Brazilian Journal of Physics (2024) 54:188
https://doi.org/10.1007/s13538-024-01565-0

Assessment of the Thermoluminescent Properties of Epidote

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Received: 24 March 2024 / Accepted: 15 July 2024 / Published online: 1 August 2024

Abstract

In the literature, little information is found about the crystal structure of epidote; however, there is limited knowledge about the thermoluminescent properties of this mineral. The mineral epidote has the chemical formula $Ca_2Al_2Fe^{3+}[Si_2O_7][SiO_4]O(OH)$ and exhibits a dark green coloration. A sample of the mineral epidote, collected in Peru, was investigated. As these are naturally occurring samples, the crystallography of each mineral may vary due to damage caused by natural radiation and the climatic conditions of pressure and temperature to which this mineral has been exposed. Therefore, to determine if the thermoluminescent behavior of different epidote samples would be similar, a mineral collected in Brazil was investigated. The samples were pulverized, and grain sizes ranging from 80 to 180 μm in dimension were utilized. The experiments were conducted employing different thermal treatments and gamma radiation doses aiming identifying the best thermal treatment that allows the obtention of an intense and distinct TL signal. Preliminary TL results demonstrated a clear response of samples irradiated with high doses, exceeding 10 kGy, and thermally treated at 900 °C for 1 h, indicating its potential as a dosimeter for industrial applications. The results of the Thermoluminescence (TL) analysis conducted on the epidote sample from Brazil revealed similarities when compared to the TL analyses of the epidote sample from Peru.

Keywords Thermoluminescence · Epidote · Irradiation · Thermal treatment

1 Introduction

The fundamental process in any type of luminescence is the emission of electromagnetic radiation from a substance. Prefixes are used before the word luminescence to qualify the signal extraction mode; for example, thermoluminescence (TL) means that the original excitation is induced by radiation, and the signal is released through the action of heat [1].

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In 1663, Sir Robert Boyle observed the phenomenon of thermoluminescence. In 1895, Wiedeman and Schmidt introduced the term “thermoluminescence”, which was mentioned in Marie Curie’s doctoral thesis in 1904. However, only in 1945 was a theoretical explanation given using the electron trap model, by Randall and Wilkins [2, 3].

The thermoluminescence method has become one of the most widespread in the field of dose determination, for monitoring purposes, radiation protection, and archaeological dating of materials such as rocks, sediments, dunes, meteorites, ceramics, bricks, among others [4].

Considering the energy band diagram, the forbidden gap in an ideal crystal contains no energy levels, and all electronic transitions caused by radiation between the valence and conduction bands and vice versa are direct. Real crystals contain some network defects such as vacancies, dislocations, or impurities. These defects can lead to the appearance of various types of local energy levels in the forbidden gap. From the TL perspective, the types of levels play an important role: electron traps (T), hole traps (H), and luminescence or recombination centers (R). The basic principles of thermoluminescence (TL) are described in Fig. 1 in terms of the energy band model of hole and electron production after irradiation [4].

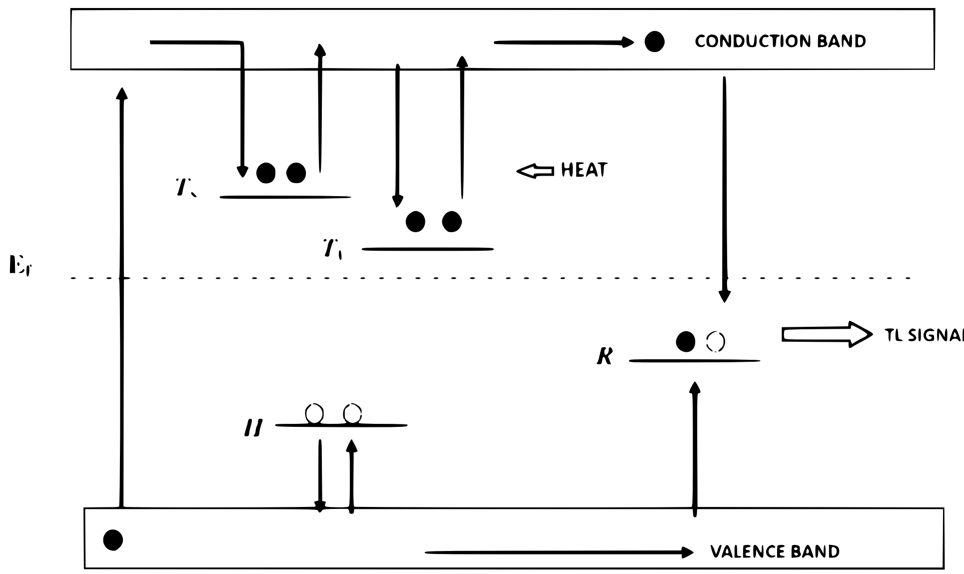

Fig. 1 Basic principles of the TL process

Ionizing radiation creates pairs of electron holes. These electrons and holes become trapped in T and H defects. The Ts trap represents an unstable trap, with a high probability of escape. It is a trap for electron storage, where the probability of escape (without external stimulus) is negligible. If the traps are energetically deep enough, the trapped electrons will remain there until they acquire sufficient energy to be released when the material is heated or irradiated with UV light, for example [5].

