Radiation Measurements 174 (2024) 107138

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

A first look at phototransferred thermoluminescence of rose quartz

I.A. Ferreira [a,b], M.C.S. Nunes [c], E.M. Yoshimura [a], N.M. Trindade [a,*], M.L. Chithambo [d]

[a] Instituto de Física, Universidade de São Paulo, São Paulo, SP, Brazil
[b] Departmento de Física, Instituto Federal de São Paulo, São Paulo, SP, Brazil
[c] Programa de Pós-Graduação em Ciência e Tecnologia dos Materiais, Universidade Estadual Paulista, Sorocaba, SP, Brazil
[d] Department of Physics and Electronics, Rhodes University, Grahamstown, South Africa

ARTICLE INFO

Keywords:
Phototransferred thermoluminescence
Rose quartz
Dosimetry

ABSTRACT

We report a preliminary study of phototransferred thermoluminescence (PTTL) induced by 470 nm light source in rose quartz. The glow curve corresponding to 1 Gy consists of five peaks at 76, 115, 180, 290 and 423 °C labelled I through V in that order. In the PTTL experiments employing blue light. PTTL was regenerated at peak I following preheating to remove peak I only and at peaks I and II otherwise. The dependence of the PTTL intensity on duration of illumination is analyzed in terms of a system of one acceptor and two donors in both cases. The mechanisms for the PTTL phenomena in the rose quartz are comprehensively discussed in this paper.

1. Introduction

Quartz (SiO_2) is an abundant mineral in the Earth's crust and is commonly found in rocks and soils near the Earth's surface (Götze et al., 2021). Studies have shown that the natural growth of quartz involves a combination of chemical and physical processes that lead to the development of a variety of physical properties (McKeever, 1985; Topaksu et al., 2012). This diversity in properties makes quartz valuable for numerous applications including serving as a source of silicon for the technology industry as well as a substrate for material engineering and the fabrication of biological and chemical devices (Nur et al., 2015). Moreover, luminescence properties inherent to quartz enable its use in geological and archeological dating techniques, as well as in nuclear accident dosimetry (Preusser et al., 2009).

Quartz occurs in different types including as smoky, rose, citrine, green, amethyst, and blue quartz (Henn and Schultz-Güttler, 2012). The rose color of quartz has been variously attributed to Mn^{3+} cations the quartz, charge transfer processes of the form $Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}$, the presence of trace elements such as P and Al or even the inclusion of dumortierite within its matrix (Götze et al., 2004; Hosaka et al., 1986; Kibar et al., 2007).

The thermoluminescence (TL) of quartz has been widely studied (Folley and Chithambo, 2021; Hunter et al., 2018; Martins et al., 2023; Preusser et al., 2009). TL is emitted during controlled heating of an irradiated material (McKeever, 1985). The TL characteristics of quartz such as its glow curves vary widely due to differences in type and origin (Kalita and Wary, 2016). For instance, Martins et al. (2023) investigated the TL of beta irradiated rose quartz from Brazil that showed three glow peaks at 80 °C, 110 °C and 145 °C for measurements made at 1 °C/s (Martins et al., 2023). In another study also on rose quartz, Farias and Watanabe (2012) also found three glow peaks between 110 °C, 220 °C and 375 °C using gamma radiation and measurement at 4 °C/s. Interestingly a recent study by Márquez-Mata et al. (Márquez-Mata et al., 2023) on seven types of quartz excited by gamma irradiation showed their rose quartz to have two peaks near 200 °C and 300 °C using a 10 °C/s temperature gradient. This selection of examples emphasizes the point that variabilities in the glow curve of rose quartz are considerable.

Our report is concerned with the phototransferred thermoluminescence (PTTL) of rose quartz. PTTL is a thermoluminescence phenomenon whereby exposure of an irradiated and preheated sample to light of a specific wavelength reproduces some glow peaks removed by the preheating (Folley and Chithambo, 2021). The electrons involved are phototransferred from deeper filled electron traps (donors) to shallower depleted ones (acceptors). The PTTL of quartz has been studied a number of times (Chithambo et al., 2019; Chithambo and Dawam, 2020; Folley and Chithambo, 2021). For example, Folley and Chithambo (2021) studied material quartz with six peaks and observed PTTL at the first three peaks. It was observed that whichever one of the three was regenerated by phototransfer depended on the preheating temperature. Their findings were described with reference to a model proposed by Chithambo (Chithambo et al., 2017) which analyses the PTTL as a system of acceptors and donors where the number of the latter is dependent

* Corresponding author.
E-mail address: neilotrindade@usp.br (N.M. Trindade).

https://doi.org/10.1016/j.radmeas.2024.107138
Received 28 December 2023; Received in revised form 17 March 2024; Accepted 23 April 2024
Available online 26 April 2024

on the preheating temperature. Additionally, Chithambo and Dawan (Chithambo and Dawan, 2020) investigated PTTL in synthetic quartz annealed at 900 °C for different times and found that duration of annealing affects its PTTL.

