Non-luminescent nature of the planar deformation features in shocked quartz from the Ries impact structure, Germany: A new interpretation

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Quartz grains from the Ries impact structure containing shock-induced microstructures were investigated using Scanning Electron Microscopy in cathodoluminescence (SEM-CL), secondary electron (SEM-SE) and back-scattered electron (SEM-BSE) modes as well as Mott–Seitz analysis. The purpose of this study is to evaluate the mechanism by which CL detects Planar Deformation Features (PDFs) in quartz, which is one of the most important indicators of shock metamorphism in rock-forming minerals. PDFs are micron-scale features not easily identified using optical microscopy or scanning electron microscopy. The CL spectrum of PDFs in quartz that has suffered relatively high shock pressure shows no or a relatively weak emission band at around 385 nm, whereas an emission band with a maximum near 650 nm is observed independent of shock pressure. Thus, the ~385 nm intensity in shocked quartz demonstrates a tendency to decrease with increasing shock metamorphic stage, whereas the 650 nm band remains fairly constant. The result indicates that the emission band at 385 nm is related to the deformed structure of quartz as PDFs.

Keywords: planar deformation features, cathodoluminescence, shock waves, quartz, meteorite crater

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Introduction

Planar Deformation Features (PDFs) of rock-forming minerals, especially in quartz, are one of the most important mineralogical indicators of shock metamorphism, which is considered evidence for the impact origin of certain geological structures (French and Short 1968; Stöffler 1974; Hörz 1982; Grieve 1987, 1991; Grieve et al. 1996; Koeberl 1997). PDFs are defined as sets of closely spaced (< 5 μm), narrow (1–3 μm), parallel planar substructures occurring along certain crystallographic slip planes (Engelhardt and Bertsch 1969; John et al. 1993; French 1998; Langenhorst 2002; French and Koeberl 2010). The planar substructures typically contain amorphous or glassy material of the composition of the host mineral.

PDFs have already been investigated by transmission electron microscopy (TEM); however, these studies were unable to determine the formation mechanism of these structures (Goltrant et al. 1991, 1992; Leroux et al. 1994). The CL spectroscopic properties of shocked quartz, as well as its PDFs, have been described from various shock metamorphic environments such as terrestrial impact structures (e.g., Ramseyer et al. 1992; Dypvik et al. 1996; Seyedolali et al. 1997; Boggs et al. 2001; Trepmann et al. 2005; Götte 2009; Hamers and Drury 2011 and references therein) and shock recovery experiments (Gucsik et al. 2003). The question of whether shock metamorphic effects can modify the luminescent nature of quartz under high pressure was first addressed in a pioneering study by Boggs et al. (2001). However, these authors were not able to explain the CL behavior of PDFs, in particular, their non-radiative character shown in the CL images. More recently, the shock-induced amorphization in PDFs of quartz samples from the Ries impact structure (at the Polsingen sampling site) was analyzed by micro-Raman spectroscopy (Gucsik et al. 2011). They found that Raman intensity exhibits a moderate increase in the range of 230 to 450 cm⁻¹ indicating that PDFs are in-filled by an amorphous phase. They concluded that the SiO₄ tetrahedral cluster-type structure is generated along the breaking of Si–O–Si bonds in the quartz structure by shock pressure (Gucsik et al. 2011 and references therein).

The luminescence properties of shocked quartz and its shock-induced microstructures both in natural and experimental cases are poorly understood (e.g., Ramseyer et al. 1992; Dypvik et al. 1996; Seyedolali et al. 1997; Boggs et al. 2001; Gucsik et al. 2003, 2004; Trepmann et al. 2005; Götte 2009; Okumura et al. 2009; Hamers and Drury 2011 and references therein). In this study our primary aim was to explain the CL behavior of shocked quartz, including the origin and characteristics of the CL signal in PDFs. These results not only contribute to an improved understanding of the formation conditions of PDFs in quartz (e.g. during a meteorite impact), but also reveal the potential for shock-induced effects, such as new electronic transitions in shocked quartz samples.

The strengths of SEM-CL in this study are that it allows high resolution imaging of defects and changes in recombination centers in materials such as PDFs, which optical microscopy and SEM-BSE cannot achieve. Further, by exploring the mechanism that separates SEM-CL from the other spectroscopic methods, BSE in particu-
lar, we can make inferences about the physico-chemical nature of PDFs. SEM-BSE imaging is an important tool in petrology as it is able to identify phases based on their atomic numbers, facilitating the identification of minerals, mineral zoning and intergrowths. However, SEM-BSE cannot discern the degree of crystallinity, recombination or polymerization of a sample. It cannot tell you whether you are looking at a glass or a crystalline phase, except by texture, as they appear the same under SEM-BSE. SEM-CL imaging is an optical method that exploits the phenomenon of electron excitation in the visible spectrum using a high energy electron beam. The resultant emissions arise from defects in the crystal lattice. CL presents petrologists interested in deformation structures and mechanisms at the micro-scale with a method to analyze minerals based on the nature and distribution of their defects. CL-SEM defect mapping could be a potentially more user-friendly method of mapping than complex numerical modeling. Furthermore, the two methods could be used in conjunction with each other for corroboration.