The released electrons move through the conduction band, and upon returning to the valence band, electrons can recombine with holes in luminescence centers. The induced electron trapping is proportional, over a wide range of doses, to the radiation dose. Therefore, the TL intensity is a function of the absorbed dose in a sample and can be used as the basis for radiation dosimetry methods [5].

There are trap depth levels in a material. As the temperature increases, electrons are gradually released from increasingly deeper traps, corresponding to the release of electrons from specific types of traps (TL peaks). This phenomenon can be observed in the emitted light vs. temperature curve (the "glow curve"). The shape of the glow curve thus reflects the number of network defects and impurity atoms of various types in the material network and their characteristics for a given material [4].

This work aims to evaluate the thermoluminescent (TL) properties of the mineral epidote.

2 Methods

Thermoluminescence readings were conducted using the Harshaw model 4500 TLD reader at the LACIFID laboratory. In all analyses, the fine-grain technique developed by Zimmerman [6] was employed. This technique serves as one option to mitigate inhomogeneities caused by non-uniform radiation fields within grains of large diameter. Only grains small enough are utilized, typically on the order of micrometers. Thus, it is possible to assume that the absorbed dose is uniform.

Preliminary TL analyses of the natural sample of epidote, thermally treated at 500 °C for 30 min to deplete traps and eliminate previous effects caused by natural irradiation, were conducted. Additionally, the sample was irradiated with gamma radiation at doses ranging from 1 Gy to 10 kGy. The obtained results revealed that the epidote sample irradiated with doses from 1 Gy to 200 Gy did not exhibit sufficient intensity to identify characteristic peaks. However, in samples irradiated with doses ranging from 200 Gy to 2 kGy, TL peaks were observed at approximately 180 °C, 270 °C, and 350 °C. These peaks exhibited an increase with the dose, although the intensity remained relatively low, resulting in a significant amount of equipment noise in the signal. Despite the persistent noise, well-defined peaks could be identified in samples irradiated with 5 kGy and 10 kGy, appearing around 180 °C and 325 °C, respectively.

The study was conducted using a natural epidote sample collected in Peru. For comparison purposes, a natural epidote sample collected in Brazil was also used. The methodology employed and the results are presented in Analysis 6.

Therefore, to examine the TL behavior of natural epidote, a study of varying thermal treatments and gamma radiation doses was conducted.

The respective methodologies are presented below:

Analysis 1 The samples were irradiated at the Center for Radiation Technology (CTR-IPEN) with gamma radiation from a ^{60}CO source under conditions of electronic equilibrium at room temperature. The TL readings were always performed a few hours after irradiation.

TL analysis was conducted on natural epidote (PE) irradiated with higher doses, aiming to verify if higher doses would yield a prominent TL signal. The doses used were 20, 40, and 60 kGy. The samples were irradiated at the Center for Radiation Technology (CTR-IPEN) with gamma radiation from a ^{60}CO source under conditions of electronic equilibrium at room temperature. The TL readings were always performed a few hours after irradiation.

Analysis 2 To analyze the TL curve of samples subjected to different thermal treatments, the following procedure was executed:

1. Samples of powdered epidote with grain size between 0 and 180 μm separated.
2. Approximately 100 mg aliquots of the sample were subjected to thermal treatment for 1 h at temperatures of 500, 600, 800, 900, and 1000 °C.
3. After cooling, each aliquot was divided into 3 parts for gamma-ray irradiation with doses of 100 Gy, 1 kGy, and 10 kGy.
4. The TL readings were performed a few hours after irradiation.

Analysis 3 This analysis was conducted to observe the TL sensitivity behavior of samples treated at 900 °C/ 1 h. Powdered epidote aliquots, after thermal treatment, were irradiated with doses of 5, 10, 20, 50, 80, 100, 200, 400, 600, 800, and 1000 Gy. The TL readings were performed a few hours after irradiation

Analysis 4 Aiming the enhancing TL signal intensity based on the article by Almogait et al. (2022), a sensitization study of epidote samples with thermal treatment and a pre-dose of high dose was conducted:

1. A portion of powdered epidote sample with grains size between 80 and 180 μm was divided into 4 parts, each one with approximately 100 mg.
2. Each sample portion was submitted to a thermal treatment for 1 h at the following temperatures: 600 °C, 800 °C, 900 °C, and 1000 °C.
3. After cooling, all samples were irradiated with a pre-dose of 10 kGy.
4. A new thermal treatment of 500 °C was performed to eliminate shallow traps.
5. The samples were irradiated again with a gamma dose of 100 Gy.