This report presents a preliminary study of the phototransferred thermoluminescence of rose quartz. As is known, TL properties of quartz vary widely dependent on various factors including thermal provenance and type (Preusser et al., 2009). A number of studies on natural and synthetic quartz (Chithambo et al., 2018, 2019; Chithambo and Dawam, 2020; Folley and Chithambo, 2021), also show interesting differences in their PTTL. The motivation for this work is therefore to study the PTTL of rose quartz, a unique quartz whose PTTL has never been studied previously in order to start to offer some understanding of the process in this material. We consider the qualitative link between PTTL peaks and source electrons traps and analyze the influence of duration of illumination on the PTTL intensity in terms of a phenomenological model.

2. Experimental methods

Measurements were conducted on granular rose quartz from Minas Gerais, Brazil. Prior to use, the sample was heated at 500 °C for 1 h to remove any residual signal. PTTL measurements were carried out at Rhodes University on a RISØ Luminescence Reader model DA-20. The sample was irradiated at room temperature using a built-in $^{90}Sr/^{90}Y$ beta source at a dose rate of 0.10 Gy/s. Luminescence was detected by an EMI 9235QB photomultiplier tube through a 7.5 nm thick Hoya U-340 filter providing an effective transmission band of 250–390 nm. Unless otherwise stated, the sample was heated at 1 °C/s.

To measure PTTL, the sample was first irradiated then preheated to a given temperature to remove glow peaks below that temperature. To effect phototransfer, the sample was thereafter illuminated at room temperature by 470 nm blue LEDs set to provide an optical power density of 90 mW/cm^2 at sample position. The sample was heated again to measure the glow curve as a means to monitor any PTTL induced at the removed glow peaks.

For pulse annealing, the sample was irradiated with 1 Gy and it was preheated to a specific temperature to gradually remove electrons from different electron traps. Subsequent illumination with 470 nm light for 50 s aimed to transfer electrons from the deep traps to the shallow traps. After that, the sample was readout to 500 °C to observe any potential PPTL signal. This process was repeated multiple times, varying the preheating temperature from 50 to 500 °C in 10 °C increments.

2.1. *Mathematical analysis of the dependence of PTTL intensity on duration of illumination*

The dependence PTTL intensity on illumination was analyzed on the basis of the method developed by Chithambo et al. (2017). In this approach, the PTTL is analyzed as a system of acceptors and donors with the number of donors dependent on the preheating temperature.

A general system comprising an acceptor and donors, each with electron concentration N_j with $j = k;1 \ldots n$, is expressed in the matrix form as:

$$N' = \begin{pmatrix} N_n' \\ N_{n-1}' \\ \cdot \\ \cdot \\ \cdot \\ N_k' \end{pmatrix} = \begin{pmatrix} -f_n & 0 & 0 & \ldots & \cdot \\ 0 & -f_{n-1} & 0 & \ldots & \cdot \\ 0 & 0 & \cdot & \ldots & \cdot \\ \cdot & \cdot & \cdot & \ldots & \cdot \\ \cdot & \cdot & \cdot & \ldots & \cdot \\ \cdot & \cdot & \cdot & \ldots & \cdot \\ \delta_n f_n & \delta_{n-1} f_{n-1} & \cdot & \ldots & -f_k \end{pmatrix} \begin{pmatrix} N_n \\ N_{n-1} \\ \cdot \\ \cdot \\ N_k \end{pmatrix} = AN \quad (1)$$

The optical stimulation rates can be found by setting the determinant of coefficients to zero namely:

$$|A - mI| = 0 \quad (3)$$

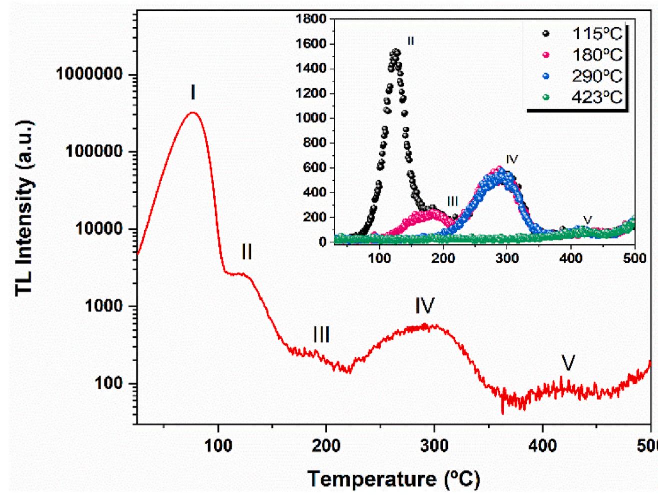

Fig. 1. A TL glow curve of rose quartz measured at 1 °C/s after irradiation to 1 Gy. The inset shows some individual peaks that come up clearer due to thermal cleaning.

