

CORRELATION BETWEEN EPR AND TL IN NATURAL ANDALUSITE

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ABSTRACT

Samples of natural andalusite (Al_2SiO_5) crystal, have been investigated in terms of thermoluminescence (TL) and electron paramagnetic resonance (EPR) measurements. The TL glow curves of samples previously annealed at 600 °C for 30 minutes and subsequently gamma-irradiated, gave rise to four glow peaks at 150, 210, 280 and 350 °C. The EPR spectra of natural samples heat-treated at 600 °C for 30 minutes, show signals at $g=5.94$ and 2.014 that do not change after gamma irradiation and thermal treatments. However, it was observed the appearance of a paramagnetic center at $g=1.882$ for the samples annealed at 600 °C for 30 minutes followed gamma irradiation. This line was attributed to Ti^{3+} centers. The EPR signals observed at $g=5.94$ and 2.014 are due to Fe^{3+} . Correlations between EPR and TL results of these crystals show that the EPR line at $g=1.882$ and the TL peak at 280 °C can be attributed to the same defect center.

1. INTRODUCTION

Andalusite is an aluminium silicate mineral belonging to the class of ortho-silicates, characterized by the presence of individual tetrahedral SiO_4^{4-} groups. Its chemical formula is variously written as $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, Al_2SiO_5 , or $(\text{AlO})\text{AlSiO}_4$. It is one of the three polymorphs of this compound, the other two being the triclinic kyanite and the orthorhombic sillimanite. The unit cell of andalusite is orthorhombic and it crystallizes in the space group $Pnmm$. The structure possesses edge-sharing aluminium octahedra in chains that extend along the c -axis accounting for half of the aluminium atoms. The other half of the aluminium atoms are five-coordinated; they alternate with silicon tetrahedra in double chains that also run parallel with the c -axis [1]

These crystals present pleochroism [2] and commonly appear in metamorphic pelitic sediments. It is generally a crystal only available as a mineral although some very small specimens have been grown in the laboratory [3].

The objective of the present work is to study the nature of centers and its correlation with the luminescence, measuring the effects of gamma irradiation and thermal treatments through TL and EPR techniques in an attempt to understand the TL mechanism of a gamma-induced peak around 280 °C in andalusite.

2. EXPERIMENTAL PROCEDURE

A natural andalusite crystal from the State of Minas Gerais, Brazil, was investigated in this work.

For TL and EPR measurements, the andalusite samples were pulverized and sieved to retain grains with diameters between 0.080 and 0.180 mm. A ^{60}Co gamma source was used for the irradiation of the samples. TL measurements at 4 °C/s were carried out in a nitrogen atmosphere on a Daybreak 1100 series automated TL reader system, equipped with a bialkali photomultiplier (PMT) EMI 9235QA for light detection. A Bruker EMX EPR spectrometer operating at X-band frequency with 100 kHz of modulation frequency was utilized for the EPR experiments. Diphenyl Picryl Hydrazyl (DPPH) was used for calibrating the g-values of the defect centers.

3. RESULTS AND DISCUSSION

3.1. Thermoluminescence.

TL glow curves of andalusite samples heat treated at 600 °C for 30 minutes, and irradiated with γ -doses from 1 to 20 kGy show four glow peaks at 150, 210, 280 and 350 °C as can be seen in Fig. 1. The 350 °C glow peak always appears broad even for higher doses. In the inset of the Fig. 1 the TL growth with γ -dose is shown. Except for the 280 °C TL peak, all other TL peaks grow linearly up to about 5 to 10 kGy and then saturate. The peak around 280 °C grows sub-linearly with γ -dose.

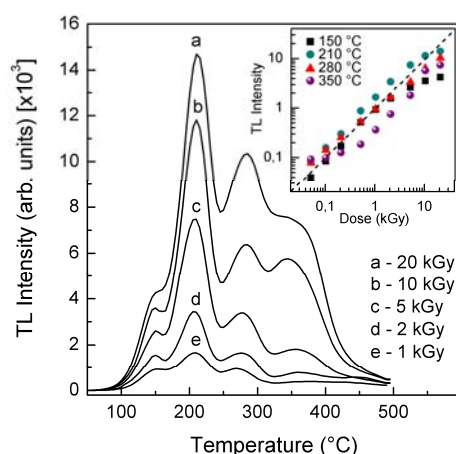


Figure 1. TL glow curves of 600 °C thermally treated natural samples for 30 min and irradiated at several γ doses. In the inset of the figure, the TL intensity versus doses of the TL peaks at 150, 210, 280 and 350 °C.

3.2. Electron Paramagnetic Resonance.

Fig. 2 shows the room temperature EPR spectrum of 50 kGy gamma irradiated andalusite previously annealed at 600 °C for 30 minutes. In the spectrum, three defect centers are identified and these centers are labeled as centers I, II and III, respectively, as is shown in Fig. 2. The center I that dominates the EPR spectra is due to Fe^{3+} .