Analysis 5 To expand this study using a fixed prior thermal treatment of 900 °C, as, until then, all results obtained indicated more intense and distinct TL analyses in samples treated at 900 °C. However, pre-doses were varied, as explained in the following procedure:

1. Thermal treatment at 900 °C for 1 h of a portion of powdered epidote sample with grains size between 80 and 180 μm.
2. The sample was divided into 8 aliquots, each one irradiated with the following pre-doses: 50 Gy, 100 Gy, 200 Gy, 400 Gy, 600 Gy, 800 Gy, 1 kGy, and 5 kGy.
3. A new thermal treatment at 500 °C was performed to eliminate shallow traps.
4. The samples were irradiated again with a gamma dose of 100 Gy.

Analysis 6 Thermoluminescence analysis was conducted on the epidote sample from Brazil. The mineral was pulverized and sieved, using grains between 0 and 180 μm. Thermal treatment at 500 °C for 1 h was applied. After cooling, the sample was divided into aliquots of approximately 50 mg each one and irradiated with gamma radiation with doses of 100 Gy, 1 kGy, and 10 kGy, to observe the sample's behavior under low and high doses. To compare the results, the same sample preparation and thermal treatment procedures were applied to the epidote sample collected in Peru.

3 Results

Analysis 1 This TL analysis was conducted using natural epidote irradiated with even higher doses, aiming to investigate whether at doses greater than those previously studied, a more prominent manifestation of the TL signal would occur. The applied doses were 20, 40, and 60 kGy. The obtained result is presented in Fig. 2.

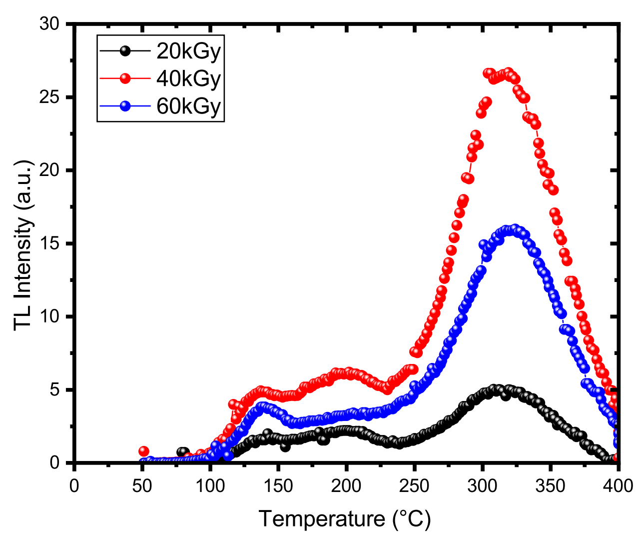

Fig. 2 Epidoto TL emission curve of samples irradiated with high gamma doses of 20, 40, and 60 kGy