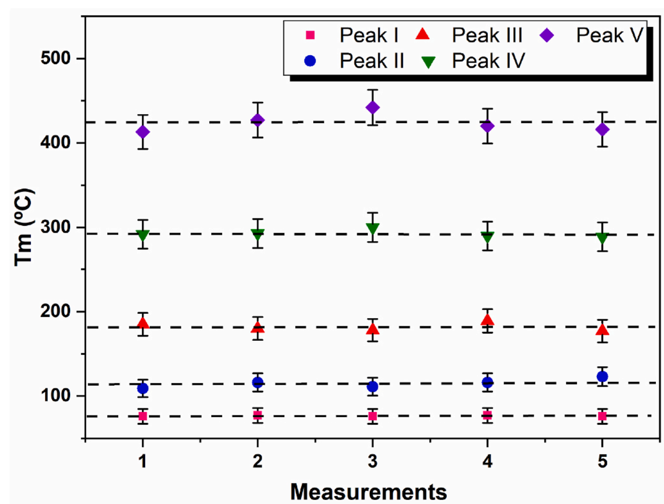

Fig. 2. Positions of glow peaks as determined in five consecutive measurements. As evident the positions are independent of sample re-use.

where I is a unit matrix and m represent the eigenvalues (Chithambo et al., 2019). The eigenvalues only exist when the determinant of the coefficients is equal to zero. As an example, using this procedure, the change of electron concentration N_k at the acceptor during illumination can be expressed as (Chithambo et al., 2019).

$$N_k = B_1\left(e^{-f_k t} - e^{-f_a t}\right) + B_2\left(e^{-f_k t} - e^{-f_b t}\right) \quad (6)$$

where $B_1 = (\alpha_a f_a N_{ai})/(f_a - f_k)$, $B_2 = (\alpha_b f_b N_{bi})/(f_b - f_k)$, where N_{ai} and N_{bi} are the initial concentration of electrons at the donor electron traps. A more expansive discussion of matrix manipulation in linear algebra and its application to PTTL was discussed by Chithambo (Chithambo et al., 2019).

3. Results and discussion

3.1. *Glow curve structure*

Fig. 1 shows a glow curve measured up 500 °C after irradiation to 1 Gy. There are five glow peaks consisting of the main peak at 76 °C and additional ones at 115, 180, 290 and 423 °C. To better show the glow

