LETTER

Effect of impurities on cathodoluminescence of tridymite and cristobalite

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Cristobalite and tridymite in andesite and obsidian exhibit bright blue emissions in color cathodoluminescence (CL) images. CL spectra of cristobalite and tridymite show emission bands at 400 and 430 nm, respectively. Their CL intensity decreases with an increase in the electron irradiation time, similar to the short-lived blue luminescence reported in hydrothermal quartz. The reduction rate of the CL intensity of hydrothermal quartz is small as compared to cristobalite and tridymite. The initial CL intensity of both minerals immediately after the electron irradiation is positively correlated with the Al_2O_3 content. This suggests that the blue emissions of cristobalite and tridymite can be attributed to the $[\text{AlO}_4/\text{M}^+]^0$ defect center (M: H^+ , Li^+ , Na^+ , and K^+). The electron irradiation of cristobalite and tridymite diffuses the monovalent cations of H^+ , Li^+ , and Na^+ and destroys their crystal structure, resulting in short-lived blue luminescence. The CL intensity after 600 s of electron irradiation depends on the K_2O impurity content. In contrast to other monovalent cations, the K^+ cation is not diffused because of its large ionic radius. The CL emissions of cristobalite and tridymite after 600 s of electron irradiation can be attributed to the $[\text{AlO}_4/\text{M}^+]^0$ defect (M: K^+). CL images of cristobalite in obsidian from Utah, USA, show a heterogeneous distribution of CL intensity, with oscillatory CL zoning on the rim and radial lath-shaped textures with bright CL superimposed on weak luminescence background. This implies that lath-shaped textures with bright emissions might have crystallized from rhyolitic magma at temperatures higher than the recrystallization temperature minerals in the other areas.

Keywords: Cathodoluminescence, Cristobalite, Tridymite, Short-lived luminescence

INTRODUCTION

Advanced applications of cathodoluminescence (CL) to silica minerals, especially quartz, have been extensively reported in geoscience literatures, e.g., for the interpretation of diagenesis and provenance (Owen, 1991; Götze et al., 2001; Goldstein and Rossi, 2002), observation of growth fabric microstructures (Boiron et al., 1992), investigation of radiation halo (Owen, 1988; Meunier et al., 1990; Komuro et al., 2002), and identification of silica minerals in meteorites (Chennaoui-Aoudjehane et al., 2005). Recently, Kayama et al. (2009) investigated the CL of tridymite and cristobalite to clarify the CL emission mechanism and luminescence centers in detail. They suggested that blue CL emissions of tridymite and cristobalite can be attributed to the $[\text{AlO}_4/\text{M}^+]^0$ defect (M^+ : H^+ , Li^+ , Na^+ , and K^+) associated with the Al^{3+} impurity substituting Si^{4+} in the Si-O tetrahedra. The intensity of these

emissions reduce during electron irradiation, where the monovalent cations (H^+ , Li^+ , and Na^+) captured by the defects are easily diffused in the lattice. This CL behavior, i.e., short-lived blue luminescence, has been also reported in a previous CL study on hydrothermal quartz (Zinkernagel, 1978; Ramseyer et al., 1988; Ramseyer and Mullis, 1990; Perny et al., 1992). Raman spectroscopy revealed that the partial structural destruction of cristobalite and tridymite by electron bombardment promoted the diffusion of monovalent cations, resulting in short-lived luminescence (Kayama, et al., 2009). Kayama et al. (2009) also suggested that the impurity concentrations of aluminum and monovalent cations might be related to the reduction process of the CL intensity of both minerals; however, there is no quantitative evidence supporting such a scheme.