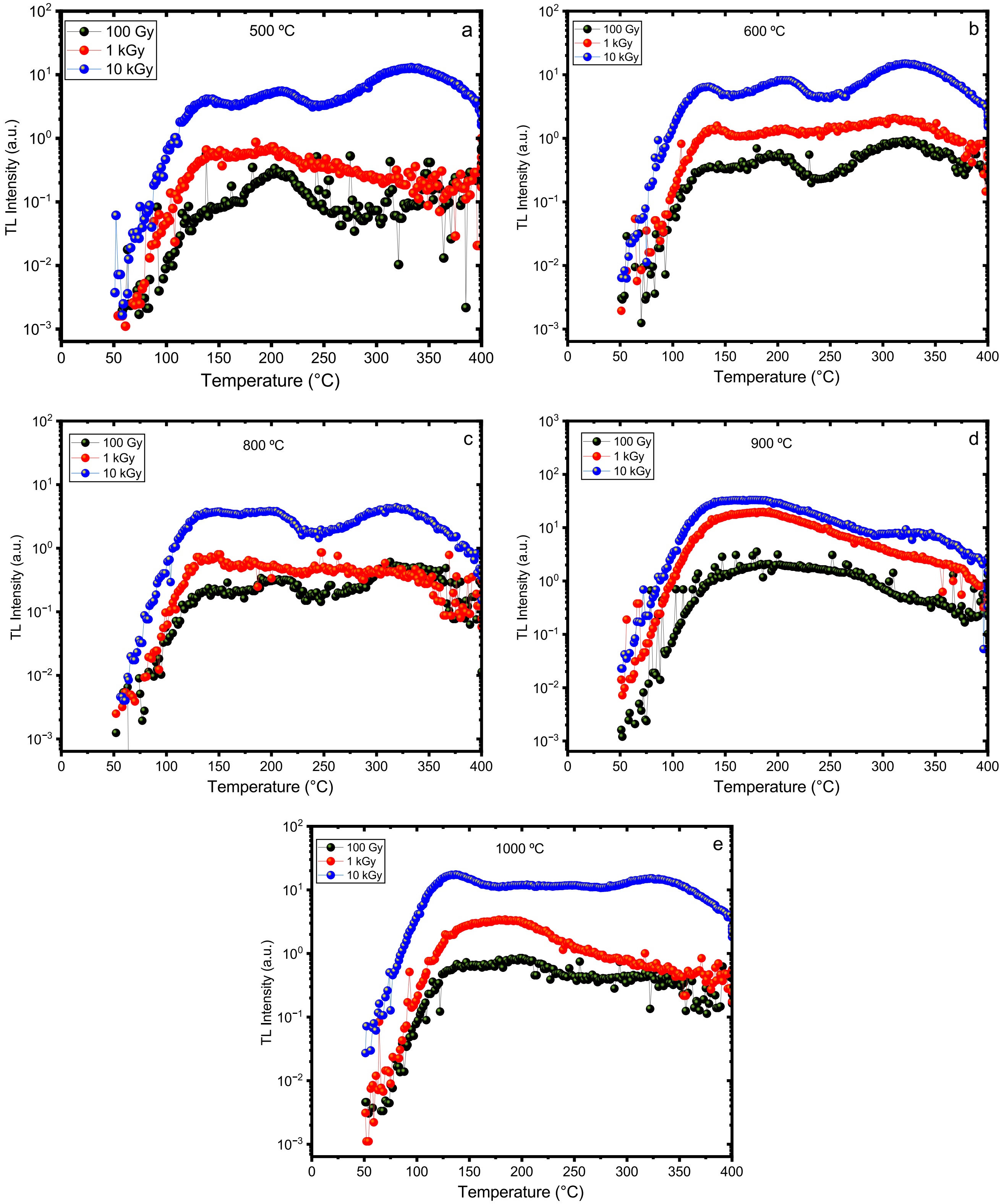

Fig. 3 TL emission curves of samples thermally treated at 500 °C (**a**), 600 °C (**b**), 800 °C (**c**), 900 °C (**d**), 1000 °C (**e**), and irradiated with gamma doses of 100 Gy, 1 kGy, and 10 kGy

Analysis 2 Qualitatively analyzing all the results presented in Fig. 3, it can be observed that in all cases, the intensity of the TL signals increased with the dose, showing at least 3 TL peaks.

With the results obtained from the samples treated at 500 °C, it was observed that samples irradiated with 100 Gy and 1 kGy exhibited a low TL signal with significant noise. However, the sample irradiated with high doses (10 kGy) presented 3 signals at 143 °C, 210 °C, and 330 °C.

The same behavior was observed for samples treated at 600 °C; however, in these conditions, the intensity of the TL signal was higher.

Samples treated at 800 °C and irradiated with 100 Gy and 1 kGy also did not show TL signals, while samples irradiated with 10 kGy presented the same signals as in the previous analyses but with a lower TL signal intensity.

In samples treated at 900 °C, a different behavior was observed. A clear and well-defined thermoluminescent signal was identified at approximately 175 °C, probably a combination of the signals observed at 143 °C and 210 °C in the other samples. For samples irradiated with low doses, 100 Gy, the signal is still not well-defined; however, the peak at 175 °C is observed in samples irradiated with 1 kGy, and the second peak does not appear. In samples irradiated with 10 kGy, the thermoluminescent signal at 175 °C is observed, and a smaller signal at 330 °C.

To allow for the visualization of curves with lower intensity, the graphs were plotted on a logarithmic scale. The obtained result is presented in Fig. 3.

Figure 4 shows the comparison between the behavior of the epidote sample subjected to different heat treatments and irradiated with 100 Gy, 1 kGy, and 10 kGy.

In Fig. 4, the influence of heat treatment on the TL analyses of epidote samples irradiated with low, medium, and high doses (100 Gy, 1 kGy, and 10 kGy) can be more clearly observed. The main graph shows the shape of the TL curve plotted on a linear scale. An inset with the graph in logarithmic scale was included in the figure to better visualize the curves with lower intensity.

Samples irradiated with 100 Gy showed thermoluminescent signals with a lot of noise and low intensity. However, it can be observed that in samples treated at 900 °C, a single TL signal is more intense than the others, at approximately 190 °C.

Samples irradiated with 1 kGy showed clearer thermoluminescent signals than in the previous result. However, in samples treated at 900 °C, the signal at 175 °C is much clearer and more intense than at other temperatures.

The behavior of samples irradiated with 10 kGy is different from previous results. In all temperatures, it is possible to observe the same thermoluminescent signals, but with distinct intensities. In this case, it is also possible to observe a more intense and well-defined signal in samples treated at 900 °C.