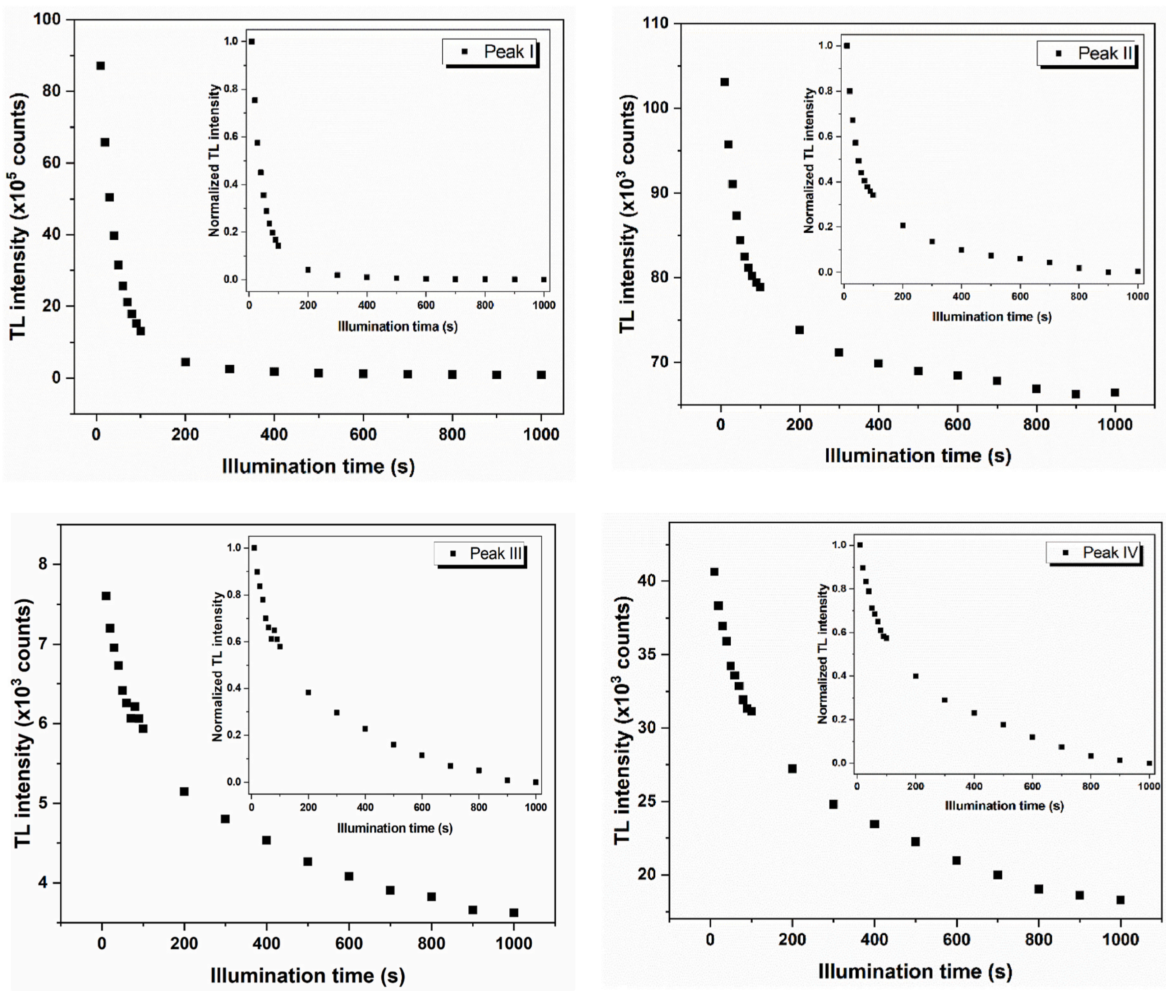

Fig. 3. Light induced fading of peaks I-IV of rose quartz. TL intensities refer to residual TL obtained following illumination of the irradiated sample each time. The insets show the normalized TL intensity.

peaks, the data is plotted in a semilogarithmic scale. The position and number of the glow peaks was confirmed using 'thermal cleaning', a technique that involves partially heating the sample to a temperature just beyond a specified peak to reveal any subsequent peak. The results of thermal cleaning are presented in the inset to Fig. 1 where four of the peaks identified earlier (II, III, IV and V) are apparent.

3.2. *Repeatability of TL glow peaks temperatures*

In PTTL measurements the same sample is used multiple times in the expectation that its glow peak positions remain stable with re-use. We experimentally checked this by running five consecutive measurements on the same sample following irradiation to 1 Gy each time. The results are displayed in Fig. 2 and show that, allowing for statistical scatter, the positions of the glow peaks are stable. The positions of the peaks are 76.4 ± 0.5, 115.0 ± 5.4, 181.0 ± 5.4, 292.8 ± 4.3 and 423 ± 11 °C.

3.3. *Light induced fading*

When an irradiated material is exposed to light between irradiation and measurement, its TL sometimes fades. The fading serves as qualitative evidence that the electron traps related to the "faded" peak may function as donor or source traps under PTTL (Chithambo et al., 2022; Emfietzoglou and Moscovitch, 1996). In this investigation, the sample irradiated to 1 Gy was illuminated by 470 nm light for durations ranging from 10 to 1000 s before measuring the residual TL signal each time. Selected results are presented in Fig. 3. All peaks, except V which was too faint to monitor, fade with illumination. This suggests that the peaks may all be involved in the PTTL as acceptors or donors.

3.4. *Preparatory check for PTTL*

With the supposition above that the peaks may be involved in TL, it was, prior to substantive measurements, necessary to determine which ones would be reproduced under phototransfer. The preparatory measurements were made following the protocol described earlier. The sample, irradiated to 1 Gy, was preheated, and subsequently illuminated for 5 s using blue light. The results are shown in Fig. 4. When the sample was illuminated after preheating to 115 °C to remove peak I only, it was reproduced under phototransfer (Fig. 4(a)). Further, when the sample was preheated to 150 °C to remove peaks I-II and illuminated, both peaks were regenerated by phototransfer (Fig. 4(b)). However, when the sample was preheated to 210 °C to remove peaks I, II and III, and then illuminated, only peak I re-appeared because of phototransfer (Fig. 4(c)). Peaks III, IV and V were not reproduced under phototransfer.