In this study, the CL of tridymite and cristobalite from various localities is examined to verify the effect of concentrations of impurities such as Al_2O_3 and K_2O on the reduction process of CL intensity. Furthermore, CL mi-

Table 1. Samples for CL measurements and their impurity contents

Mineral	No.	Locality	Mode of occurrence	Al ₂ O ₃ (wt%)	K ₂ O (wt%)
Cristobalite	C01	Coso Peak, USA	Small spherules crystals in obsidian	0.34	0.02
	C03	Shizuoka, Japan	Small spherules crystals in andesite	1.41	0.02
	C05	Kagoshima, Japan	Small spherules crystals in andesite	0.75	0.01
	C11	California, USA	Small spherules crystals in obsidian	0.88	0.03
	C-Ob	Utah, USA	Small spherules crystals in obsidian	0.76	0.11
Tridymite	T01	Vehech, Slovakia	Small tabular crystals in andesite	1.12	0.27
	T03	Gunma, Japan	Small tabular crystals in andesite	0.98	0.24
	T07	Kumamoto, Japan	Small tabular crystals in andesite	1.02	0.25

croscopy of cristobalite in obsidian is carried out to determine the relationship between the characteristic CL textures and the impurity content.

SAMPLES AND METHODS

Tridymite and cristobalite in andesite and obsidian from various localities were employed for CL spectral measurements (Table 1). Tridymite from Vehech, Gunma, and Kumamoto and cristobalite from Shizuoka and Kagoshima used in a previous study (Kayama et al., 2009) were considered as reference samples and their CL data were compared with the CL data of cristobalite from Coso Peak, California, and Utah. Hand-picked crystals were embedded in a small dimple (ϕ : 2 mm) on a brass disk using a nonluminescent epoxy resin and were polished and mirror-finished using diamond powder with particle size of 1 μ m. The prepared samples were coated with a carbon film, $\sim$ 2 nm thick, to prevent charge build-up on the surface during electron irradiation. Polished thin sections of cristobalite (C01, C11, and C-Ob) occurring as small spherules in obsidian were also examined to characterize their CL textures by CL imaging.

Color CL images were obtained using a cold-cathode microscope (luminoscope), which consisted of an optical microscope, an electron gun, and a cooled charge-coupled device (CCD) camera. The instrument was operated at an accelerating voltage of 15 kV and a beam current of 0.5 mA with 360-s exposure. A scanning electron microscopy-cathodoluminescence (SEM-CL) analysis was carried out using an SEM (JEOL: JSM-5410) combined with a grating monochromator (Oxford: Mono CL2) to measure CL spectra ranging from 300 nm to 800 nm in 1-nm steps. All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp. This correction prevents errors in the peak position of emission bands and allows the quantitative evaluation of CL intensity. To prevent electron irradiation damage and a high S/N ratio of CL signals, CL spectra should be measured at low current intensity. In this study, CL emissions of cristobalite (C-Ob) are found to be quite bright as compared to other samples. Hence, a low beam current

has to be maintained to prevent the saturation of the photomultiplier detector. Therefore, CL spectral measurements on all tridymite and cristobalite samples are performed in the scanning mode across an area of 220 μ m $\times$ 165 μ m at an accelerating voltage of 15 kV and a beam current of 0.1 nA; these conditions are different from those used in our previous study (Kayama et al., 2009). The change in the CL intensity at the peak positions with an increase in electron irradiation time is also monitored under a low current intensity of 1.0 nA in the focused mode (ϕ : 1 μ m) for 600 s. Panchromatic CL images are obtained at high magnification using a CL detector (Gatan: MiniCL) that can be used for SEM-CL analysis; the spectral response of this detector has a maximum in the blue region and gradually decreases with an increase in the wavelength up to 800 nm. The equipment construction and the analytical procedure are strictly followed from the reports of Ikenaga et al. (2000) and Kayama et al. (2009). Electron microprobe analysis was carried out to determine impurity contents in all samples using JEOL: JXA-8900R.

RESULT

All the cristobalite and tridymite samples exhibit bright blue emissions in the color CL images obtained using the luminoscope. Blue emissions of cristobalite and tridymite, however, diminish during electron irradiation. Every sample exhibits bright CL emissions in the initial period of electron irradiation. However, prolonged irradiation causes a progressive decrease in their CL intensity, and CL emissions become almost invisible to the naked eye after 1 h of irradiation.

