively ascribed to an F$^+$-center. It is observed in thermal annealing experiments that center II becomes unstable around 200 °C and decays in the temperature range 200–350 °C. Therefore, it is possible that center II may relate with the TL peak at 250 °C as well as the peak at 310 °C.

Fig. 8 shows optical absorption spectra of green tourmaline slab. Strong bands at 430, 730 and 1100 nm are observed in the sample. According to Deer et al. [8], in tourmaline, containing about 3.5% Fe, the principal colors come from Fe$^{2+}$ d-d bands in the 700 nm region; they are usually blue or green. Burns [53] attributes to Fe$^{3+}$ d-d transitions $^6A_{1g} \rightarrow ^4T_{1g}$ producing $v_1$-band, $^6A_{1g} \rightarrow ^4T_{2g}$ $v_2$-band and $^6A_{1g} \rightarrow ^4A_{1g}, ^4E_g$ $v_3$-band in green tourmaline. $v_1$, $v_2$- and $v_3$-bands occur at 430 nm (23,256 cm$^{-1}$), 730 nm (13,699 cm$^{-1}$) and 1100 nm (9091 cm$^{-1}$), respectively. Since $v_1$-band is blue-violet absorption and $v_2$-band is yellow-red absorption the crystal appears to be green colored.

4. Conclusions

The XRD and XRF analysis have shown that sample here investigated have the tourmaline crystal structure with the basic composition of the main oxides corresponding to the tourmaline crystal.

The TL glow curve of the samples heat-treated at 500 °C for 30 min and irradiated with different γ doses present three peaks at 170, 250 and 310 °C. The glow-curve deconvolution shows that in the region from 50 to 400 °C, three overlapped TL peaks of kinetic second order are observed. The TL intensity as function of dose of 250 and 310 °C peaks have shown that its TL intensity grows linearly in the region between 10 and 1000 Gy. As a consequence of the present results, these two TL peaks may be used for radiation dosimetry.

A EPR signal characterized by a single isotropic line at about $g = 4.28$ with large intensity due to Fe$^{3+}$ ion is observed in the EPR spectrum of green tourmaline. This signal is not affected by γ-radiation. Furthermore, two defect centers are identified in the irradiated green tourmaline. Center I exhibiting a doublet signal at $g = 2.0146$ with A...
Data correlation analysis of EPR and TL results showed that the center I and the TL peak at 170°C can be attributed to the same defect. In both cases, the centers disappear at the same temperature and are restored after γ irradiation. Center II appears to correlate with the 250°C TL peak and has the possibility to be associated with the high temperature 310°C TL peak, due to their slow decay.

Acknowledgments

The authors wish to thank Ms. E. Somessari and Mr. C. Gaia, Instituto de Pesquisas Energeticas e Nucleares (IPEN), Brazil, for kindly carrying out the irradiation of the samples. This work was carried out with financial support from Fundação de Amparo à Pesquisa do Estado de São Paulo - FAPESP (Process number 2014/03085-0).

References

[2] P.G. Manning, Optical absorption spectra of chromium-bearing tourmaline, black tourmaline, and tourmaline restored after γ irradiation. Center II appears to correlate with the 250°C TL peak and has the possibility to be associated with the high temperature 310°C TL peak, due to their slow decay.

2. P.G. Manning, Optical absorption spectra of chromium-bearing tourmaline, black tourmaline, and tourmaline restored after γ irradiation. Center II appears to correlate with the 250°C TL peak and has the possibility to be associated with the high temperature 310°C TL peak, due to their slow decay.

N.F. Cano et al.