



Mechanisms of TL for production of the 230 °C peak in natural sodalite

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ABSTRACT

The thermoluminescence (TL) peak in natural sodalite near 230 °C, which appears only after submitted to thermal treatments and to gamma irradiation, has been studied in parallel with electron paramagnetic resonance (EPR) spectrum appearing under the same procedure. This study revealed a full correlation between the 230 °C TL peak and the eleven hyperfine lines from EPR spectrum. In both case, the centers disappear at the same temperature and are restored after gamma irradiation. A complete model for the 230 °C TL peak is presented and discussed. In addition to the correlation and TL model, specific characteristics of the TL peaks are described.

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1. Introduction

Luminescent materials, synthetic as well as naturally available, find many applications, which include radiation dosimetry. The defect centers created by ionizing radiation are responsible for TL. The identification and characterization of these centers form an essential step in understanding the mechanism of TL. 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 species detected by TL technique.

Sodalite is a silicate mineral of chemical formula $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$. It occurs in nature in blue color. The crystal structure of sodalite consists of an ordered framework of AlO_4 and SiO_4 tetrahedra, in such a way that cubo-octahedral cages are formed, where each atom of Al or Si is located at the center of a tetrahedral cage of oxygens. In each cage there is a Cl ion tetrahedrally coordinated by Na ions, forming a body-centered cubic structure with lattice parameter between 0.0887 and 0.892 nm [1]. Its optical absorption, dielectric relaxation phenomena, as well as EPR spectra are studied in some detail by several workers, reference to which can be found in the recent paper of Cano et al. [2]. However, no serious attempt has been made to study its TL in spite of the fact that TL of other silicates minerals are studied by a large number of workers [3–9].

The purpose of the present investigation is to study the nature of traps and its correlation with luminescence, measuring the

effects of gamma irradiation and thermal treatments through TL and EPR techniques, elucidating the defect center responsible for production of 230 °C TL peak in natural sodalite.

2. Experimental procedure

In the study, a natural blue sodalite stone from the State of Bahia, Brazil was investigated. X-ray fluorescence analysis was used to determine the main impurity contents and X-ray diffraction technique was utilized for structure analysis. The irradiations were carried out at room temperature using a ^{60}Co γ -source and under conditions of electronic equilibrium. The TL measurements were carried out in a Daybreak TL Reader, model 1100, equipped with a bialkali photomultiplier (PMT) EMI 9235QA for light detection. The applied heating rate was 4 °C/s in nitrogen atmosphere. EPR measurements were performed in a Bruker EMX spectrometer with a rectangular cavity (ST ER4102) using a microwave frequency of 9.75 GHz, microwave power of 20 mW and a modulation field of 100 kHz. Diphenyl Picryl Hydrazyl (DPPH) was used for calibration of the g values of the defect centers.

3. Results and discussion

Table 1 shows the composition in weight % of the oxide components of the sodalite. Besides basic oxide components, SiO_2 , Al_2O_3 and Na_2O , oxides such as CaO , Fe_2O_3 , K_2O , MnO , TiO , MgO and others in smaller concentration are found.

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The TL glow curves of samples previously annealed at 500 °C for 30 min and irradiated to several gamma doses are shown in Fig. 1(a). For the TL measurements, the 500 °C/30 min pre-heat was chosen because after this annealing the TL peaks at 110, 230 and 270 °C are found well defined.

Fig. 1(b) shows the dose–response curve of the 230 °C TL peak of the sodalite thermally treated at 500 °C and irradiated to doses between 1 Gy and 10 kGy of ⁶⁰Co. This TL peak shows linear behavior up to 500 Gy, saturating afterward. For low doses less than 1 Gy the sample is not very sensitive. This indicates that this

sample is promising for use as a detector of gamma radiation from 1 to 500 Gy.

It is interesting to observe in Fig. 1(a) that the high temperature peak around 270 °C appears only for higher doses, above 2 kGy and from then on it grows very rapidly.

The TL glow curve of the sodalite crystal was analyzed by the $E-T_{\text{stop}}$ [10,11] and CGCD [12] methods and the characteristic parameters (i.e. E , s , and the lifetime) for each peak were calculated.