3.5. *Pulse annealing*

A useful means to determine whether an electron trap functions as an acceptor or donor is through the use of the so-called pulse annealing technique e.g. (Chithambo and Dawam, 2020; Emfietzoglou and Moscovitch, 1996). In this method, the preheating temperature that

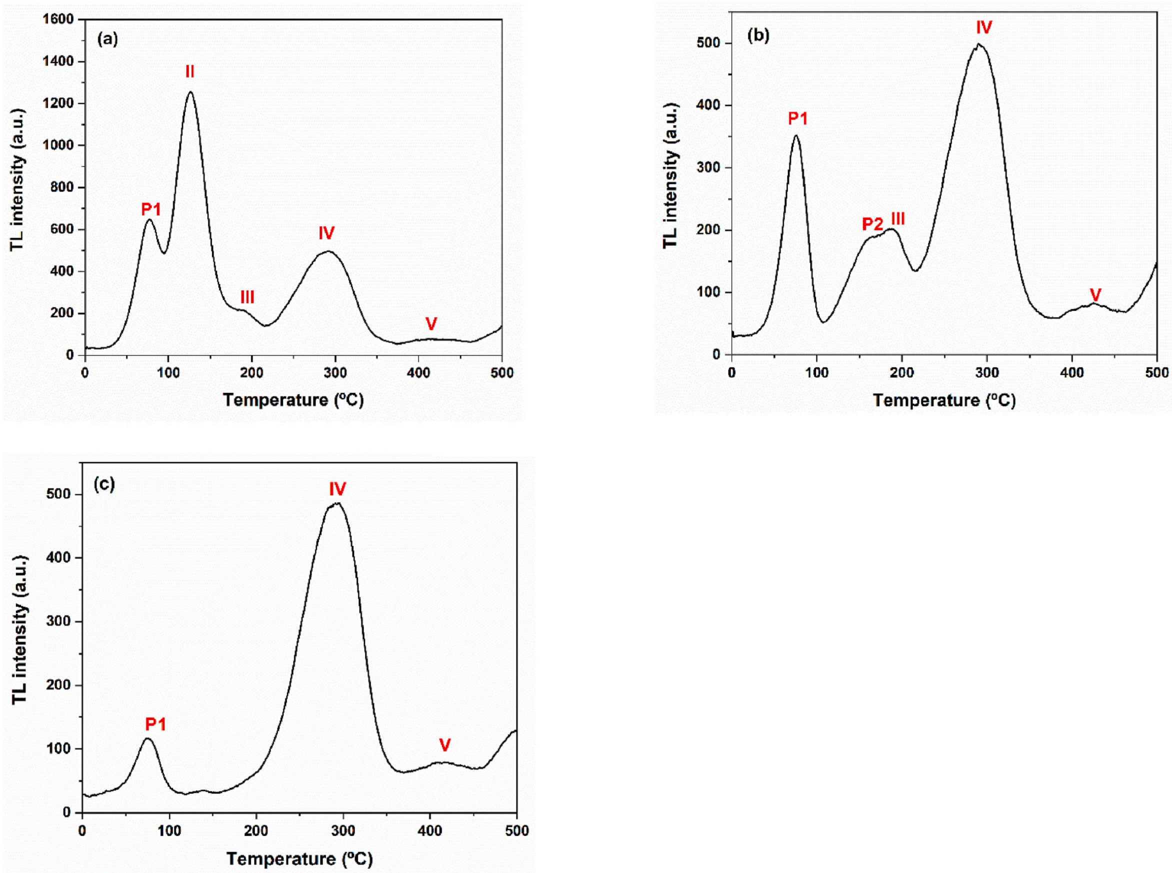

Fig. 4. Glow curves of a sample irradiated to 1 Gy and illuminated after preheating to 115 °C to remove peak I (a) to 150 °C to remove peak II (b) and to 210 °C to remove peak III (c). The PTTL peaks reproduced are named P1 and P2.

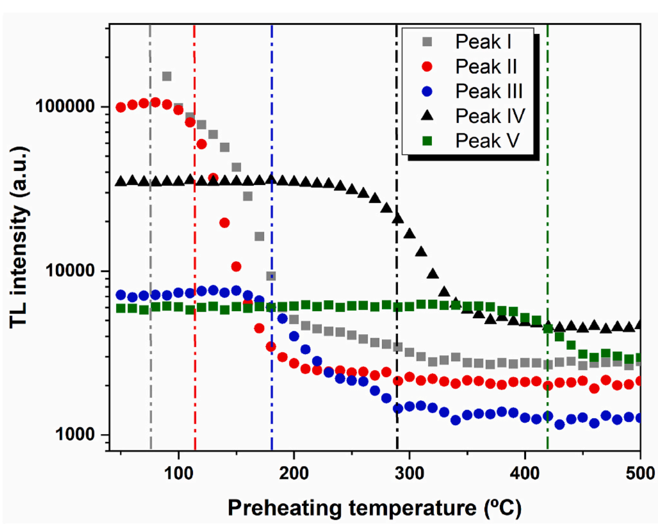

Fig. 5. Effects of partial heating on peak intensity in a pulse annealing experiment.

precedes illumination is gradually changed. In our measurements, the sample was irradiated to 1 Gy, preheated to temperatures from 50 to 500 °C in 10 °C increments, and illuminated for 50 s each time before the measurement of a full glow curve. The intensity of all peaks was monitored. Fig. 5 shows results of the pulse annealing experiment.

