Comparative study of the thermoluminescence properties of natural metamorphic quartz belonging to Turkey and Spain

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HIGHLIGHTS

- The thermoluminescence (TL) peak of metamorphic quartzes was investigated.
- Comparable differences were seen between low and high dose levels.
- AD and CGCD methods were used.

ARTICLE INFO

Article history:
Received 1 September 2013
Accepted 22 October 2013
Available online 30 October 2013

Keywords:
Metamorphic quartz
Thermoluminescence
Dose linearity
Pre-heat

ABSTRACT

The aim of this study is to investigate the sensitization of the thermoluminescence (TL) peak of metamorphic quartzes from Adiyaman in Turkey (TMQ) and from Madrid in Spain (SMQ). Quartz samples of two different origins were β-irradiated between ~6.689 Gy and 4816 Gy at room temperature. X-ray diffraction analysis has indicated that both TMQ and SMQ have the same crystal structure. Chemical analyses of both TMQ and SMQ were performed using the XRF technique. The preheat processes were carried out at 125 °C for 10 s in the TL measurement. TMQ and SMQ samples have different TL properties in two ways. First TMQ has four first order TL glow peaks while SMQ has five first order TL peaks and secondly, the observed dose sensitivity of TMQ samples is higher than the SMQ samples.

1. Introduction

Quartz, as one of the most abundant minerals, is an important rock-forming mineral. It is estimated that about 12% of the mass of the Earth's crust is made of it. Quartz is chemically an almost inert and passive substance at the surface and a very active agent under conditions deep within the Earth's crust. The changes of pressure (P)–temperature (T) conditions, natural irradiation or alteration cause variations in the structure of quartz during the hydrothermal and metamorphic processes (Gotze, 2009). At higher temperatures and pressures, it participates in many complex chemical reactions during rock and mineral formation. Metamorphism is the only major process in which quartz is either produced or consumed and it disappears from the environment during the formation of new minerals (http://www.quartzpage.de/gen_rock.html, 2013). New formation of natural crystal known as the metamorphic quartz generally in aquatic media occurs at high pressures and temperatures as respectively > 20 MPa and > 200 °C up to 6000 bars and temperatures over 500–600 °C (Gothe et al., 2011).

Quartz, one of the natural dosimeters used in luminescence studies, has great importance by means of mineral formation for quantifying the radiation history of materials in a variety of applications such as testing the authenticity of art objects, nuclear accident dosimetry (Bailiff et al., 2000), food irradiation control (Yazici et al., 2008) and dating of archeological materials and sediments (Adamiec, 2005; Porat et al., 2007; Preusser et al., 2009). Using quartz as a dosimeter, it is important to characterize it in terms of general properties such as dose response, preheat related to its mineral structure (Pagonis et al., 2002; Toktamiş et al., 2007; Topakcu et al., 2013).

The dosimetric characteristics of TL materials mainly depend on the kinetic parameters quantitatively describing the trapping–emitting centers responsible for the TL emission. The studies of natural/synthetic quartz show that quartz displays a number of TL peaks when it was heated from room temperature up to 500 °C after irradiation (Spooner and Questiaux, 2000; Yazici and Topakcu, 2003).
The shock-metamorphosed quartz, caused by the impact of an asteroid or meteor quartz, showed TL properties with maximal TL at 365 nm, 470 nm and 610–680 nm band. Electron and hole centers which originate from vacancies including those from the substitution of Al$^{3+}$ and/or Fe$^{3+}$ for Si$^{4+}$ by the electron paramagnetic resonance (EPR) have been found in them (Serebrennikov et al., 1982). Mineralogical formation, crystallinity index and the content of the impurities seem to be the main parameters of influence in the shape intensity of the cathodoluminescence (CL) and TL glow curve emission of hydrothermal and metamorphic quartzes (Topaksu et al., 2012).

In this study, we compared TL behaviors of metamorphic quartz samples which were collected in Turkey and Spain. For this purpose, X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses were performed in order to give a rough description of the crystalline structure and elemental-chemical composition of the TMQ and SMQ samples. Experimental TL glow peaks from two different metamorphic quartzes were also decomposed using the GlowFit programme (Puchalska and Bilski, 2006) with the computer glow curve deconvolution (CGCD) method. Then the β-dose linearity of these TL glow peaks were tested from /C2420 Gy to 4816 Gy. In addition to these, the temperature of TL glow peaks, the order of kinetics $b$, the trap depth/activation energy ($E$) and frequency factor ($s$) were determined.