Samples and experimental procedure

Samples

The Ries impact structure (26 km in diameter, 15 Ma), a complex meteorite impact crater located in Southern Germany (N 48°53’, E 10°37’), provides some of the best-preserved samples to illustrate the formation conditions of terrestrial impact cratering and its geologic as well as geochemical consequences (Staudacher et al. 1982; Engelhardt 1990; Deutsch 1998; Stöffler and Grieve 2007).

In this study, quartz samples with well-developed sets of planar microstructures (PFs and PDFs) were selected from a total of 16 thin sections from two sampling sites: (1) suevite from Seelbronn (which is situated near Amerdingen, about 20 km SSW of Nördlingen) and (2) impact rock containing a cemented matrix from Polsingen (which is located about 20 km NNE of Nördlingen), Ries crater, Germany (Fig. 1). Both quarries contain impact breccia, suevite and highly shocked biotite and plagioclase, which fall into the shock stage ranging between 15–25 GPa. Well-developed multiple sets of PDFs coexisting with Planar Fractures (PFs) were observed in the shocked quartz grains from the above-mentioned sampling sites.

Methodology

CL imaging and spectral analyses (secondary electron and back-scattered electron imaging) were performed using Scanning Electron Microscope cathodoluminescence (SEM-CL), on an SEM (JEOL JSM-5410LV) (Oxford Mono CL2) at Okayama University of Science, Okayama, Japan. The system configuration has been described in detail in Okumura et al. (2006) and Kayama et al. (2010). Operating conditions for all SEM-CL images and spectroscopy as well as SE imaging
were 15 kV accelerating voltage and beam current 2.0 nA at room temperature. CL spectra were recorded between 350–850 nm, with 1 nm resolution, using the photon counting method and a photomultiplier (PMT) detector, Hamamatsu Photonics R2228. The CL spectral data were acquired as a function of wavelength (nm), and were corrected for calibration. SEM-CL studies used polished thin sections, with the sections being prepared using a non-luminescent epoxy material (Devcon ET, ITW Industries, Co. LTD., Japan) and coated with a 20 nm thickness of carbon in order to avoid charge build-up. The final polishing was done using colloidal silica. An un-shocked quartz sample from Minas Gerais was used for testing acquisition time of the spectra to determine whether CL spectral properties of quartz are affected by CL-irradiation.
Results

Scanning Electron Microscope cathodoluminescence (SEM-CL) observations

A selection of representative grains (from 36 grains in total) for optical, secondary electron (SE) and SEM-CL imaging, as well as CL spectral measurements of shocked quartz grains were obtained in a suevite (an impact breccia) from Seelbronn. The planar microstructures of quartz grains observed show roughly straight cracks using optical microscopy (Fig. 2a) and SEM-SE (Fig. 2b) images. In SEM-CL images (Fig. 2c), well-developed PDFs are observed occurring as dark parallel sets with < 1 µm width and spacing 1~5 µm. Compared to the SEM-SE and optical micrographs, the SEM-CL image shows PDFs in significantly more detail (Fig. 2c).

Cathodoluminescence spectroscopy

CL spectra of PDFs from both sampling sites are dominated by an emission band centered at ~385 nm (near UV) and a broad band at ~650 nm (red region) (Fig. 3a and b). The CL emission intensities at 385 nm differ significantly in the shocked quartz grains, where the peak intensities of PDFs are lower by 25% than those in the crystalline phase. In contrast, CL spectroscopy shows almost no difference of the emission intensities at 650 nm between PDFs and host in the shocked quartz grains (Fig. 3a and b).
Arrhenius plot of PDFs

The probability of non-irradiative transitions depends on temperature and is represented as

\[ s \exp(\varepsilon/kT) \]  

where \( s \) is frequency factor, \( k \) is Boltzmann constant, \( \varepsilon \) the activation energy (eV) for temperature quenching and \( T \) is absolute temperature (K). The luminescence efficiency (\( \eta \)) is then proportional to the probability of radiative, \( A \), and that of non-radiative transitions and can be described as

\[ \eta = A/[A + s \exp(\varepsilon/kT)]. \]  

