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Radiation-induced charge trapping and recombination process in natural topaz studied by TL, EPR and XRD

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Abstract

Thermoluminescence (TL) was combined with X-ray diffractometry and electron paramagnetic resonance (EPR) to identify charge traps and recombination centres in natural topaz and to help the understanding of the process of light emission in this solid. According to the results, colourless samples presented higher TL intensities than coloured samples, and they also exhibited the highest [OH]/[F] occupation factors. The thermal treatments were found to change the [OH]/[F] ratios since samples treated at about 400 °C present higher TL response and occupation factors. These results indicate that the OH^- group is directly connected to the trapping centres in topaz. The EPR signal with $g \approx 2.02$, due to $(AlO_4)^0$ centres, increases with the dose. From the TL and the EPR results, it was possible to confirm that the $(AlO_4)^0$ centre is the luminescent centre in topaz.

Keywords: Topaz; TL; Powder X-ray diffraction; EPR

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1. Introduction

Topaz is an aluminium fluorosilicate with chemical composition $Al_2SiO_4(OH,F)$ [1–3]. The crystal chemistry of natural topaz is relatively invariant, the exception being the partial OH–F substitution in the anionic F site. In the natural samples the [OH]/[F+OH] concentration very rarely exceeds 0.30 mol % [1,2].

Colourless topaz pellets were proven to be promising materials for dosimetric applications [4–7]. Several colourless Brazilian samples exhibited good thermoluminescent (TL) response to radiation, and the TL intensity showed a linear response to gamma rays between 10^{-1} and 10^2 Gy [6–8]. It was observed in a previous work that topaz samples from different origins present distinct TL emission glow curves. The most significant change on TL emission was related to the number and relative intensities of the TL peaks [5,6]. However, the defects that are responsible for the light emission processes in this material are not understood yet.

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Wunder et al. [10], using powder X-ray diffraction (XRD) analyses, found that in topaz there is a correlation between the [OH]/[OH+F] concentration ratio and the lattice constants by comparing the synthetic $Al_2SiO_4(OH)_2$ ("topaz OH") with the natural F-rich topaz. Northrup et al. [9] used the same techniques to determine the positions of H in another fully hydrated high-pressure synthetic sample analogue to topaz $Al_2SiO_4(F,OH)_2$.

EPR in topaz has been studied [11–13] aiming the determination of the colour centres in natural topaz and in samples with colours enhanced by radiation. Dickinson and Moore [11] found ten distinct EPR centres, four of them associated to impurities and six related to defect centres. The EPR peaks at *g* value approximately 2 are affected by heating or irradiation or both. Yukihara et al. [13] identified the most intense EPR line as being due to paramagnetic impurities Fe^{3+}, Ti^{3+} and the complexes $(PO_4)^0$ and $(AlO_4)^0$.

The aim of this work is to discuss the correlation between TL, powder XRD and EPR results aiming at the identification of the charge traps and recombination centres in natural topaz and to help the understanding of the process of light emission of this mineral.

2. Experimental

Five natural topaz samples batches of different origins from Minas Gerais, Brazil, were analysed and identified in Table 1 according to their colours.

The samples were powdered. Those with grain sizes between 0.075 and 0.150 mm were used in TL analyses, while the grains between 0.045 and 0.065 mm were used in the powder X-rays diffraction and EPR measurements. All samples were measured without any previous thermal treatment except for the samples of batch #2. The latter were also measured after thermal treatments at 400, 500, 600, 700 and 800 °C. The irradiation of the samples was done with a gamma source (^{60}Co).

The TL measurements were performed in a home-made TL reader equipped with a THORN EMI photomultiplier, model 9789QB, with a sample compartment and associated electronic. The TL readouts were performed from room temperature up to 350 °C following a linear heating program.

The EPR measurements were done with a Brucker EMX spectrometer operating at 9.7 GHz. The sweep of the magnetic field was from 100 to 5000 G. Powder samples were put in quartz capillary tubes and fitted inside the EPR cavity. Standard data reduction and analysis were done using the WinEPR software package accompanying the equipment.

The X-ray measurements were collected in a Powder Diffractometer Rigaku, DMAXB, with a Cu radiation tube operated at 40 kV/25 mA with counting time of 5 s and step size of 0.02°. A curved graphite crystal monochromator for diffracted beam was used to assure that only the Cu

Table 1
Colours, relative concentration of topaz and quartz and [OH]/[F] ratio as determined from the XRD refined pattern of the topaz samples

Sample	Colouration	[OH]/[F]	Composition (% Mass)		Thermal treatment temperature (°C)
			Topaz	Quartz	
#1	Colourless	0.85	99	1	–
#2	Colourless	1.63	96	4	–
		1.36			400
		0.92			500
		0.79			700
		0.52			800
#3	Light grey	1.32	99	1	–
#4	Blue	0.49	99	1	–
#5	Dark yellow	0.37	99	1	–

Kα radiation reaches the detector. The crystalline phases were identified using the *International Centre for Diffraction Data* catalogue. Rietveld refinement procedures were done using the DBWS9807 as described by Young et al. [14]. The pseudo-Voigt function was used to fit the peak profiles of the identified crystalline phases [15]. FWHM of the peaks, asymmetry coefficients, scale factors and lattice parameters for each phase and the background polynomial parameters, were simultaneously refined. After this step, refinements of the fractional occupancy factor for OH^- and F^-, which are sharing the same crystallographic site, were repeated several times, giving the [F]/[OH] molar ratios for each sample.