Peak I first decrease in intensity as the preheating removes the electron trap associated with the peak. After that, the peak is reproduced under phototransfer. The removal of peaks II and III causes a further decrease in the intensity of peak I. In this context, the PTTL signal observed for peak I may be qualitatively linked to electron traps of peaks II and III as donors. Concerning peak II, it is apparent that the intensity of peak II mostly decreases with the removal of peaks III and IV. Thus, we can also attribute the PTTL of peak II to charges originating from the electron traps of peaks III and IV. Peaks III, IV, and V are not reproduced under phototransfer. The results of pulse annealing are summarized in Table 1.

Table 1
Systems of acceptor, labelled A, and donor(s), labelled D, involved in the PTTL in the rose quartz sample as deduced from the pulse annealing experiment.

Peak	Tm (°C)	Preheating temperature (°C)	Donors	System
I	75	103	II, III	1A2D*
II	115	175	III, IV	1A2D

3.6. *Influence of illumination time on PTTL*

The influence of duration of illumination on PPTL intensity was investigated for peaks I and II. For this, the sample was irradiated to 1 Gy, preheated to temperatures of either 115°C or 150 °C, and illuminated with blue light to induce phototransfer. Fig. 6(a) shows the PTTL intensity of peak I plotted as a function of the illumination time. According to pulse annealing result (Table 1), the PTTL observed at peak I can be described as corresponding to a system of one acceptor and two donors. The line through data in Fig. 6(a) is a fit of equation (6) along with a curve fitted by this model (Eq. (6)).

