Abstract. Pellets of lizardite crystals (\(\text{Mg}_3\,[\text{Si,Fe}]_2\text{O}_5\,(\text{OH})_4\)) and teflon powder have been investigated to identify the centers related to thermoluminescence (TL) emission. All the TL peaks are well fitted by using a second order kinetic model and the related trap parameters and activation energy are evaluated. Moreover, the measured optical absorption bands, in the visible and UV ranges, and in the infrared region, are attributed to charge transfer involving Mn and Fe ions and to vibration modes of Mg-O-H groups, respectively.

1. INTRODUCTION
Lizardite, Antigorite and chrysotile are silicate minerals belonging to a group called serpentine. Their chemical formula is \(\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4\), however they differ from each other by crystal structure. Lizardite crystallizes into trigonal, antigorite into monoclinic and chrysotile into orthorhombic system.

Most of papers on these crystals are of mineralogical nature nothing on their thermoluminescence was found in the literature. Hunt et al. [1] investigated reflectance spectra in visible and near infrared region of 87 silicates minerals, including two samples one called serpentine 318B and the other asbestos 323B – Arizona which presented bands at 0.65, 0.45 and 0.8 \(\mu\text{m}\) due to ferric ion and also bands at 1.4 and 2.34 \(\mu\text{m}\) related to hydroxyl ion. The lizardite is the most abundant and the least is chrysotile, but this one has been most important source of asbestos.

An antigorite \([\text{Mg}_{1-x}(\text{Si}_2\text{O}_4)(\text{OH})_{4-2x}]\) sample from India was investigated by Reddy et al. [2], using Optical absorption technique. They found bands related to \(\text{Fe}^{3+}\) ion at 15428, 17852, 19602, 22773, 24869 and 26448 cm\(^{-1}\) and the others at 9122, 10635, 11679, 15380 and 2292 9 cm\(^{-1}\) due to \(\text{Fe}^{2+}\). Using EPR they verified the presence of \(\text{Fe}^{3+}\), with g-values ranging from 5.4 to 3.1, and a sextet lines of the \(\text{Mn}^{2+}\) ion, which substitute \(\text{Mg}^{2+}\) in the crystalline lattice, with g-values near 2.0.

Götze et al, [3], investigated clay minerals using cathodoluminescence (CL), EPR, X-ray diffraction, scanning electron microscopy and trace element analysis; the selected mineral groups are the serpentine-kaolin, talc-pyrochlorite, smectite and illite. They concluded that the minerals kaolinite, dickite, nacrite, halloysite and pyrophyllite are characterized by a blue CL emission (400 nm), and EPR results indicated that this blue emission can be related to radiation induced defects centres, as electron holes trapped on apical oxygen atoms (Si-O centre) or located at the Al-O-Al group. They also verified that serpentine does not show visible CL.

In this work, we investigate the thermoluminescence and optical absorption properties of Lizardite mineral specimens from Brazil, collected in the state of Goiás.
2. MATERIALS AND METHODOLOGY

Our specimens exhibit the characteristic green coloration of the commercial Lizardite crystal, which is named “Chinese Jade” because of its Jade-like coloration. The triclinic Lizarite structure (Mg$_3$[(Si,Fe)$_2$O$_5$](OH)$_4$) of our samples was confirmed by X-rays diffraction measurements.

It is known in the literature that the lizardite changes to forsterite, when it is heated up to 350 °C [4].

By using ICP technique the major elements concentrations and impurities were identified in the sample. Their list in weight unit is: SiO$_2$ = 35.76; Al$_2$O$_3$ = 0.09; Fe$_2$O$_3$ = 0.49; MgO = 45.24; CaO < 0.01; Na$_2$O < 0.01; K$_2$O = 0.93; P$_2$O$_5$ = 0.034; MnO = 0.028. The silicon in the SiO$_4$ tetrahedron can be replaced by aluminum and the magnesium by aluminum, ferric and ferrous ions in different environments.

For thermoluminescence (TL) investigations samples were prepared as follow. Specimen parts were first grind with a mortar and a pestle, then sieved to separate grains between 75 and 150 µm. They were subsequently pressed with teflon powder producing pellets of 5 mm diameter and 1 mm thickness. Finally, the samples were irradiated with γ-rays in a $^{60}$Co source; doses from 20 to 500 Gy were applied with a rate of 253.7 Gy/h, high doses until 172 kGy were applied with a rate of 2.82 kGy/h. TL measurements were performed in an oxygen-free nitrogen atmosphere using a Daybreak Nuclear and Medical Systems Inc, Model 1100-series, with a photomultiplier EMI 9235QA coupled to optical filters: Corning 7-59 and Schott BG–39, resulting in a transmittance at 335-470 nm and heating rate was 10 °C/s.

Optical absorption (OA) measurements, in the range of 300-2700 nm, were carried out with a Carry 500 spectrometer on 2 mm thick polished samples.

The initial results using only Lizardite grains were not reproducible, On the other hand, reproducible results could be obtained using teflon pellets along with Lizardite grains. In this configuration, the grains are embedded on the upper surface of the teflon pellet.

3. RESULTS AND DISCUSSION

Two prominent TL peaks at 153 and 250 °C were observed in the TL glow curve of irradiated pellets, as shown in figure 1. The TL glow curves can be fitted by using second order kinetics model [5, 6], the equation for TL intensity ($I$) for each peak is:

$$I(T) = n_0 s \exp(-E/kT) \left[ s/\beta \right] \frac{\tau}{\tau_c} \exp(-E/kT)dT + 1 \right]^{-2} \quad (1)$$

where $s$ is the frequency factor, $n_0$ is the initial concentration of trapped electron, $E$ is the activation energy, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $\beta$ is the linear heating rate.