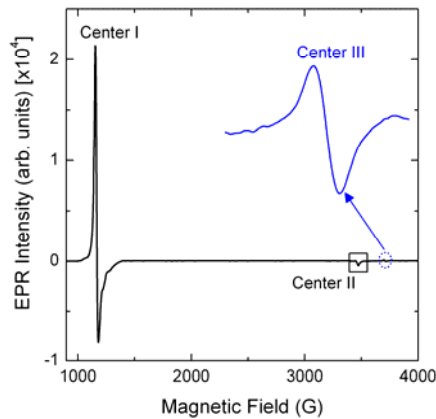


Figure 2. Room temperature EPR spectrum of the 50 kGy gamma-irradiated andalusite crystal.

In the present study, the EPR lines labeled as centers I and II, observed at $g=5.94$ and $g=2.014$ in Fig. 2, may be attributed to the Fe^{3+} ions substituting the Al^{3+} ions in the host matrix of andalusite crystals [4]. Center III does not exhibit any hyperfine structure and is characterized by a single broad EPR line with an isotropic g -value equal to 1.882. In general, not many defect centers are expected to be formed in a crystal system of silicates with this g -value, except for the Ti^{3+} center. Toyoda and Ikeya [5] found, in the irradiated quartz, a Ti^{3+} center and demonstrated that it begins to decay around 160 °C, vanishing at 260 °C. Experimentally, we found the similar behavior for center III at $g=1.882$. The same behavior of the two decays indicates a correlation between the 2 centers as can be observed in Fig. 3.

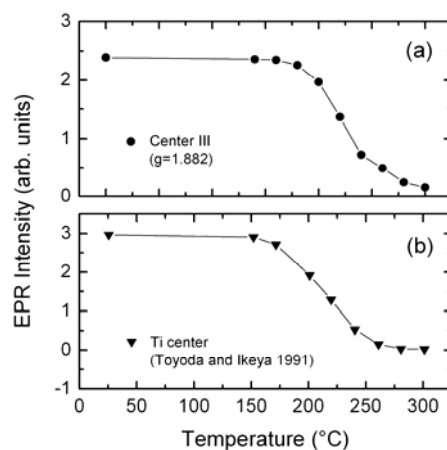


Figure 3. Decay of the 210 °C (■) and 280 °C (▲) TL peaks and the $g=1.882$ EPR signal (○) of the andalusite samples submitted to different thermal treatments.

It is interesting to observe in Fig. 4 that the microwave power dependence of the EPR signal intensity of center III in andalusite (a) and of the Ti^{3+} center (b) taken from the work of Ikeya [6], this result confirm the observed correlation above.

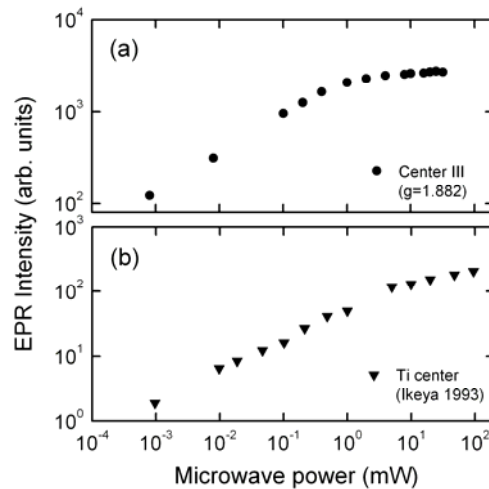


Figure 4. Microwave power dependence of the center III EPR signal intensity in andalusite (a) and of the Ti center (b) taken out from the work of Ikeya (1993).

3.3. Correlation between TL and EPR

The center III and TL peak stability was measured using the isochronal thermal method at various temperatures. In the method, the sample is heated up to a given temperature, maintained there for 15 minutes, and then rapidly cooled down to room temperature. The results of the thermal annealing behaviour of the TL peaks and of center III are presented in Fig. 5.

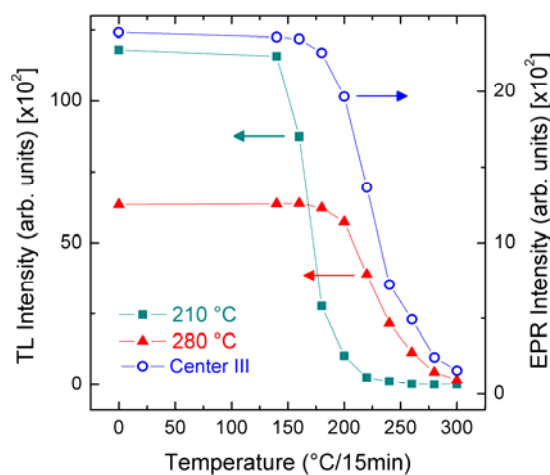


Figure 5. 210 °C (■) and 280 °C (▲) TL peaks and the $g=1.882$ EPR signal (○) of the andalusite samples submitted to different thermal treatments.