When the sample was preheated to 150 °C to remove peaks I-II and

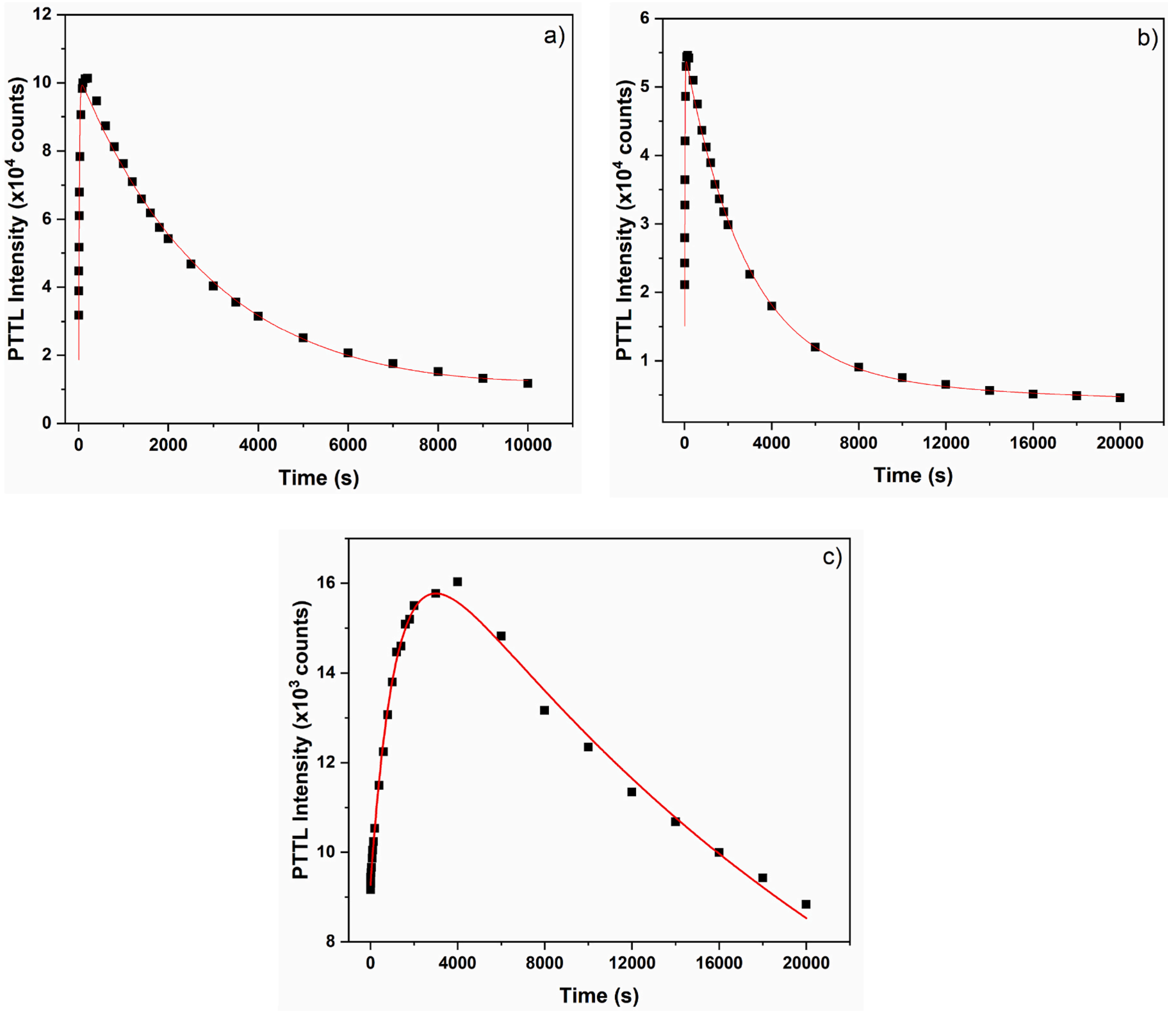

Fig. 6. Dependence of PTTL for peak I after preheating to 115 °C (a), for peak I after preheating to 150 °C (b) and for peak II after preheating to 150 °C (c).

illuminated, both peaks were reproduced. According to pulse annealing, the PTTL at peak II also corresponds to two donors. Therefore, Eq. (6) satisfactorily describes the data for peak II as shown in Fig. 6(c) and for peak I in Fig. 6(b) mentioned previously as one acceptor and two donors. It was found that the R^2 value in all fits is not less than 0.98.

4. Conclusions

We have explored the phototransferred thermoluminescence properties of rose quartz. Its glow curve has five glow peaks, but its PTTL is only observed at peaks I and II. Using pulse annealing, it was possible to qualitatively conclude that the PTTL at that peaks I and II correspond to two donors. The dependence of PTTL intensity on duration of illumination has been analyzed using a phenomenological model on this basis.

CRediT authorship contribution statement

I.A. Ferreira: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **M.C.S. Nunes:** Formal analysis, Investigation, Methodology, Software. **E.M. Yoshimura:** Writing – review & editing, Validation, Resources, Methodology, Formal analysis. **N.M. Trindade:** Writing – review & editing, Funding acquisition, Formal analysis, Methodology, Project administration, Resources, Validation. **M.L. Chithambo:** Validation, Supervision, Resources, Project administration, Formal analysis, Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Neilo Marcos Trindade reports financial support was provided by Sao Paulo Research Foundation. Neilo Marcos Trindade reports financial support was provided by National Council for Scientific and Technological Development. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was made possible due to generous funding from various sources. On this, I. A. Ferreira thanks the FAPESP (#2021/05042-0) and (#2022/14925-5); M.C.S. Nunes is grateful to FAPESP (#2021/12758-1) and (#2022/14516-8); E.M. Yoshimura appreciatively lists FAPESP (#2018/05982–0) and CNPq (#311657/2021–4); N. M. Trindade, FAPESP (#2018/05982-0, #2019/05915-3) and CNPq (#409338/2021-4); M. Chithambo is indebted to Rhodes University and the National Research Foundation of South Africa.

References

Chithambo, M.L., Dawam, R.R., 2020. Phototransferred thermoluminescence of annealed synthetic quartz: analysis of illumination-time profiles, kinetics and competition effects. Radiat. Meas. 131, 106236 https://doi.org/10.1016/J.RADMEAS.2019.106236.

Chithambo, M.L., Folley, D.E., Chikwembani, S., 2019. Phototransferred thermoluminescence from natural quartz annealed at 1000 °C: analysis of time-dependent evolution of intensity and competition effects. J. Lumin. 216, 116730 https://doi.org/10.1016/j.jlumin.2019.116730.

Chithambo, M.L., Kalita, J.M., Trindade, N.M., 2022. Processes related to phototransfer under blue- and green-light illumination in annealed Al_2O_3:C,Mg. J. Appl. Phys. 131, 245101 https://doi.org/10.1063/5.0094547.

Chithambo, M.L., Niyonzima, P., Kalita, J.M., 2018. Phototransferred thermoluminescence of synthetic quartz: analysis of illumination-time response curves. J. Lumin. 198, 146–154. https://doi.org/10.1016/J.JLUMIN.2018.02.029.