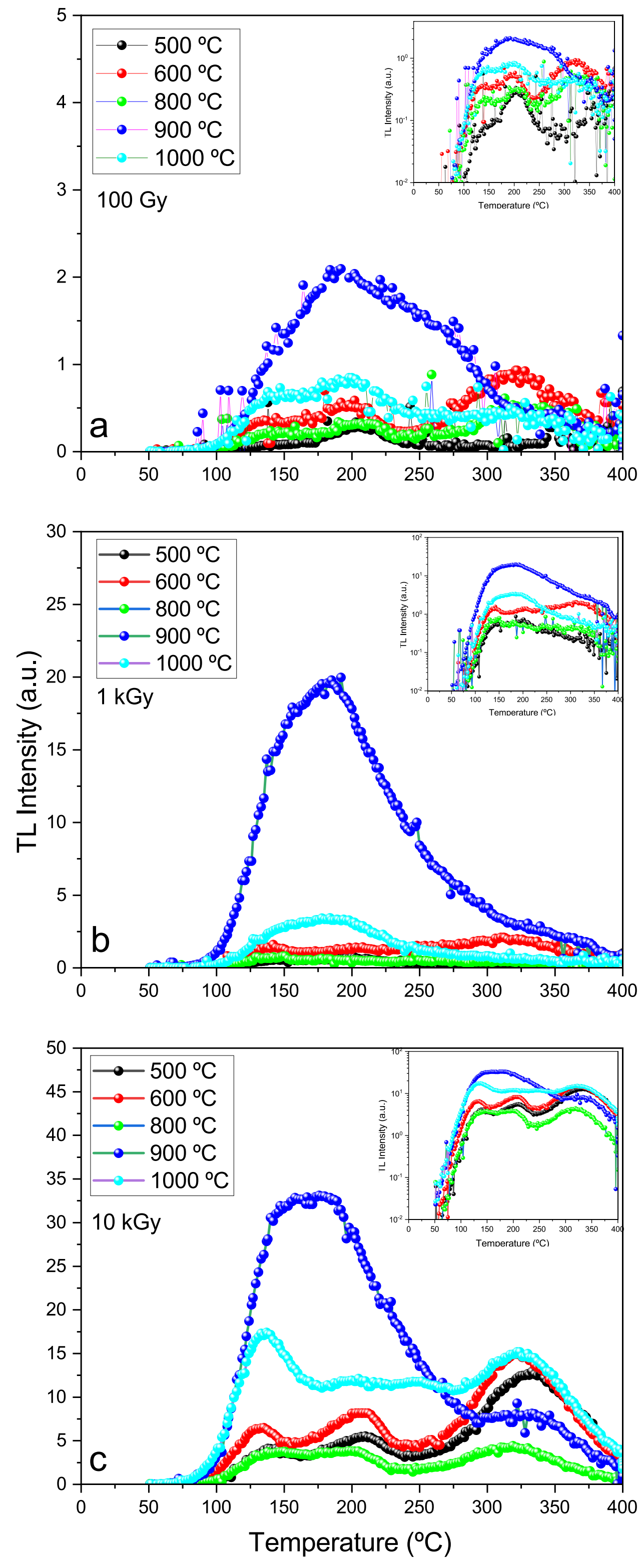

Fig. 4 Comparison between Epidoto TL emission curves of samples treated at 500, 600, 800, 900, and 1000 °C and irradiated with gamma doses of 100 Gy (**a**), 1 kGy (**b**), and 10 kGy (**c**). In the insets, the graphs were plotted on a logarithmic scale

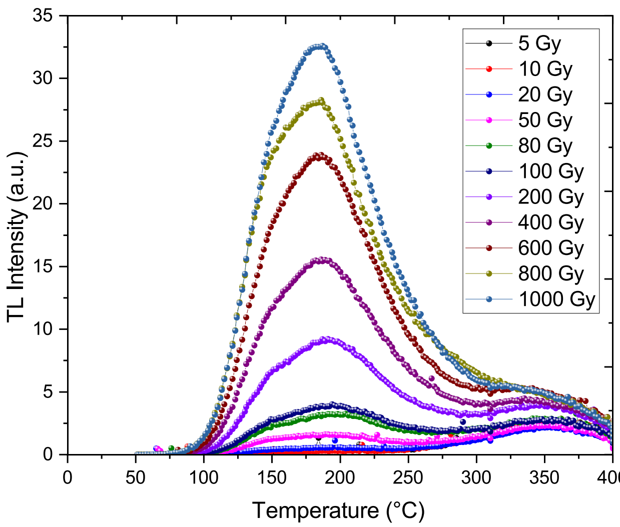

Fig. 5 Epidoto TL intensity curve of samples thermally treated at 900 °C and irradiated with gamma doses from 5 Gy to 1000 Gy

