FTIR spectra and TL properties of quartz annealed at high temperatures

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Abstract: A study has been made of the infrared absorption bands behavior in different Brazilian quartz types submitted to thermal treatments. Heating promotes changes in the internal structure of the crystal forming vacancies through the dissolution of some components and forming of others and this has reflected in the TL emissions and optical absorption of the quartz samples. Thermally annealed quartz samples have, however, shown similar infrared spectra.

Introduction:
The tetrahedron SiO₄ is the basic structure unit of quartz (SiO₂). A quartz crystal, natural or synthetic, contains point defects from which several properties results. Thermoluminescence (TL) is one of the most revealing properties and it has been subject of an innumerable studies (McKeever, 1985). Most of these studies refer to α-quartz, which usually has TL peaks at 110, 220 and 325 °C. The 110°C peak is short lived, however it has interesting behavior and was investigated by several authors (for instance McKeever, 1985 and Chen and McKeever, 1997). The 325°C peak is used in TL dosimetry and dating. The results obtained during a spectral thermal stimulation (thermoluminescence) combined with the vibration behavior results, can explain phenomena of the color centers in these crystals. The TL sensitivity of many materials is increased after it has received a large dose of ionizing radiation. This is characteristic of geologic minerals such as quartz (Fleming 1968). The TL sensitivity arises primarily in the luminescence process, the major cause being the activation of luminescence centers. According Khoury (2008) the heat-treatments performed at 500 °C prior to γ dose did not change the TL intensity of this peak but contributed to decrease the standard deviation around the TL mean values. These results indicate that the increase of TL sensitivity results primarily from an increase in the number of activated luminescence centers participating in TL emission, the centers are being activated by charge capture. In general, the TL sensitivity increase is seen in two ways. Firstly, the growth of accumulated TL with total received dose is ‘supralinear’ (that is, faster than linear) for doses well below saturation. Secondly, after the TL produced by a first irradiation dose (called the ‘initial’ dose in this context) has been thermally drained, the TL response to a second dose (the ‘test’ dose) is increased; the phosphor is said to show the ‘predose’ phenomenon. The emission spectrum provides information on the recombination centers. (Gordon et al 1956). Natural quartz exposed to ionizing radiation emits two different types of thermoluminescence: blue and red TL. The blue TL emission is attributed to the recombination of released electrons with of holes of Al centers (Yang and Mckeever, 1990). Aluminum is always present in quartz and gives rise to the well known aluminum center and strongly participate in TL emission. Other important defect is the oxygen vacancy originating the E₁ and E₂ centers. Blue TL emission is correlated with aluminum impurities and OH ions in samples of synthetic quartz (Hashimoto et al. 2003). Centers associated with red TL emission are not yet clearly identified. Some authors have proposed that these emissions are correlated with oxygen holes centers or peroxy radicals (Fattahi and Stokes, 2003). The effect of OH impurity on the TL emission in Madagascar and Brazilian quartz, have been investigated by infrared spectroscopy (Hashimoto, 2007). The Madagascar and Brazil quartzes samples were compared and it is noted the Madagascar crystalline rock sample had low red TL emission and intense blue TL emission, unlike the Brazilian quartz. Its spectroscopy data had shown the impurities were present in low concentration and also there are very few defects in the two quartz samples, suggesting low aluminum concentrations produce higher blue TL emissions. In this work, a correlation between TL emission spectra of three varieties of quartz, with the impurities content is presented. The samples annealed were analyzed by XRF, ICP-MS and FT-IR.

Experimental Sample Preparation: To evaluate the effect of heat treatments were used green quartz, due its higher response TL radiation, hyaline once its behavior is well known, and synthetic quartz because its low impurities content. The samples were initially grounded and sieved to obtain a 0.080 and 0.180mm size diameter particles. In this study, all thermal treatments (600 to 900°C by 1h) were made using a furnace, which may reach temperatures as high as...
1200°C. After the thermal treatment the samples were exposed to gamma rays, using a 60Co source at room temperature receiving a 25KGy dose.

**Infrared measurements:** An infrared spectrometer FT-IR (Spectrum GX – Perkin Elmer) was used. Due the sample characteristics the infrared spectra was obtained using a reflectance accessory (HATR).

**TL-emission spectrometry:** TL emission spectrum measurements were performed in home made equipment mounted by one of the authors (Ferraz et al.). More details about it can be found on Ferraz et al 2008.

**Chemical analysis.** An inductively coupled plasma mass spectrometry ICP-MS (Elan 6100 – Perkin Elmer) was used to determination of micro elements and an X-Ray Fluorescence Spectrometer (PW 2404 Philips) was used for macro elements determination.

**Results and discussion**

First of all, TL response in function of gamma irradiation dose was studied. The samples were submitted to four thermal treatments (600, 700, 800 and 900°C), and after it a 5KGy dose was applied. The results are presented on the figure 1. It is possible to observe in figure 1 there is an intensity increase when the samples are thermal treated with temperatures higher than 700°C. The peak around 220°C has grown more than one million and a half regarding natural sample. The TL peak around 110°C has changed its maximum to the higher temperatures.

Figure 1. TL emission curves of annealed and irradiated quartz samples.