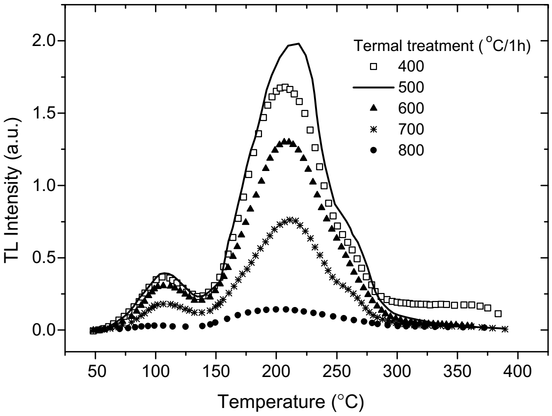

Fig. 1. TL emission curves of the samples #2 as a function of the thermal treatments at different temperatures for 1 h and subsequent irradiation with 10 Gy.

3. Results and discussions

In most samples, the Rietveld refinement of the XRD patterns indicated that a small amount of quartz was found together with topaz, as can be seen in Table 1. From the refinements it is also possible to obtain the [OH]/[F] ratio, also listed in Table 1. We can see that each sample presents a different [OH] to [F] ratio and that the thermal treatment can change their concentration ratios.

In a previous work [6] we have observed that the TL emissions are mainly composed of a broad emission centred at about 420 nm, which spreads from 330 to 500 nm. This emission is similar to that observed in thermally treated quartz being attributed to $(AlO_4)^0$ and $(H_3O_4)^0$ centres. The former leads to an emission centred at 460 nm while the latter gives the emission at 380 nm [9]. These defects are formed when Al^{3+} or $3H^+$ ions substitute Si^{4+} and the resulting dangling bond is neutralised by a trapped hole forming a neutral defect [16]. Due to the similarities between the spectra, we have proposed in the previous work [6] that these centres might also be the main emission centres in topaz.

Thermal treatments before the irradiation induce changes in the TL emission peaks. Fig. 1 shows the TL emission curves of the samples #2 as a function of thermal treatment at different temperatures for 1 h and subsequent γ irradiation with 10 Gy. The main effect of the thermal treatment is the reduction of the TL peaks at temperatures higher than 280 °C. Treated samples showed two main TL peaks, the first at 110 °C and the second at 210 °C. The latter overlaps with a less intense peak at 240 °C. For treatment at temperatures higher than 400 °C the TL peaks above 300 °C vanish. All the other TL peaks have the same behaviour. They both increase when the temperature of the thermal treatment increases reaching the maximum intensities for treatments at 500 °C. Further increase in temperature decreases the peaks. On the other hand, in a previous paper [6] we have shown that the thermal treatment did not change the emission spectra of the glow curve. These effects indicate that the thermal treatment is probably changing the amount of charge traps responsible for each TL peak, rather than changing the distribution of recombination and/or luminescent centres.

In Fig. 2 we plot the TL intensity of the 210 °C TL peak as a function of the [OH]/[F] ratio for the natural samples and for the thermally treated samples of batch #2. The figure shows that the TL intensity of topaz depends on the [OH]/[F] ratio and samples with higher [OH]/[F] ratios are the ones that exhibit the highest TL glow peaks. It is possible to conclude from these results that there must be a correlation between the [OH] concentrations and the TL traps.

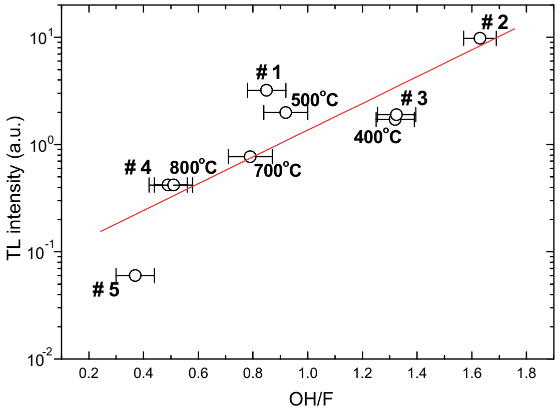

Fig. 2. Maximum TL intensities of the natural topaz samples (indicated by sample #) and of the thermally treated samples (indicated by the temperature of the thermal treatment), as a function of their respective [OH]/[F] ratios.