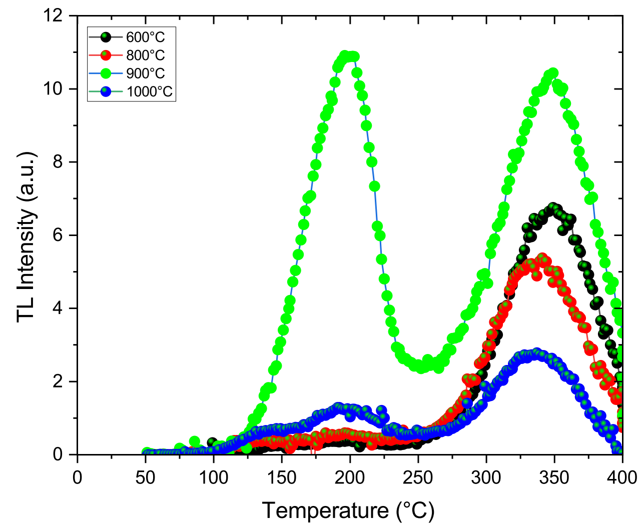

Fig. 7 TL curve of sensitized epidote sample, varying heat treatments: 600 °C, 800 °C, 900 °C, and 1000 °C

Samples treated at 900 °C show two signals, one intense and well-defined at 175 °C and another less intense at 330 °C when irradiated with 10 kGy. Compared with the other results, it can be concluded that with the heat treatment at 900 °C, the thermoluminescent signal becomes clearer, more intense, and better defined than at other temperatures studied.

Analysis 3 The obtained results are presented in Figs. 5 and 6.

So far, this result has been the most satisfactory, allowing the identification of clear, noise-free, and more intense signals compared to the analyses conducted up to this point. Two TL signals were identified one at approximately 187 °C and another at 355 °C. Both signals increase with the dose, and the behavior of this growth is observed in Fig. 6. At the 187 °C peak, the curve starts to saturate in samples irradiated with a dose of 1000 Gy, while at the 355 °C peak, saturation already occurs in samples irradiated with a dose of 200 Gy.

Analysis 4 In Fig. 7, it is possible to observe two TL signals, the first around 200 °C, visible, intense, and well-defined only in the sample treated at 900 °C, and a stable and well-defined second peak at approximately 330 °C.

The intensity of the signals exhibited an anomalous behavior; it can be noted that the TL intensity does not increase with the increase in the temperature of the heat treatment, as shown in Fig. 8.

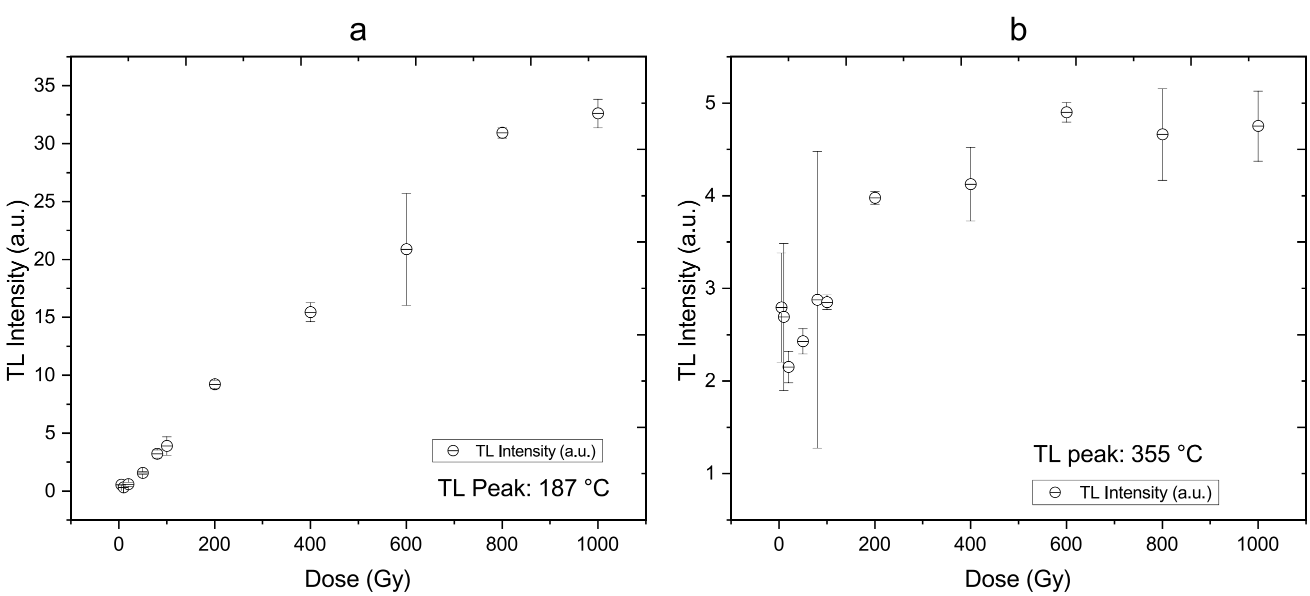

Fig. 6 Epidoto TL dose-response curve as a function of the gamma dose of the TL peaks at 187 °C (**a**) and 355 °C (**b**)