Chawla and Singhvi (1992) describes the TL response variation with gamma irradiation for quartz as a quickly growing until 200Gy, constant in the range of 200 to 800Gy and growing again above of 800Gy. Despite halide crystals, sulphates, carbonates and oxides have the supralinearity, in the silicates crystals, in general, the supra linearity is nonexistent, except for quartz, which is extremely supralinear. Not yet understood the supralinearity mechanism especially in quartz. However, Huntley (1988) described that heating at temperatures of 400°C and additional dose of 1.6KGy can cause changes in quartz TL emission curves. Samples of alpha and green quartzes had great TL response with the dose if they are thermally treatment to 600°C/1h.

A study on the effect of high doses and temperatures in the quartzes samples was done. Initially the TL emission spectrum was obtained for different types of quartzes samples. It can be seen on the figures 2, 3 and 4 the differences in emissions wavelengths for these varieties of quartz. The luminescence visible from the natural quartz generally consists of two emission bands centered on 450nm (blue emission) and 650nm (red emission), according Marfunin (1979). Emissions in the samples of pure quartz synthetic (artificial quartz) contains emissions (low intensity) around 400nm. As mentioned previously by Kibar et al, (2007) this emission is due to the high-thermal sensitivity and to the formation of AIO4/M+ centers originated due the sample irradiation. Exception of quartz that has a green emission centered around 350nm, this emission is associated to holes or vacancies of oxygen and silicon (Kibar, 2007). Once the macro elements concentrations are important in the TL emission X-Ray Fluorescence analysis (XRF) was done. The XRF results are presented on Table I. The micro element determination done by ICP-MS did not showed any correlation FT-IR or TL spectra.

Figure 2. TL emission spectrum of hyaline quartz

Some authors as Fujita et al. (2006) suggested the hydroxyl radical and other impurities may be responsible for weak blue TL emission. Measures of electronic paramagnetic resonance (EPR) at -196°C and thermoluminescence (TL) showed that the (TiO4/H+)0, (TiO4/Li+)0, (TiO4/Na+)0 centers are affected by heat treatment. This suggests that these treatments also affect the trapped electrons producing the luminescence centers. Recent studies show that the emission bands between 380-390nm are extremely sensitive to radiation and correlated...
with impurities of Al, and centers of paramagnetic (Al/M⁺).

Infrared spectra were obtained for the quartzes varieties studied in this work, with the aim of observe behavior changes in the spectrum in powder samples submitted to different heat treatments. Initially were obtained spectra of natural quartz without heat treatment and compared with the spectra obtained in the Minerals Spectroscopy site. It was necessary to use a reflectance accessory (HATR) in infrared measurements, (see figures 6, 7 and 8) and, to be easier the spectra comparison with the data in the literature, the Kubelka-Munk function was used. Analyzing the FT-IR spectra the following stretch modes were observed: 1) OH stretch in region of 3300cm⁻¹, 2) asymmetric stretch in the region of 1500cm⁻¹, and 3) SiO stretch in the range of 900-750cm⁻¹. The obtained spectra is very similar to the published one, it shows an intense absorption band between 4000 to 3000cm⁻¹, below 3000cm⁻¹, there are strong absorptions, overtones and frequencies combinations from 2500 until approximately 1500cm⁻¹, including the vibration of the fundamental lattice and in the vicinity of 1200cm⁻¹ there is a strong absorption band related to the essential lattice. The samples of synthetic or artificial quartz, hyaline quartz and green quartz were used to obtain spectra, without and with thermal treatment to 600, 700, 800 and 900°C for 1 hour.

Table I. Macro element concentration obtained by X-Ray Fluorescence Analysis

<table>
<thead>
<tr>
<th>Concentration Impurities (%)</th>
<th>Hyaline</th>
<th>Quartz grown artificially</th>
<th>Green</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>99.4</td>
<td>99.7</td>
<td>98.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.22</td>
<td>0.021</td>
<td>0.82</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.002</td>
<td>0.0007</td>
<td>0.06</td>
</tr>
</tbody>
</table>

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It is possible to observe that the intensity and forms of peaks related to the vibrational bands change significantly when the samples are subjected to high temperatures. The peaks in the region of 3000cm⁻¹, identified as vibration due to contributions from molecules of H₂O, so that when exposed to annealing, these molecules are evaporated showing more visible spectrum and easier identification of impurities.
Hashimoto et al. (1994/2007) examined natural quartz, even coming from Brazil and synthetic through techniques of FTIR, TL and EPR and correlated data.

When comparing the composition of the samples and associate with the intensity of the blue TL emission, it is noted that there is no a direct proportionality between Al concentration and intensity of TL emission. It can be concluded that there is no correlation between the Al concentrations of impurities and the blue TL emission, and then this result of inconsistent with Hashimoto et al, 1994.

The data obtained are correlated and discordant with the obtained by Hashimoto et al (1994), so that it is possible to conclude the concentrations of impurities of Al have no correlation with the intensity of blue TL emission in most of the variety of quartz.

In terms of spectrophotometric analysis it was not observed the bands of absorption of Al-OH in the region of 3200 cm\(^{-1}\) and OH-bands of Li in the region of 3600 cm\(^{-1}\), a proof of an inconsistency, with the data of Hashimoto et al (1994/2007).

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**References**