An excellent theoretical fit using second order kinetics model was obtained for all the peaks, however the theoretical deconvolution showed two additional peaks at 204 and 311 °C, as is shown in figure 1. The presence of 4 peaks is also confirmed by $T_m$-Tstop method [7].

Electron traps parameters $s$ and $E$ were evaluated through peak shape, initial rise and Glow Curve Deconvolution methods [8, 9]. All the results are summarized in table 1.
Figure 1. Theoretical and experimental TL glow curves of Lizardite-teflon pellets and the inset shows the TL from only teflon pellets.

Table 1. Calculated activation energies (E) and frequency factors (s) of the TL peaks found in Lizardite-Teflon pellets. A= Glow Curve Deconvolution, B= Peak Shape, C= Initial Rise.

| Tm (°C) | E (eV) | s (10^{12} s^{-1}) | E (eV) | s (10^{12} s^{-1}) | E (eV) | s (10^{12} s^{-1}) |
|--------|--------|---------------------|--------|---------------------|--------|---------------------|
| 153    | 0.95   | 0.11                | 1.00   | 0.09                | 0.95   | 0.14                |
| 204    | 1.12   | 0.35                |        |                     |        |                     |
| 250    | 1.35   | 5.24                | 1.39   | 18.79               | 1.53   | 22.76               |
| 311    | 1.49   | 3.28                |        |                     |        |                     |

Figure 2 shows the intensity of TL peaks 153, 204 and 311 °C peaks increasing up to 2 kGy almost linearly and after this dose the intensity falls off due to the onset of saturation; however the 250 °C one still increased up to a dose of 172 kGy. Actually, measurements on pellets only prepared with Teflon demonstrated that the 250 °C peak is not related to the Lizarite but to the Teflon itself (as seen on figure 1), and must be therefore considered as an artifact in the mixed pellets.

Figure 2. TL growth curves of 153, 204, 250 and 311 °C peaks irradiated with γ-rays.
The individual mean life of the peaks were deduced by using formula 2 and the E and s values listen I table 1 for T= 27 °C.

\[
\tau = \frac{\exp\left(-\frac{E}{kT}\right)}{s}
\]

We found the following values of \( \tau \): 1 day, 200 days and 93 kyears for 153, 204 and 311 °C peaks respectively for lizardite sample.

The OA spectra of a polished Lizardite crystal sample recorded from 300 to 2700 nm is given in figure 3. The increase of the absorbance for wavelengths lower than 1000 nm can be attributed to charge transfer bands of 3d transition ions [10], in particular of Fe\(^{3+}\), and Mn\(^{2+}\), in agreement with our ICP results showing the presence of these ions. Moreover, several bands are observed in the near and infrared intervals, due to primary and secondary combinations of modes of Mg-OH groups, while the fine structure observed at 1400 nm can be assigned to the first overtone of the O-H stretching mode [11, 12]. It is worth noting that irradiation with \( \gamma \)-rays does not affect the OA bands intensity for the used doses (20-750 Gy).

![Figure 3. Optical absorption spectra of lizardite showing several peaks.](image)

4. CONCLUSIONS

Our optical absorption measurements show that the green coloration of the studied Lizardite mineral specimen is due to the high absorbance in the UV and blue region. The OA bands intensity does not change with \( \gamma \)-irradiation and cannot be therefore related to the TL emission bands measured in the visible range.

Moreover, the observed linear relationship on more than three decades between the TL bands and the ionizing irradiation dose could be applied both for dating and dosimetry. Thanks to its very high estimated thermal stability (93 k years), the high-temperature TL peak (at 311°C) is particularly suitable for high dose dosimetry applications (up to 2 KGy).

Acknowledgments
Authors wish to thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for providing financial support.
References
[1] Hunt G R, Salisbury J W and Lenhoff C J 1973 Modern Geology 4 85.
[2] Reddy S N, Ravikumar R V S S N, Reddy B J, Reddy Y P and Rao P S 2001 Neus Jahrbuch fur Mineralogy-Monatshefte 6 261.
[3] Götze J, Plötze M, Götte Th, Neuser R D and Richter D K 2002 Miner. Petrol. 76 195.
[4] Deer W A, Howie R A, Zussman J 1966 An Introduction to the Rock-Forming Minerals (Longman London).
[5] Garlick G F J and Gibson A F 1948 Proc. Roy. Soc London A60 574.
[6] Chen R, Kristianpoller N and Davidson Z 1981 Journal of Luminescence 23 293.
[7] McKeever S W S 1985 Thermoluminescence of solids (Great Britain, Cambridge U. Press.).
[8] Chen R, 1969 J. Appl. Phys. 40 570.
[9] Kitis G, Gomez-Ros J M and Tuyn J W N 1998 Journal of Physics D: Aplied Physics 31 2639.
[10] Manning P G 1970 Canad. Mineral. 10 (4) 677.
[11] King T V V and Clark R N 1989 Journal of Geophysics Research 24 (B10) 13997.
[12] Clark, R.N., T.V.V. King, M. Klejwa, G. Swayze, and N. Vergo 1990 J. GeophysRes. 95, 12653-12680.