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Blue and red thermoluminescence of natural quartz in the temperature region from −196 to 400 °C

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Abstract

Quartz samples of three different origins were γ-irradiated with 20 kGy at room temperature or at the temperature of liquid nitrogen (−196 °C), and analyzed by on-line TL-emission spectrometry over two temperature ranges: above 200 °C (high-temperature region) and −196 to 200 °C (low-temperature region). The emission spectra in the high-temperature region could be separated into intense blue TL (BTL) or red TL (RTL) properties. All quartz samples displayed more or less both properties of BTL and RTL in the low temperature region, shifting the BTL-emission spectra towards violet. Particularly, volcanically originated quartz (RTL, Medeshima) showed highly complex BTL and RTL peaks in the low-temperature region, and a stronger simple RTL peak in the high temperature. These complex glow-curve peaks are considered to reflect the presence of many crystal defects and much content of impurities in the volcanically formed quartz. In the glow-curve measurements, Brazilian quartz (quartz-vein origin) gave weak RTL and intense BTL in the low-temperature range, followed by faint emission of BTL in the high-temperature side. On the other hand, the radiation-induced colored (CC) part of a Madagascan crystal rock slice (hydrothermal origin) showed intense BTL together with slight RTL in the low temperatures, followed by strong BTL and appreciable strength of RTL in the high temperatures.

The BTL-emission pattern (TL-color image) of a Madagascan slice showed a complementary relationship between irradiations at liquid-nitrogen temperature and at room temperature. To explain these radiation-induced phenomena from quartz, hydrogen radicals and Li^+ ions, derived from radiolysis products of OH-related impurities, could operate to eliminate the BTL centers by recombination below the room temperature.

Keywords: Natural quartz; Thermoluminescence (TL); TL-emission spectrum; TL glow-curve; BTL; RTL; Liquid-nitrogen temperature; Artificial irradiation; Radiation damages

1. Introduction

Natural quartz exposed to ionizing radiation emits two different types of thermoluminescence (TL), distinguishable into blue and red (BTL and RTL). BTL from natural quartz is attributed to the recombination of Al hole centers with electrons released from trapped sites (Nattall and Weil, 1980; Yang and McKeever, 1990). The BTL-center formation has been found to be correlated with Al and OH-impurities in synthetic quartz samples as well as in hydrothermally originated quartz and plutonic quartz (Hashimoto et al., 2003; Tajika and Hashimoto, 2006). On the other hand, RTL phenomena were found in volcanically originating quartz grains as well as those extracted from burnt archaeological materials. The RTL centers have not yet been clearly identified although some candidates have been proposed, such as non-bonding oxygen hole centers or peroxy-radicals (Fattahi and Stokes, 2003) or lattice defects (Itoh et al., 2002). Additionally, some samples from pegmatite veins have shown both BTL and RTL properties within the same quartz specimen, emitting RTL under a low radiation dose but BTL under a high dose (Hashimoto et al., 1987). More recently, most quartz sands originating from granite rocks have unexpectedly been found to show RTL even though the granite rocks should be classed as plutonic. Subsequently, thermal annealing has changed the BTL property into RTL in a slice of Madagascan

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crystal rock containing relatively high amounts of impurities, such as Al–OH and molecular water (Hashimoto et al., 1997a).

In order to gain a deeper understanding of the TL mechanism, it is important to study quartz samples of different origins over a wide temperature range including the range below room temperature.

This research aims to study the properties of BTL and RTL, such as emission spectra and glow curves, of some typical quartz samples across a range of temperatures from that of liquid nitrogen (−196 °C) up to 400 °C. Subsequently, the effects of OH impurities on the BTL of sliced quartz are examined by IR (infra-red) spectrometry.

2. Experimental

2.1. Samples and sample preparation

Three samples of natural quartz were collected from Brazil (quartz-vein origin), Madagascar (hydrothermal origin) and Medeshima (volcanic origin, Japan). The Medeshima quartz sample was also employed in a previous paper (Hashimoto et al., 1993). Samples were selected on the basis of their BTL/RTL properties. The Brazilian quartz in lasca form was crushed to grain size and etched with HF solution to remove the crushing effects before use in the subsequent experiment. The Madagascan samples were prepared in two forms: Z-cut slices whose surface was mirror-polished to a thickness of 1 mm, and grains obtained by crushing colored (CC) or colorless (CL) portions of the sample after exposure to high radiation (Hashimoto et al., 2006). The slices were subjected to TL-color imaging (TLCI) and IR-maps. Medeshima grains were purified from other minerals by the normal procedure described in a previous paper (Hashimoto et al., 1997a); including simple hand picking and gently crushing and HF-etching treatments.