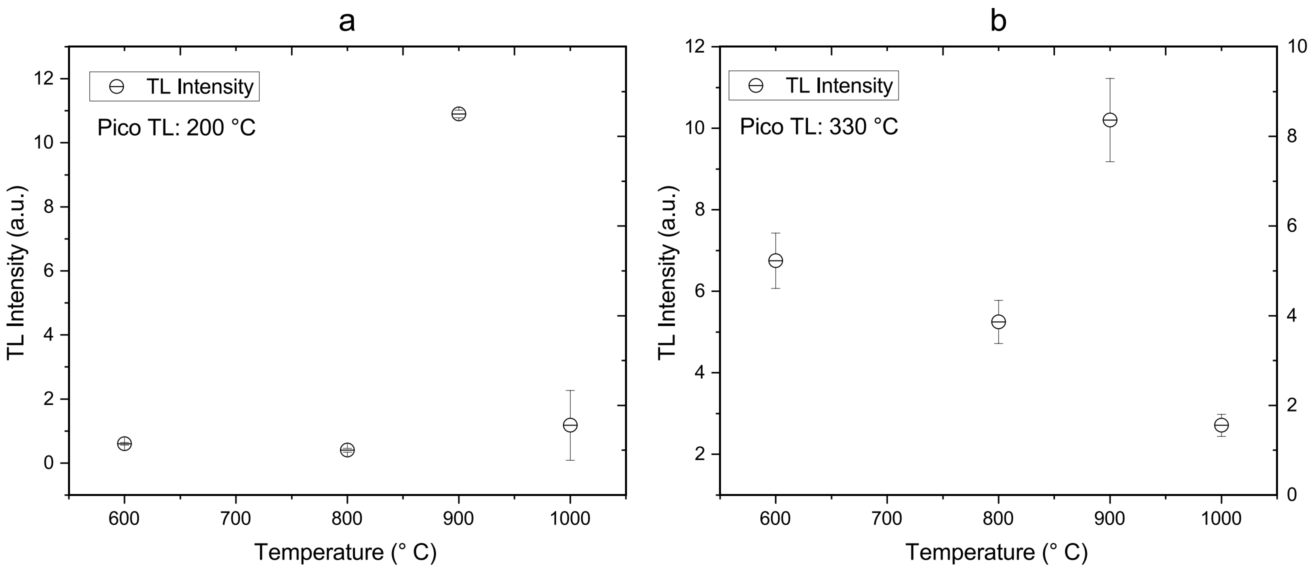

Fig. 8 Epidoto TL intensity of the 200 °C (**a**) and 330 °C (**b**) TL peaks concerning the activation temperature

Analysis 5 In this analysis, the position of the first TL signal varies from approximately 185 to 205 °C, and the second TL signal varies from 350 to 355 °C. With the pre-dose values used, no improvement in the TL signals was observed; there are still many noises and signals of low intensity. Compared with the results of samples irradiated with a pre-dose of 10 kGy, the intensity of the current result is lower.

The result is presented in Fig. 9.

Analysis 6 In Fig. 10, similarities between the Peruvian and Brazilian epidote samples can be identified. The graphs

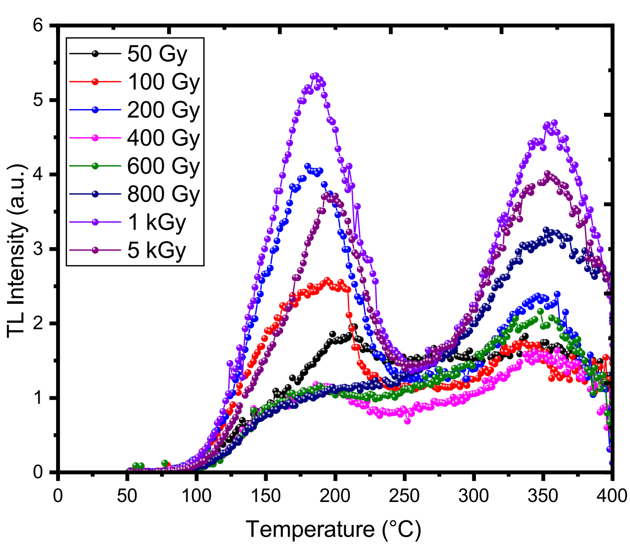

Fig. 9 TL curve of sensitized epidote sample with different pre-doses: 50Gy, 100 Gy, 200 Gy, 400 Gy, 600 Gy, 800 Gy, 1 kGy, and 5kGy