The CL images obtained using the MiniCL imaging system show a homogeneous distribution of emission intensity, except for cristobalite in obsidian (C01, C11, and C-Ob). C01 and C11 exhibit oscillatory CL zoning, which shows bright areas on the rim and dull ones in the core. C-Ob shows radial and lath-shaped textures (area B) with bright CL superimposed on weak luminescence background (area C) as well as oscillatory CL zoning (area A) (Figs. 1c and 1d). No features corresponding to such CL textures can be found in optical microscopic and back-

Figure 1. Cristobalite in obsidian (C-Ob). (a) Optical microphotograph (parallel nicol). (b) BSE image. (c) CL image. (d) CL image at high magnification.

Figure 2. CL spectra of cristobalite in andesite and obsidian.

scatter electron (BSE) images (Figs. 1a and 1b).

CL spectroscopy in the scanning mode across an area of $220 \mu\text{m} \times 165 \mu\text{m}$ reveals that all cristobalite samples show an emission band at around 400 nm in the blue region (Fig. 2). The CL intensity of cristobalite from obsidian is higher than that of andesite. Additionally, CL spectra of C01, C03, and C05 show an emission band at around 650 nm with weak intensity. All tridymite samples show a CL spectral pattern with an emission band at around 430 nm in the blue region and at around 650 nm in the red region; the intensity of their red emissions are considerably lower than that of the blue ones (Fig. 3). The CL intensity of blue emissions of tridymite is higher than that of cristobalite in andesite. The integrated CL intensity

Figure 3. CL spectra of tridymite in andesite.

of the blue emission of both minerals is more than four times that of hydrothermal quartz from Poona, Maharashtra, India, whose CL spectra show a peak wavelength in the blue region at 390 nm.

Electron irradiation causes a rapid decay of blue emissions of cristobalite and tridymite. The changes in CL intensities at the peak positions for all the cristobalite and tridymite samples are monitored during electron irradiation at 1.0 nA in the focused mode for 600 s (Figs. 4 and 5). CL intensities of all samples decrease with an increase in the irradiation time, which is the characteristic behavior of short-lived luminescence. In all samples, the CL intensity abruptly dropped immediately after electron irradiation and then gradually decreased up to 600 s. The

Figure 4. Decrease in CL intensity of cristobalite in blue region after electron irradiation at 15-kV accelerating voltage and 1.0-nA beam current in focused mode (ϕ : 1 μ m) for 600 s.

Figure 5. Decrease in CL intensity of tridymite in blue region after electron irradiation at 15-kV accelerating voltage and 1.0-nA beam current in focused mode (ϕ : 1 μ m) for 600 s.

CL intensity reduction rate with respect to the electron irradiation time, however, is different for the samples. After 100 s of electron irradiation, the CL intensity at the peak maximum becomes 22%–38% of the initial intensity for tridymite (T01, T03, and T07) and cristobalite (C03 and C05) in andesite, whereas a small change in the reduction rate of CL intensity is observed during electron irradiation from 100 s up to 600 s, where the minima of the reduction rate reached 11%–17% after 600 s of irradiation (Figs. 4 and 5). During 100-s irradiation, the CL intensity of cristobalite in obsidian, i.e., C01, C11, and C-Ob, however, decreases down to 38%, 84%, and 63% of the initial intensity, respectively (Fig. 4). After prolonged irradiation for 600 s, their intensity reduces to approximately 8%, 45%, and 35% of the initial intensity, respectively.

DISCUSSION

The measured CL spectra of cristobalite and tridymite show emission bands at around 400 and 430 nm, respec-

Figure 6. Plot of initial intensity of blue emission immediately after electron irradiation against Al₂O₃ content.