For the TL spectrometry and TL measurement, grain samples were sieved to adjust sizes ranging of 150–250 μm in diameter. Prior to irradiation, they were annealed at 450 °C for 5 min in an electric furnace to erase natural TL signals. All grain and slice samples were γ-irradiated with 20 kGy at −196 °C or at room temperature, and this was followed by measurement of TL.

2.2. TL-emission spectrometry, TL glow-curve measurement, and TLCI

TL-emission spectrometry used an IPDA (Intensified Photo-Diode Array) spectrophotometric system to measure successive TL spectra ranging from 350 to 700 nm summed for 45 cycles at 20-ms intervals. The measured emission spectra were corrected for differences in sensitivity as a function of wavelength by reference to the known spectrum from a standard electric lamp (Hashimoto et al., 1997b). These data were reconstructed as a contour map. The heating rate was adjusted to 1 °C/s in the low temperature range (hereinafter designated low-temperature TL, LT-TL) from the temperature of liquid nitrogen up to 200 °C by adjusting nitrogen gas from a liquid nitrogen reservoir, using the same temperature controller (Linkam L-600A) throughout the temperature range (Hashimoto et al., 2006). Two aliquots from each quartz sample were used for TL spectrometry after irradiation; one sample was irradiated at the temperature of liquid nitrogen, followed by LT-TL emission spectrometry, and the other was irradiated at room temperature, followed by high-temperature (HT-TL) emission spectrometry above 200 °C.

On the basis of TL-spectrometric results, BTL and RTL glow curves were measured with a combination of filters and a photomultiplier tube (PMT) sensitive to either the blue or the red region; the optical filters B-340 and IRC-65L were used with a PMT (R-585) for measurement ranging across 350–500 nm, whereas the filter combination R-60 with CF (cold filter) and a PMT (R-649s) was used for measurement of RTL within the 600–750 nm region (Hashimoto et al., 1987).

Additionally, two TLCIs from a Madagascan Z-cut slice were photographed at two temperatures to obtain LT-TL and HT-TL measurements (Hashimoto et al., 2003).

After the irradiation of grain samples at −196 °C the glow curves in either BTL or RTL were measured from

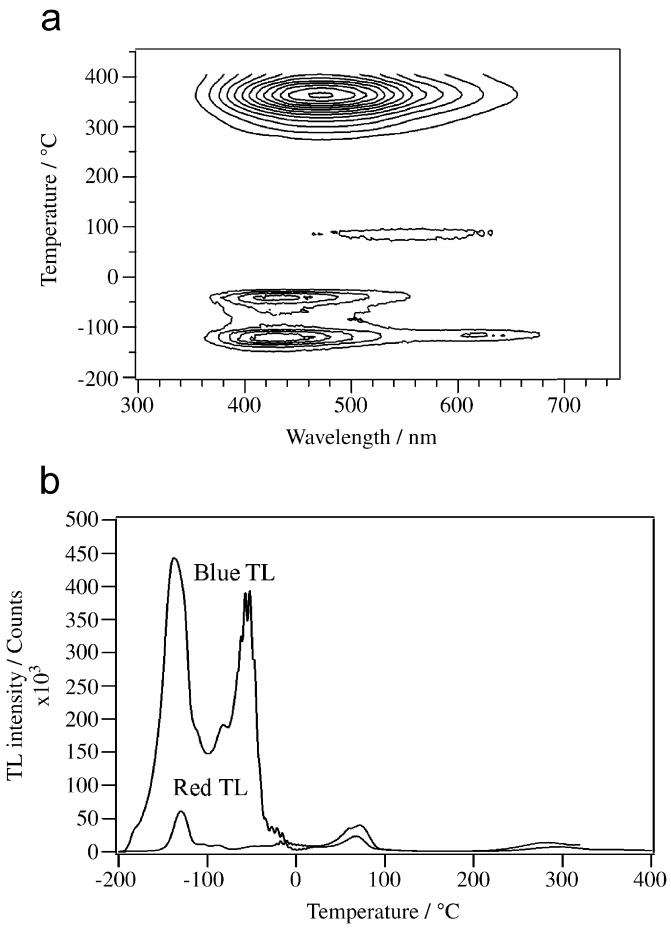

Fig. 1. Thermoluminescence contour map (a) and glow curves (b) for Brazilian quartz. After γ-irradiation (20 kGy) at −196 °C or at room temperature, on-line TL spectrometry was performed for HT-TL and LT-TL regions, respectively. In two other samples, γ-irradiation (20 kGy) at −196 °C was followed by measurement of BTL and RTL glow curves from −196 to 400 °C. TL-intensity was normalized in terms of sample weight.