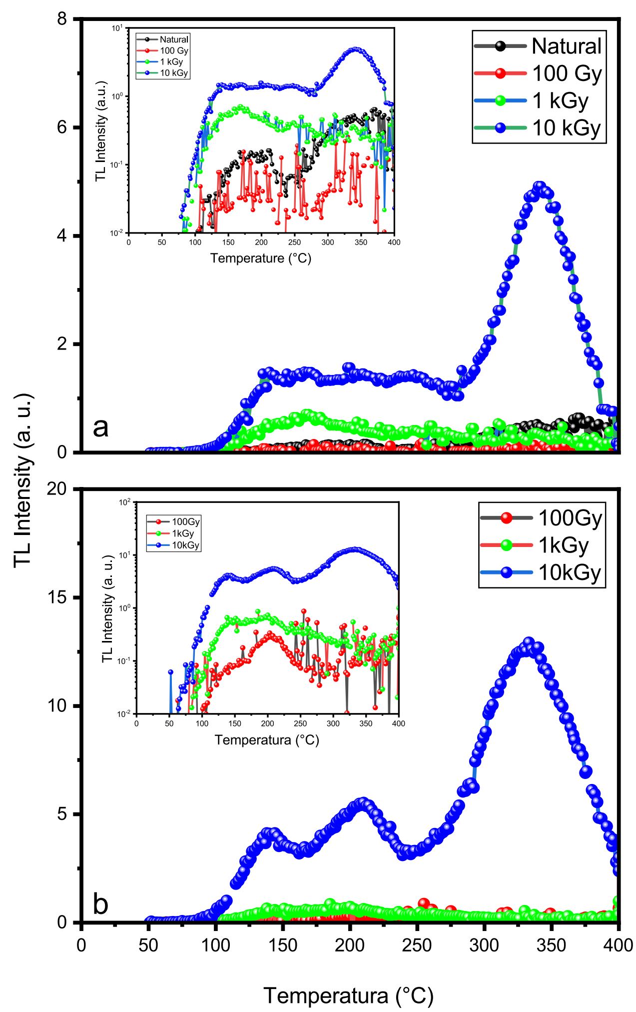

Fig. 10 TL glow curves of the epidote samples collected in Brazil (**a**) and Peru (**b**), irradiated with gamma doses of 100 Gy, 1 kGy, and 10 kGy. In the insets, the graphs were plotted on a logarithmic scale

included in the main figures were plotted on a logarithmic scale to better visualize the curves with lower intensity.

The samples irradiated with 100 Gy and 1000 Gy show low intensity and high noise. However, in the samples irradiated with 10 kGy, the TL peaks at 140 °C and 205 °C are more clearly identifiable in the Peruvian sample.

The final peak appears at approximately 330 °C in both samples, but the intensity is higher in the Peruvian sample.

4 Conclusion

With TL analyses, it was possible to observe that the natural crystal irradiated with gamma rays at low doses (1 Gy to 1 kGy) exhibits low signal intensity. From 2 kGy onwards, the thermoluminescent signal becomes more noticeable, although there are still noise issues in the signal.

Temperature tests led to the conclusion that the most effective thermal treatment was at 900 °C for 1 h, where the signals show clear growth with dose, demonstrating sharpness and intensity. Subsequently, the stability of these signals and the occurrence of TL peak overlaps will be evaluated through TmTstop analysis.

In sensitivity tests of the TL signal with pre-dose and thermal treatment, a more favorable behavior was observed in samples treated thermally at 900 °C and irradiated with a pre-dose of 10 kGy.

The results of the TL analysis performed on the epidote sample from Brazil showed similar outcomes compared to the analyses of the epidote sample from Peru. Therefore, further studies with the Brazilian sample will not be pursued.

The results of Thermoluminescence (TL) demonstrated a positive response in samples irradiated with high doses (greater than 10 kGy), indicating its potential as a dosimeter for industrial applications.

Acknowledgements To Professor Dr. Shigueo Watanabe, my research supervisor during my undergraduate, master's, and doctoral studies. Your teachings will always be remembered by me. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 88887.506305/2020-00.

Author Contributions LMF wrote the main manuscript text and prepared figures. All authors reviewed the manuscript.

Funding This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 88887.506305/2020-00.

Data Availibility No datasets were generated or analyzed during the current study.

Declarations

Ethics Approval Compliance with ethical standards is not required as this study involved no human or animal subjects.

Ethical Conduct The authors affirm that the research presented in this manuscript was conducted with the highest standards of ethical conduct. The authors declare no Conflict of interest and Affirm that the results reported in this article are a true and accurate representation of the conducted research.

Competing Interests The authors declare no competing interests.

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