Fig. 2(a) shows the obtained activation energies (E) using the $E-T_{\text{stop}}$ method. With these results and applying the CGCD equations proposed by Kitis et al. [12] we obtain the deconvolution of the TL glow curve of natural sodalite thermally pre-heated at 500 °C for 30 min and then γ -irradiated with a dose of 2 kGy. Fig. 2(b) shows the five TL peaks separated using first- and second-order kinetics in the region between 50 and 350 °C. The deconvolution analysis has shown that the TL glow curve of the sodalite crystal is composed of five peaks in the region between 50 to 350 °C. The positions, frequency factors (s), activation energies (E) and lifetimes (τ) of the TL peaks are presented in Table 2. The obtained lifetime high values of the 230 and 270 °C TL peaks indicate its stability at room temperature, allowing us to use the natural sodalite previously annealed at 500 °C for 30 min for dosimetric purposes.

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. 3. The EPR spectra show lines at $g=2.01132$, $g=2.0008$ lines and 11 hyperfine lines superimposed on the $g=2.0008$ signal. The observed intense EPR line at $g=2.01132$ has been attributed to the $[\text{AlO}_4]^0$ (this center corresponds to a hole trapped at a non-bridging oxygen ion adjacent to the Al^{3+} ion)

Table 1
Composition of natural sodalite using X-ray fluorescence analysis.

Compound	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	Fe ₂ O ₃	K ₂ O	MnO	MgO	Ti ₂ O	P ₂ O ₅
(wt%)	38.93	32.27	25.68	0.21	0.08	0.07	0.035	0.02	0.014	0.01
Elements	U	Th								
(ppm)	0.985	0.54								

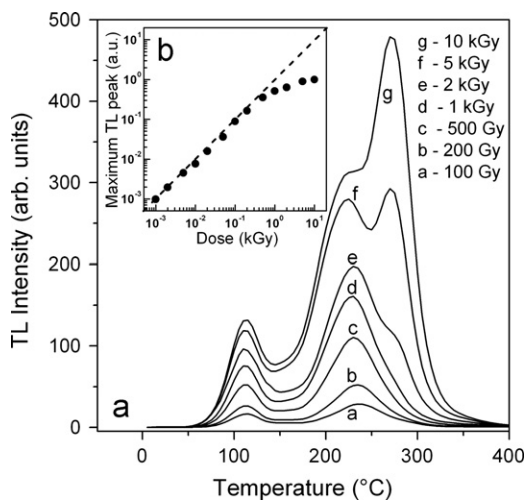


Fig. 1. (a) TL glow curves of sodalite crystals pre-annealed at 500 °C for 30 min and irradiated at several γ doses. (b) TL intensity behavior of the 230 °C peak as a function of gamma radiation doses, the dashed line indicates linearity.

Table 2
Activation energy (E), frequency factor (s) and lifetime (τ) of TL traps of sodalite.

TL peak (°C)	E (eV)	s (s ⁻¹)	τ (years; at 15 °C)
110	1.038 ± 0.007	$(1.478 \pm 0.011)10^3$	$(3.091 \pm 0.007)10^{-3}$
153	1.125 ± 0.005	$(5.805 \pm 0.029)10^{12}$	(0.262 ± 0.002)
187 ^a	1.250	1.558×10^{13}	17.352
227	1.343 ± 0.008	$(8.509 \pm 0.053)10^{12}$	$(1.162 \pm 0.010)10^3$
272	1.530 ± 0.024	$(3.337 \pm 0.052)10^{13}$	$(5.525 \pm 0.123)10^5$

^a In the $E-T_{\text{stop}}$ method the error could not be evaluated.