2. Material and methods

All measurements were made on an automated Risø TL/OSL-DA-20 reader having an EMI 9235 QA photomultiplier tube (PMT) attached to filter pack consisting of Hoya U-340 (290–370 nm) filter. To prevent the scattered stimulation light from reaching the PMT, the reader is equipped with a 7.5 mm Hoya U-340 detection filter which has a peak transmission around 340 nm. β-irradiation was performed using an 1.48 GBq (40 m Ci) $^{90}$Sr/$^{90}$Y beta source with a maximum energy of 2.27 MeV. It was calculated that the absorbed dose rate of quartz at the sample position on the carrousel is 6.689 Gy/min.

The crystalline structures of the samples were analyzed by Rigaku Miniflex II model X-ray diffractometer at 30 kV (scanning rate: 2 /min, 15 mA with $\lambda=1.5406$ Å Cu-Kα radiation) using X-ray diffraction (XRD) technique.

To give a rough description of the elemental–chemical composition of the TMQ sample, Wavelength Dispersive X-ray Fluorescence (WDXRF) analysis was performed using an X-ray Fluorescence spectrometer Rigaku ZSX Primus II.

2.1. Sample preparation

The three samples used for this study were gently crushed to prevent crystal damaging effect (Toyoda et al., 2000). After that, samples were washed with distilled water, then dried in the incubator and sieved to obtain the suitable size of fine grain (90 $\mu$m grain size $\leq 140$ μm). Finally, the grains were deposited with aluminum discs of 10 mm diameter and 0.5 mm thickness as aliquots for measurements. The samples were weighed 5.0 mg powder samples and these samples were used for measurements. The incandescent background was subtracted from the TL data.

3. Result and discussions

X-ray diffraction pattern is shown in Fig. 1 and the obtained results from the pattern are also demonstrated in Table 1. All diffraction peaks match well with the characteristic peaks of SiO2. X-ray diffraction measurements show that TMQ and SMQ have the same hexagonal crystal structure. The type and concentration of different impurities are also observed and given in Table 2 as a result of XRF analysis of the TMQ and SMQ samples. Si, Cu, Fe, Mg and S appeared as the major trace elements of the sample.

**Table 1**
The XRD results for TMQ and SMQ samples.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Crystal structure</th>
<th>Unit cell parameters</th>
<th>Volume</th>
<th>$Z^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Close formula</td>
<td>$a$ ($\mu$m)</td>
<td>$b$ ($\mu$m)</td>
<td>$c$ ($\mu$m)</td>
</tr>
<tr>
<td>TMQ Quartz</td>
<td>SiO$_2$</td>
<td>Hexagonal</td>
<td>4.9146</td>
<td>4.9146</td>
</tr>
<tr>
<td>SMQ Quartz</td>
<td>SiO$_2$</td>
<td>Hexagonal</td>
<td>4.9141</td>
<td>4.9141</td>
</tr>
</tbody>
</table>

TMQ sample Space Group: P3221 (154) and SMQ sample Space Group: P3121 (152).

**Table 2**
Chemical analysis of two natural metamorphic quartzes from TMQ and SMQ performed by XRF.

<table>
<thead>
<tr>
<th>Elements</th>
<th>SMQ (%)</th>
<th>TMQ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>99.400</td>
<td>94.621</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.320</td>
<td>2.817</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.010</td>
<td>1.174</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.060</td>
<td>0.776</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.140</td>
<td>0.295</td>
</tr>
<tr>
<td>MgO</td>
<td>–</td>
<td>0.210</td>
</tr>
<tr>
<td>CaO</td>
<td>–</td>
<td>0.042</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>–</td>
<td>0.036</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.010</td>
<td>0.020</td>
</tr>
<tr>
<td>MnO</td>
<td>–</td>
<td>0.009</td>
</tr>
<tr>
<td>Trace ppm</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>Zr</td>
<td>76</td>
<td>80</td>
</tr>
</tbody>
</table>

0 20 40 60 80 100 120 140

**Fig. 1.** XRD results of the TMQ and SMQ samples.
XRF analysis showed that the natural TMQ and SMQ used in the given study contain mainly silicon bearing minerals with some amounts of magnesium, calcium, iron, potassium, aluminum, manganese and trace elements as impurities. The bulk chemical analysis of the samples indicates that the proportion of SiO₂ of SMQ is 99.400% and of TMQ is 94.621%. The result of XRF analysis for both samples is given in Table 2 in detail. As can be seen from Table 2, XRF analysis gives good information about the geological origin of the sample from a pegmatite body. Because it contains elements raised from fluids rich in vaporizable (chlorine, fluorine, boron, and water vapor) materials (Kibar et al., 2007).