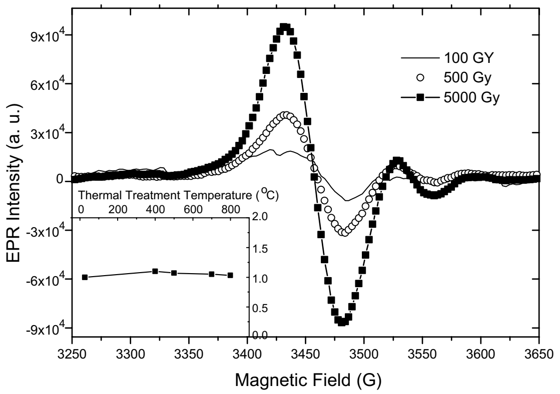

Fig. 3. Typical EPR lines of the $(AlO_4)^0$ and Ti^{3+} centres of a topaz sample irradiated with a ^{60}Co γ source. The relative intensities of the EPR line related to the $(AlO_4)^0$ centres are shown in the insert as a function of the temperature of the thermal treatment previous to irradiation.

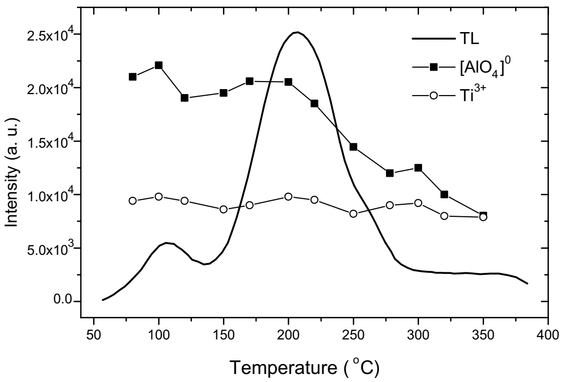

Fig. 4. Intensities of the $(AlO_4)^0$ and Ti^{3+} EPR lines as functions of the temperature of the isochronal annealing of the samples previously treated at 400 °C and irradiated with a dose of 5000 Gy associated to typical TL glow curve of the same sample.

Fig. 3 presents a typical EPR spectrum of a thermally treated topaz sample at 500 °C irradiated with 100, 500 and 5000 Gy from a ^{60}Co γ source. The typical EPR lines of the $(AlO_4)^0$ and Ti^{3+} centres are located at $g \cong 2.02$ (3434 G) and $g \cong 1.97$ (3530 G), respectively [12,13]. In the same figure it is possible to see that the intensity of the $(AlO_4)^0$ increases as the radiation dose increases. Moreover, if we change the temperature of the thermal treatment before irradiation, the $(AlO_4)^0$ EPR line does not change as shown also in this figure.

In Fig. 4 is shown the dependence of the intensity of these two EPR lines on the temperature of the isochronous thermal treatment. A sample of batch #2 was powdered, thermally treated at 400 °C and irradiated with 100 Gy from a ^{60}Co γ source. The sample was then divided into different parts that were again thermally treated at different temperatures for 10 min. These isochronous treatments were done in the temperature range from 80 to 350 °C. It can be observed that while the Ti^{3+} lines did not change, the $(AlO_4)^0$ decreases. It is also clear that the step decreases in the $(AlO_4)^0$ are approximately correlated to the TL peaks, i.e. the first decrease in the intensity of the EPR line is at the temperature of the first TL peak and the second markedly decrease in the intensity of the EPR line is associated with the highest TL peak of the sample, a TL glow curve of the sample treated at 400 °C is also shown for comparison. This clearly points out to that there should be a connection between the $(AlO_4)^0$ and the TL peaks, as we have observed from the TL spectra in a previous paper [6]. On the other hand, it is also possible to conclude that Ti^{3+} centres cannot account for the TL emission in topaz.

Combining all these results it is possible to conclude that the $(AlO_4)^0$ centres cannot be connected to the TL charge traps but should be connected to the luminescence centre that is destroyed as the temperature of the post irradiation thermal treatment increases, but is quite stable as the temperature of the thermal treatment before the irradiation increases. This conclusion is also supported by the observation that the spectra of the TL emission are quite similar to the one observed in Al-containing quartz.

4. Conclusions

Combining all the results presented in the present work with the results found in the literature it is possible to propose a model for the charge trapping and recombination process in topaz. When the samples are irradiated, OH centres and Al^{3+} substituting the Si^{4+} centres act as charge trapping centres. During the heating up stage, a charge trapped in the OH centres is released and recombines with those trapped in the $(AlO_4)^0$ centres, emitting the light. The number of OH trapping centres can be changed via thermal treatments and the amount of $(AlO_4)^0$ centres is quite high since Al^{3+} is a normal constituent of the topaz matrix. The spectra of the light are related to $(AlO_4)^0$ centres and there is a close relationship between the [OH]/[F] concentration ratio and the intensity of the TL glow curves.

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