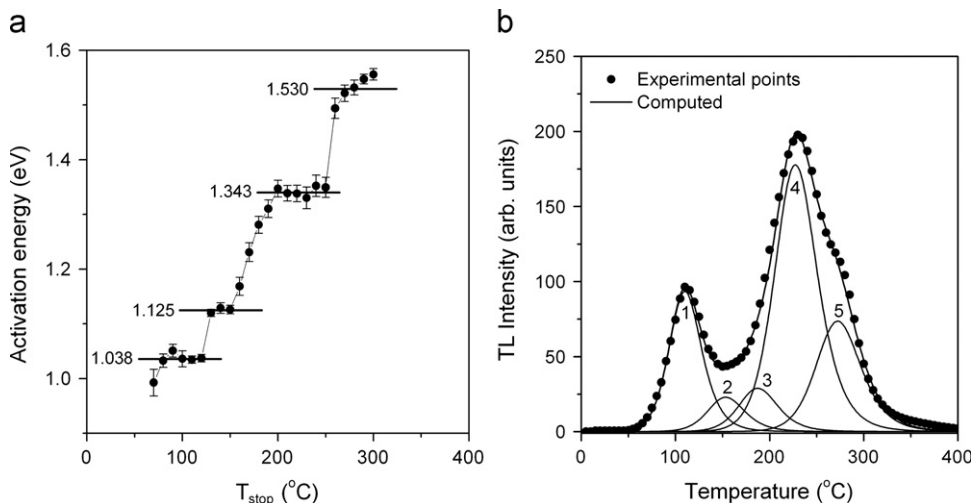


Fig. 2. (a) Activation energy vs. T_{stop} obtained by the $E-T_{\text{stop}}$ method. (b) TL glow curve from natural sodalite pre-annealed at 500 °C for 30 min and subsequently receiving a γ -ray dose of 2 kGy. A good fit between the experimental glow curve (circles) and the simulated glow curve (full line) can be achieved by assuming the presence of five peaks.

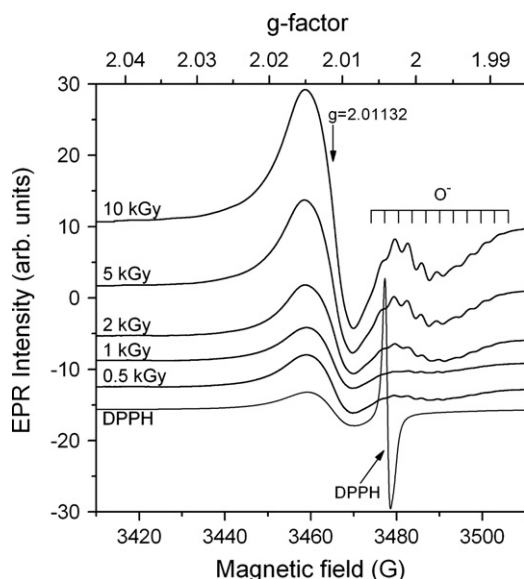


Fig. 3. EPR spectra of natural sodalite pre-annealed at 500 °C for 30 min in air and then irradiated to different gamma doses up to 10 kGy.

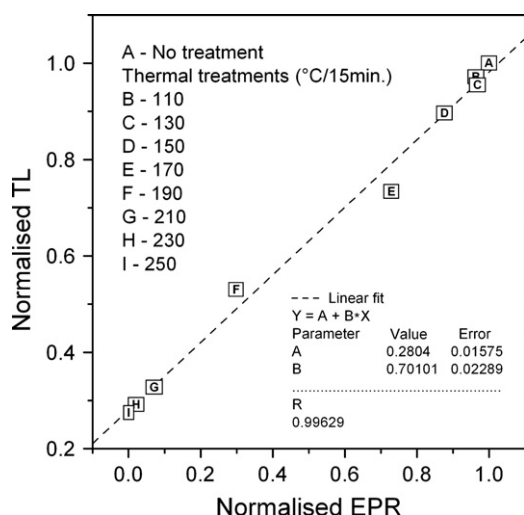


Fig. 4. Correlation between the thermal decay of the 230 °C TL peak and the eleven hyperfine lines (centered at $g=2.0008$).

defect following the works of Hassib et al. [13], Van den Brom et al. [14] and Annersten and Hassib [15]. The eleven EPR lines with a hyperfine coupling constant of 3.5 G is associated with an O^- ion in an intermediate position with respect to two adjacent Al nuclei ($I=5/2$), one in a lattice site and one replacing a Si^{4+} of the crystal structure breaking the usual alternation of aluminum and silicon that occurs in the perfect lattice, this group of eleven hyperfine lines (centered at $g=2.0008$) was also observed by Annersten and Hassib [15] on an irradiated blue sodalite crystal.