To quantitatively evaluate the temperature dependence of CL intensity obtained by spectral measurements on room and liquid nitrogen temperatures (Fig. 4a), the activation energy for temperature quenching was estimated using equation (2) and assuming the Mott–Seitz model (Seitz 1939; Mott and Gurney 1948). This estimation is essential for conversion of CL spectra collected as a function of wavelength (nm)

\[ \text{Fig. 3} \]
CL spectra from a Planar Deformation Feature (PDF) and the host (crystalline) part of shocked quartz grains from Seelbronn (a) and Polsingen (b). CL spectra obtained from spots on PDF and crystalline host in inset SEM-CL images, which were taken at low temperature (less than 400 °C).

\[ \text{Fig. 4} \]
(a) CL spectra of unshocked and shocked quartz samples at various temperatures. (b) Compared to the shocked quartz samples, the unshocked quartz exhibits two temperature quenching processes (E is 0.03 eV up to −110 °C and 0.235 eV above −110 °C) shown in the Arrhenius diagram.
into such in energy space (eV). It follows from equation (2) that in an Arrhenius plot of $\ln[1/(1/\eta)]-I$ against $1/T$ as shown in Fig. 4b the activation energy in temperature quenching processes can be estimated for each quartz sample from the slope of the least-square linear fit. Arrhenius plots are shown for two shocked quartz samples and lead to estimated activation energies of ~0.072 and ~0.085 eV in the temperature range from −180 to −30 °C. In contrast to shocked quartz, which can be described by a single activation energy over the full temperature range, unshocked quartz shows evidence for two temperature quenching processes: $\varepsilon$ is ~0.032 eV below −110 °C and ~0.222 eV above −110 °C (Fig. 4b).

Discussion

Broad emission bands at 385 and 650 nm in the shocked quartz

The CL spectra of our shocked quartz samples are dominated by broad bands at ~385 and 650 nm, which show an almost total absence of any sharp emission lines or the blue center (380 nm). The emission band at ~385 nm in natural quartz has been associated with an aluminum (Al) impurity represented as $[\text{AlO}_4^{-}/\text{M}^+]^0$ ($\text{M}^+ : \text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+$) (Alonso et al. 1983; Itoh et al. 1988; Luff et al. 1990; Perny et al. 1992; Stevens-Kalceff et al. 2000; Götze et al. 2001). Gorton et al. (1997) also confirmed a weak emission band at 390 nm in ultra-pure synthetic quartz (< 0.1 ppm Al contents). According to Toyoda and Ikeya (1991), the amount of Al centers in α-quartz, in their studies on thermal stabilities of paramagnetic defects in Electron Spin Resonance (ESR) measurements, remarkably decreases over the range of ~200 to 450 °C, with the Al center disappearing at 450 °C. It is important to note that CL spectroscopy and ESR detect different Al-centers, which are related and transformed into each other by irradiating and annealing due to heating (cf. e.g. Götte et al. 2011, and references therein). The weaker emission band at 385 nm in quartz grains from Polsingen suggests that these grains suffered relatively higher shock metamorphism than those from Seelbrom, which was further confirmed using micro-Raman spectroscopy (Gucsik et al. 2011). However, determining the shock stage in impactites is complicated, as the suevite is composed of various types of impact rocks which indicate heterogeneous shock metamorphic effects, such that the degree of shock recorded is different in each quartz grain in the rock. The quenching of the emission band at ~385 nm might be due to several processes: the migration of monovalent ions (e.g. $\text{H}^+$, $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$) with an increase in temperature by shock metamorphism. The Al center might disappear due to the modification of energy levels accompanying amorphization, or the breakdown of the SiO$_4$ tetrahedral structure by shock metamorphism (Boggs et al. 2001). Therefore, the emission band at ~385 nm has potential for indicating the types of deformation affecting quartz in different shock ranges, in which no other crystallographic changes have been observed. However, the assignment of the broad emission band centered at 385 nm to a particular transition
is difficult because of widespread distribution of possible processes over a range of < 350 to 500 nm.

The broad emission band at 650 nm in quartz appears in both the CL spectra of the PDFs and its crystalline host. For the emission band at ~650 nm, CL spectroscopy revealed no remarkable differences in the emission intensity between samples. According to Stevens-Kalceff et al. (2000) and Götze et al. (2001), the emission band at around 620–650 nm has generally been noticed in both synthetic and natural quartz samples, and in cryptocrystalline silica such as agate and SiO₂ glass (amorphous silica). Stevens-Kalceff and Phillips (1995) indicated that this emission is attributed to either a non-bridging oxygen hole center (NBOHC) or a trapped-electron Si³⁻ center in crystalline quartz. Sigel and Marrone (1981) suggested that an emission band centered at ~650 nm in silica glass is associated with a defect in the Si–O network involving non-bridging oxygen ions. Since the ~650 nm feature is observed in both crystalline and defective parts of the quartz crystals, the luminescence center attributed to 650 nm emission is interpreted as intrinsic to SiO₂ and possibly impervious to shock metamorphism.