We conducted a study in dose linearity and TL kinetics to compare TMQ and SMQ samples using the results of TL glow curves for all peaks. These quartz samples were irradiated with a β-source ~20.067–401.34 Gy and then heated from room temperature up to 600 °C with a heating rate 2 °C/s and the TL glow curves were plotted (Fig. 2).

Fig. 2 illustrates TL glow curves without the preheat process for SMQ and TMQ. As seen from Fig. 2, there are comparable differences between low and high dose levels for both samples. 90 °C TL peak was seen for both low and high dose levels for SMQ, while for high dose level there is also a shoulder at about 130 °C TL for TMQ. The preheat process at 125 °C was performed to see high temperature TL peaks in all experimental processes. The short lived 90 °C TL peak faded after the preheat process. Then the samples were irradiated between ~6.689 Gy and 4816 Gy and TL

![Fig. 2. Comparison of TL intensities of TMQ and SMQ samples (a) low doses and (b) high doses.](image)

![Fig. 3. TL dose response curves for TMQ and SMQ samples after 125 °C preheat (a, a’) TMQ (b, b’) SMQ sample.](image)
measurements were performed after the irradiation using the heating rate of 2 °C/s. Some of the selected TL glow curves after different dose levels are shown in Fig. 3.

As seen from Fig. 3 TMQ gives high TL intensity than SMQ. The higher intensity of TMQ might be due to (i) the mineralogical formation, at higher pressures and temperatures that should cause the creation of a larger number of traps (McKeever, 1985) and (ii) the high content of impurities, detected in the TMQ by XRF (Table 2), that may substitute for Si$^4+$ in the tetrahedra, producing charge imbalance compensated by interstitial cations in the SiO$_2$ framework (Topaksu et al., 2012). When the crystal lattice is subjected to stress, Garcia-Guinea et al. (2007) correspond the 340 nm TL band emission of many silicate minerals, including quartz, to silicon–oxygen bonding defects produced.

Al and Ti substitute Si in [SiO$_4$] tetrahedron giving rise to the Al-center and Ti-centers (Toyoda and Ikeya, 1991). Palão and Watanabe (2008) showed that the Al has a strong effect on the TL intensity compared to Fe, Ca, Ti and Mg. Especially, Al$_2$O$_3$ enhances low temperature peaks.

Fig. 3(a, a’) and (b, b’) displays the TL signals consequent preheating when TMQ and SMQ samples demonstrated increased doses. Three or more peaks are clearly observed when the lowest doses used for TMQ sample. However, during the highest doses, TL signal has been corroborated as a collective single peak. The TL signals of SMQ sample are confirmed five peaks during low doses (see Fig. 3(b, b’)). When high doses are applied; despite the peak that remains dominant at 200–250 °C, other peaks observed to bond and come together to guard their image.

![Figure 4](image4.png)

**Fig. 4.** The dose response of glow peaks (P1–P4) of TMQ samples by the CGCD method.

![Figure 5](image5.png)

**Fig. 5.** The dose response of glow peaks (P1–P5) of SMQ samples by the CGCD method.

![Figure 6](image6.png)

**Fig. 6.** An analyzed glow curve of preheated samples at 125 °C for 15 s measured after irradiation at room temperature for TMQ samples (FOM=2.60).

![Figure 7](image7.png)

**Fig. 7.** An analyzed glow curve of preheated samples at 125 °C for 15 s measured after irradiation at room temperature for SMQ samples (FOM=2.44).

### Table 3

Linear dose range of decomposed TL peaks for TMQ and SMQ samples.

<table>
<thead>
<tr>
<th>Quartzes</th>
<th>P1 + P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMQ</td>
<td>Linear dose range (Gy)</td>
<td>6.689–20.067</td>
<td>20.067–133.78</td>
<td>6.689–33.445, 401.34–2408</td>
</tr>
</tbody>
</table>

**References**


Both samples were analyzed with the CGCD method in order to determine the influence of the exposed dose on the superposed TL glow peaks. Superposed TL glow peaks of these samples were decomposed using the GlowFit programme (Puchalska and Bilski, 2006). As a result of this analysis, TMQ samples have four TL peaks at 179, 217, 290 and 364 °C, while SMQ samples have five TL peaks at 172, 220, 314, 412 and 511 °C, seperately. It is generally known that quartz crystals have common peaks occurring at 110 °C, 160 °C, 220 °C, 325 °C and 375 °C (Murray and Wintle, 1999).