Chithambo, M.L., Seneza, C., Kalita, J.M., 2017. Phototransferred thermoluminescence of α-Al_2O_3:C: experimental results and empirical models. Radiat. Meas. 105, 7–16. https://doi.org/10.1016/j.radmeas.2017.08.009.

Emfietzoglou, D., Moscovitch, M., 1996. Phenomenological study of light-induced effects in alpha-Al_20_3:C. Radiat. Protect. Dosim. 65, 259–262. https://doi.org/10.1093/OXFORDJOURNALS.RPD.A031637.

Farias, T.M.D.B., Watanabe, S., 2012. A comparative study of the thermoluminescence properties of several varieties of Brazilian natural quartz. J. Lumin. 132, 2684–2692. https://doi.org/10.1016/J.JLUMIN.2012.04.047.

Folley, D.E., Chithambo, M.L., 2021. Analysis of thermoluminescence and phosphorescence related to phototransfer in natural quartz. J. Lumin. 238, 118217 https://doi.org/10.1016/J.JLUMIN.2021.118217.

Götze, J., Pan, Y., Müller, A., 2021. Mineralogy and mineral chemistry of quartz: a review. Mineral. Mag. 85, 639–664. https://doi.org/10.1180/MGM.2021.72.

Götze, J., Plötze, M., Graupner, T., Hallbauer, D.K., Bray, C.J., 2004. Trace element incorporation into quartz: a combined study by ICP-MS, electron spin resonance, cathodoluminescence, capillary ion analysis, and gas chromatography. Geochem. Cosmochim. Acta 68, 3741–3759. https://doi.org/10.1016/J.GCA.2004.01.003.

Henn, U., Schultz-Güttler, R., 2012. Review of some current coloured quartz varieties. J. Gemmol. 33, 29–43.

Hosaka, M., Miyata, T., Shimizu, Y., Okuyama, O., 1986. Synthesis of rose-quartz crystal. J. Cryst. Growth 78, 561–562. https://doi.org/10.1016/0022-0248(86)90162-4.

Hunter, P.G., Spooner, N.A., Smith, B.W., 2018. Thermoluminescence emission from quartz at 480 nm as a high-dose radiation marker. Radiat. Meas. 120, 143–147. https://doi.org/10.1016/J.RADMEAS.2018.04.001.

Kalita, J.M., Wary, G., 2016. Thermoluminescence response of natural white quartz collected from Gelephu, Bhutan. Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 383, 177–182. https://doi.org/10.1016/J.NIMB.2016.07.012.

Kibar, R., Garcia-Guinea, J., Çetin, A., Selvi, S., Karal, T., Can, N., 2007. Luminescent, optical and color properties of natural rose quartz. Radiat. Meas. 42, 1610–1617. https://doi.org/10.1016/J.RADMEAS.2007.08.007.

Márquez-Mata, C.A., Vega-Carrillo, H.R., et al., 2023. Thermoluminescent characteristics of seven varieties of quartz. Mater. Chem. Phys. 295, 126999 https://doi.org/10.1016/J.MATCHEMPHYS.2022.126999.

Martins, R.T.E.K., Ferreira, I.A., Silva, A.O., Nunes, M.C.S., Ulsen, C., Künzel, R., Souza, M.M., Chithambo, M.L., Yoshimura, E.M., Trindade, N.M., 2023. Thermoluminescence of rose quartz from Minas Gerais, Brazil. Radiat. Phys. Chem. 209, 110960 https://doi.org/10.1016/J.RADPHYSCHEM.2023.110960.

McKeever, S.W.S., 1985. Thermoluminescence of Solids, Thermoluminescence of Solids. Cambridge University Press. https://doi.org/10.1017/cbo9780511564994.

Nur, N., Yeğingil, Z., Topaksu, M., et al., 2015. Study of thermoluminescence response of purple to violet amethyst quartz from Balikesir. doi: 10.1016/j.nimb.2015.05.011.

Preusser, F., Chithambo, M.L., Götte, T., Martini, M., Ramseyer, K., Sendezera, E.J., Susino, G.J., Wintle, A.G., 2009. Quartz as a natural luminescence dosimeter. Earth Sci. Rev. 97, 184–214. https://doi.org/10.1016/j.earscirev.2009.09.006.

Topaksu, M., Correcher, V., Garcia-Guinea, J., Topak, Y., Göksu, H.Y., 2012. Comparison of thermoluminescence (TL) and cathodoluminescence (ESEM-CL) properties between hydrothermal and metamorphic quartzes. Appl. Radiat. Isot. 70, 946–951. https://doi.org/10.1016/J.APRADISO.2012.03.017.