**Non-radiative nature of PDFs in CL**

It was observed that the energy difference (a band gap or BG) between the top of the valence band (VB) and the bottom of the conduction band (CB) in quartz is ~9 eV (O’Reilly and Robertson 1983) (Fig. 5a). Thus, even a small amount of energy from the electron beam will cause electrons to enter the CB, from where they then fall back and move randomly through the crystal structure until they encounter a trap or recombination center existing between the VB and CB (Hayward 1998). Photon emission in the visible light range of the electromagnetic spectrum is produced by electrons that return to lower energy states via traps. However, light emission in the UV region of the spectrum is based on a direct return from the CB to the VB (Yacobi and Holt 1990; Gaft et al. 2005). According to Boggs et al. (2001) and Nasdala et al. (2003), quartz is an insulator mineral, in which the band gap between CB and VB is too large for thermal (at relatively low temperatures) excitation to promote electrons from lower-energy states to the higher-energy states.

These paths in the visible range are schematically illustrated in an idealized crystal structure in Fig. 5a. A band gap (BG) exists between VB and CB. As discussed below, the shock-induced amorphization initiates electronic transition processes in defect centers (e.g., by breaking Si–O bonds and destroying the symmetry by shifting of the atoms from the lattice sites), which are correlated to the 350 nm CL emission. The amorphous infilling of the PDFs modifies the energy level arrangement of electron traps existing in the BG, such that the luminescence process observed in the near-ultraviolet to blue range does not operate or is very ineffective. This means that the amorphous material causes new closely-spaced energy levels due to its disordered nature, which indicates the electrons can easily return to their initial state with the emission of low-energy photons, or by losing energy to the lattice in the...
form of heat (phonon emission) (Fig. 5b). These results may corroborate the observations of Boggs et al. (2001) and agree with the conclusions obtained from our Raman spectroscopic observations (Gucsik et al. 2011). Alternatively, the non-luminescent nature of PDFs may be due to the absence of traps or recombination centers because of amorphization.
Conclusions

Cathodoluminescence (CL) microscopy on PDFs in shocked quartz grains from the Ries impact crater, Germany, shows these features as dark lines (no visible light emitted). The CL spectra of these samples exhibit broad bands at ~385 nm in the near-ultraviolet to blue range, and at ~650 nm in the red range, which might be associated with Al centers and a non-bridging oxygen hole center (NBOHC), respectively. This indicates that recombination centers or traps for photon emission are more closely-spaced within the BG (Fig. 4), which is probably caused by the partial amorphization of the quartz and/or an instantaneous increase in temperature up to 500 °C. Thus, the intensity of the emission band at 385 nm has potential as a shock indicator of shock in quartz.

Concerning the CL spectral features as well as Mott–Seitz analysis, we conclude that the phase transformation of quartz leads to small symmetry and electronic structure-breaking displacements of atoms resulting in non-radiative processes in the luminescence emission. We note that the CL technique employed here is a useful and powerful tool for the identification of shock-induced micro-deformation in rock-forming minerals. We have interpreted the lack of emission in PDFs in shocked quartz as a lack of recombination of monovalent ions and/or Al centers within the SiO$_4$ lattice structure. This is in agreement with the high degree of disorder in the amorphous materials as detected by micro-Raman spectroscopy. SEM-BSE imaging shows no compositional zoning at the boundaries between PDFs and the quartz host, nor evidence of any nucleation or growth of new product phase indicating the glassy infilling of the PDFs is truly amorphous. However, quartz high-pressure polymorphs, stishovite and coesite, also appear dark under SEM-CL, but these minerals have distinct Raman spectra, ruling out the likelihood of a polymorphic phase transformation. Future detailed analysis using SEM-CL on PDFs, stishovite and coesite are planned. Structurally, the PDFs are brittle fractures along crystallographic planes, containing an infilling of amorphous material involving a syn-deformational shear component. These features combined with the lack of Al and/or monovalent recombination indicate the dominance of combined or competing pressure or strain rate control on PDF formation via disequilibrium martensitic transformation of the shocked quartz, rather than displacive or reconstructive mineral transformations (Sharp and de Carli 2006). The observations and inferences from this study show that SEM-CL, combined with other compositional and spectroscopic data, may prove a fundamental tool in analyzing and mapping physico-chemical microscale defect distributions and deformation processes of interest to materials, engineering and earth scientists.
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