The dose response was also investigated by the peak area method using the CGCD method for all components in the glow curve of TMQ and SMQ samples. Some of the selected glow curves after different dose levels are shown in Fig. 3. The resulting dose response of decomposed TL peaks are plotted on log-log scales and shown in Figs. 4 and 5.

The linear dose range of all glow peaks is given in Table 3. The calculation of \( E \) (activation energy) and \( s \) (frequency factor) mainly links to the prior knowledge of \( b \) (order of kinetics) and the number of glow peaks in the glow curve (Kirsh, 1992). Hence, additive dose method was practiced in this study to get an opinion about the \( b \) of each individual glow peak. TMQ and SMQ samples were irradiated to different doses to test the dose dependence on the peak position. This is a simple test for the first order kinetics. The peak maximum should not be affected by other experimental parameters for a constant heating rate. On the other hand, the peak temperatures shifted to the lower side with increasing dose levels for \( b \neq 1 \). As seen from Fig. 3, there is no significant change in the position of peak temperatures. This result explicitly shows that all the peaks in the glow curve of TMQ and SMQ should have first order kinetics.

The CGCD method is able to determine the initial number of trapped electrons and the activation energy, \( E \), with high accuracy for glow peaks with kinetics order values in the range of \( b \approx [1,2] \) and even beyond this range. CGCD analysis shows that TL glow peaks of both samples have first order kinetics, too.

The glow peaks of samples irradiated with a dose of 66.89 Gy of \( \beta \)-sources were decomposed by using a CGCD technique and these TL peaks are shown in Figs. 6 and 7, separately.

TL kinetics parameters (\( E \), \( s \), and \( b \)) and peak temperatures of the decomposed TL glow peaks for TMQ and SMQ samples are shown in Table 4. As can be seen from the Table 4, TMQ samples have four TL glow peaks while SMQ samples have five TL glow peaks.

<table>
<thead>
<tr>
<th>Quartzes</th>
<th>TL kinetics and peak temperature</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMQ</td>
<td>( E ) (eV)</td>
<td>0.92</td>
<td>0.59 × 10^{10}</td>
<td>0.22 × 10^{10}</td>
<td>0.51 × 10^{10}</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>( s ) (s^{-1})</td>
<td>0.19 × 10^{14}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>( T ) (°C)</td>
<td>179</td>
<td>217</td>
<td>290</td>
<td>364</td>
<td>–</td>
</tr>
<tr>
<td>SMQ</td>
<td>( E ) (eV)</td>
<td>0.96</td>
<td>0.82</td>
<td>1.11</td>
<td>0.91</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>( s ) (s^{-1})</td>
<td>5.0 × 10^{14}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>( T ) (°C)</td>
<td>172</td>
<td>220</td>
<td>314</td>
<td>412</td>
<td>511</td>
</tr>
</tbody>
</table>

4. Conclusion

In this study, TMQ and SMQ samples were analyzed using the XRD and XRF methods to determine the crystalline structures and elemental–chemical composition of those quartz samples. As a result the XRD measurements show that TMQ and SMQ samples have the same hexagonal crystal structure. XRF results show that TMQ contains significant amounts of \( \text{Al}_2\text{O}_3 \), \( \text{Fe}_2\text{O}_3 \), \( \text{K}_2\text{O} \) and \( \text{TiO}_2 \) while SMQ samples contain more \( \text{SiO}_2 \) compared to TMQ. The TL emission of the TMQ exhibits a higher intensity than the SMQ samples that could be associated with the parameters of mineralogical formation, crystallinity and content of impurities. TL measurements show that TMQ samples have four TL peaks at 179, 217, 290, 364 °C, while SMQ samples have five TL peaks at 172, 220, 314, 412, 511 °C, seperately. Additive dose (AD) experiments and CGCD analysis indicate that all of the TMQ and SMQ glow curves have first order kinetics. The activation energies (\( E \)), order of kinetics (\( b \)) and frequency factors (\( s \)) were determined by the CGCD method for all of the TMQ and SMQ glow curves (Table 4). Linear \( \beta \) dose ranges of TMQ and SMQ samples were determined for all of the glow peaks by using the dose response experiments. It was shown that peak 3 (P3) has a linear dose range for both TMQ and SMQ (Table 3).

Acknowledgments

This study was carried out at the Cukurova University, Adiyaman University. The authors are grateful to TUBITAK (Turkish Scientific and Technology Research Council) for its financial support under the contract number 105Y349 to purchase RISO TL/OSL DA-20 equipment.

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