The correlation between the increase of the 280 °C TL peak with gamma dose and of the center III (at $g=1.882$) is observed in Fig. 6. The linear dependence between TL and EPR results indicates that the growth of both the 280 °C TL peak and center III with gamma-dose are similar, indicating that center III and the 280 °C TL peak are related to the same defect center. Furthermore, from the isochronal thermal studies of center III EPR signals and 280 and 210 °C TL peaks, presented in Fig. 5, it can be noticed that center III decreases in intensity with annealing temperature starting at 160 °C and the signal vanishes completely when the anneal temperature is increased beyond 220 °C. The similar decay behavior between EPR center III at $g=1.882$ and the 280 °C TL glow peak can therefore tentatively be assumed to be due to the same defect center. Since, according to Toyoda and Ikeya [5] Ti-center behaves in a very similar way of center III, it is reasonable to assume that this defect center is due to Ti^{3+} .

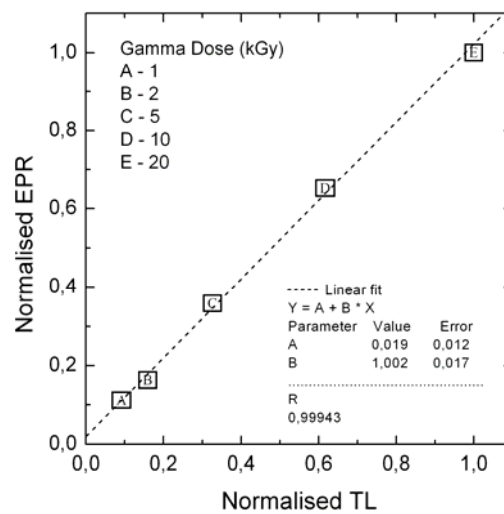
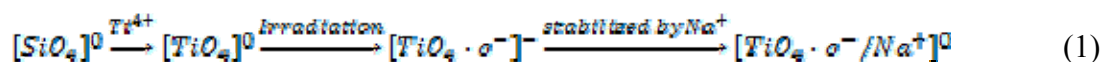


Figure 6. Correlation between the gamma-dose increase of the 280 °C TL peak and of the center III EPR signal.

Following the model proposed by Ikeya [6] for quartz and because alkali metal ions M^+ (mainly Na^+) are usually found in silicate minerals and play an important role as charge compensators, the process of center formation can be summarized as follows:



An isoelectronic Ti^{4+} substitutes for a Si^{4+} site in the andalusite lattice but its electron affinity (ionization potential) is considerably larger. This result in trapping of an electron created by ionizing irradiation to form a $[TiO_4 \cdot e^-]^-$ electron center in the andalusite lattice. The total charge of the center is -1 and thus Ti^{3+} at a Si^{4+} site in an andalusite structure has a negative effective charge, attracting an interstitial monovalent cation Na^+ to form a stable $[TiO_4/Na^+]^0$ center at room temperature.

It is well known that O^- hole centers are created in a great number of minerals [7,8]. Oxygen represents the normal components of a crystal (especially in silicates) and occurs in a normal structure position. According to Marfunin [7], when an impurity cation replaces the lattice

cation with a larger charge, the resulting deficit of the positive charge is compensated by a hole trapped at a bridging oxygen with concurrent formation of an O^- center. One well known example is the Si- O^- -Al center in quartz due to the substitution $Al^{3+} \rightarrow Si^{4+}$. Following Marfunin [7] we assume that the same process that occurs in quartz takes place in other silicate crystals.

Based on the above arguments and on the correlation analysis between TL and EPR results, an alternative interpretation of the 280 °C TL emission peak mechanism can be proposed as follows: During irradiation, the electron lost from one of the oxygen atoms captured by titanium ions ($Ti^{4+} + e^-$) leading to the formation of paramagnetic Ti^{3+} ions.

During TL read out, an electron liberated from a Ti center recombines with one hole in the O^- center giving rise to the TL peak at 280 °C. The TL mechanism concerning Ti^{3+} and O^- centers can be extended to silicate minerals including andalusite whose structure always contains the SiO_4 complex.

4. CONCLUSIONS

The TL and EPR spectra have been measured in natural andalusite crystals. Samples heat-treated at 600 °C for 30 minutes and irradiated with different gamma doses show strong peaks at 150, 210, 280 and 350 °C. The EPR spectra show lines at $g=5.94$ and $g=2.014$ that are due to Fe^{3+} ions and one signal at $g=1.882$ that was attributed to the $[TiO_4/Na^+]^0$ center. The correlation between the isochronal thermal decay of the 280 °C TL peak and the $g=1.882$ EPR signal and the correlation between the increase with gamma dose of 280 °C TL peak and the $g=1.882$ EPR signal show that the glow peak at 280 °C could be ascribed to Ti^{3+} ions acting as trap centers.

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