The correlation between the thermal decay of the 230 °C TL peak and the thermal decrease of the eleven hyperfine EPR lines (centered at $g=2.0008$) is presented in Fig. 4 (thermal treatments were performed after the sample irradiation with γ -ray dose of 2 kGy) and the correlation between the increase with gamma dose of 230 °C TL peak and of the eleven lines (centered at $g=2.0008$) is shown in Fig. 5. The observed linear dependence among TL and EPR results, in both cases presented in Figs. 4 and 5, indicates their clear connection. The centers disappear at the

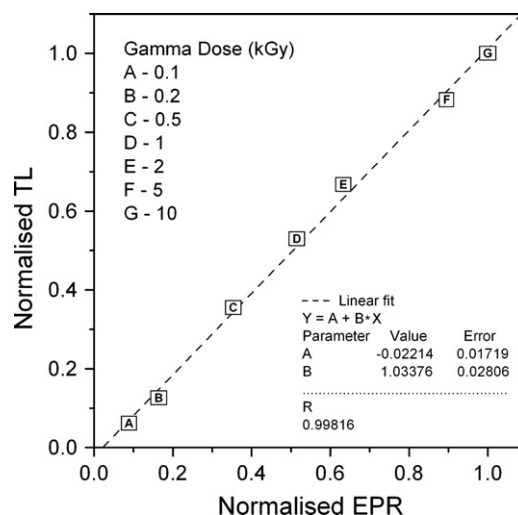
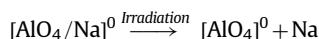


Fig. 5. Correlation between the gamma dose increase of the 230 °C TL peak and the eleven hyperfine lines (centered at $g=2.0008$).

same temperature and the gamma irradiation restores both centers simultaneously in the same way.

Aluminum and sodium play an important role in the stabilization of the observed EPR and TL centers. A trivalent Al^{3+} ion easily replaces a Si^{4+} in the ionic crystal scheme of the sodalite lattice [14]. The principle of ionic charge neutrality in an ionic crystal may require a charge compensating monovalent cation in an interstitial site. In this case, the Na^+ occupies the interstitial site and acts as a charge compensator forming the $[AlO_4/Na]^0$ center. The choice of an Al^{3+} ion as the substitutional ion and of a Na^+ ion as the charge compensator is supported by a similar case of the $[AlO_4/Na]^0$ defect observed in non-irradiated quartz [16,17].

Based on the correlation analysis between TL and EPR results, the following mechanism is suggested: the gamma irradiation liberates Na^+ from $[AlO_4/Na]^0$ complex, provides an electron trapped at the Na and a hole trapped at a bridging oxygen ion (O^- ion) in an intermediate position with respect to two adjacent Al ions. During the TL read out, the trapped electron is liberated from the Na atom and can be captured by O^- ions emitting the 230 °C TL light. This process can be described by the following equations:



4. Conclusions

The EPR spectra show lines at $g=2.01132$, $g=2.0008$ lines and 11 hyperfine lines superimposed on the $g=2.0008$ signal. The signal at $g=2.01132$ is attributed to the hole trapped at a non-bridging oxygen ion adjacent to the Al^{3+} ion. The eleven hyperfine lines are due to an O^- ion in an intermediate position with respect to two Al nuclei ($I=5/2$).

The TL glow curve of natural samples heat-treated at 500 °C for 30 min and irradiated with different γ doses present TL peaks at 110, 230 and 270 °C. The glow curve deconvolution shows that in the region from 50 to 350 °C, five overlapped TL peaks are observed.

A TL model was proposed in which a Na^+ ion acts as a charge compensator when an Al^{3+} ion replaces a Si^{4+} lattice ion, forming the $[AlO_4/Na]^0$ complex. Under the influence of gamma irradiation,

one of the oxygens, surrounding the Al^{3+} ion, loses an electron. This electron, leaving behind the hole, may be captured by the Na^+ ion. In addition, the O^- ions are trapped in an intermediate position with respect to two adjacent Al ions. During the TL read out, the trapped electron is liberated from the Na atom and can be captured by O^- ions emitting the 230 °C TL light.

As a consequence of the present study, we believe that the 230 °C TL peak of the sodalite crystal may be used for radiation dosimetry.

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