Figure 7. Plot of initial intensity of blue emission after electron irradiation for 600 s against K₂O content.

tively (Figs. 2 and 3). Both minerals show a drop in the CL intensity in the blue region immediately after electron irradiation and a subsequent gradual decrease in the CL intensity during irradiation up to 600 s (Figs. 4 and 5); this CL behavior observed in previous CL studies on cristobalite, tridymite, and quartz has been reported as short-lived blue luminescence related to the $[\text{AlO}_4/\text{M}^{+}]^0$ defect (M^+ : H^+ , Li^+ , and Na^+) (Zinkernagel, 1978; Ramseyer et al., 1988; Ramseyer and Mullis, 1990; Perny et al., 1992; Kayama et al., 2009). All of the analyzed tridymite and cristobalite samples exhibit short-lived blue luminescence. However, the reduction rates of their CL intensity in the blue region during electron irradiation are quite different. This can be correlated to the impurity content of Al₂O₃ and K₂O (Figs. 6 and 7). The Al₂O₃ and K₂O contents in the samples are found to be 0.34–1.41 wt% and 0.01–0.27 wt%, respectively, by electron microprobe analysis. The Al concentration in cristobalite in obsidian is lower than that in cristobalite and tridymite in andesite. The initial CL intensity of cristobalite and tridymite immediately after electron irradiation is positively correlated to the Al impurity content (Fig. 6). The CL intensity of

quartz in the blue region also shows such a positive correlation with the Al content and the Li^+ and Na^+ contents (Ramseyer and Mullis, 1990; Perny et al., 1992). Therefore, blue emissions of quartz can be attributed to the $[\text{AlO}_4/\text{M}^+]^0$ defect center (M: Li^+ and Na^+). Similarly, the short-lived blue luminescence observed in cristobalite and tridymite can be attributed to the $[\text{AlO}_4/\text{M}^+]^0$ defect center (M: H^+ , Li^+ and Na^+). The CL intensity after 600 s of electron irradiation depends on the K_2O impurity content (Fig. 7). The CL intensity of tridymite (K_2O content: 0.24–0.27 wt%) is higher than that of cristobalite (K_2O content: 0.01–0.11 wt%). This indicates that the CL emissions observed after prolonged electron irradiation can be attributed to the $[\text{AlO}_4/\text{M}^+]^0$ defect (M: K^+). In contrast to other monovalent cations, the K^+ cation is not diffused by electron irradiation due to its large ionic radius, on the basis of diffusion behavior of the cations (H^+ , Li^+ , Na^+ and K^+) at room temperature in quartz (Sibley et al., 1979; Halliburton et al., 1981; Bahadur, 1994). The decrease in the CL intensity of both minerals during electron irradiation might be related to the $[\text{AlO}_4/\text{M}^+]^0$ defect (M: H^+ , Li^+ , and/or Na^+), where these monovalent cations are easily diffused by electron irradiation even when exposed for a short period. Furthermore, cristobalite and tridymite in andesite exhibit an abrupt drop in the CL intensity immediately after electron irradiation up to 100 s as compared to cristobalite in obsidian (Figs. 4 and 5). After 100 s of electron irradiation, the CL intensity at the peak maximum becomes 22%–38% of the initial intensity for tridymite (T01, T03, and T07) and cristobalite (C03 and C05) in andesite and 38%–84% of the initial intensity for cristobalite in obsidian (C01, C11, and C-Ob). After the abrupt drop, the CL intensity decreases gradually up to 600 s, reaching 11%–17% of the initial intensity for cristobalite and tridymite in andesite and 8%–45% of the initial intensity for cristobalite in obsidian. These results imply that monovalent cations such as H^+ , Li^+ , and Na^+ are almost completely diffused on cristobalite and tridymite in andesite during electron irradiation for 100–600 s, but are only partly diffused on cristobalite in obsidian under this beam condition.

Oscillatory zoning with bright areas on the rim and dull ones in the core is observed in CL images of cristobalite in obsidian. However, no such features are observed in CL images of cristobalite in andesite. CL images of C01 and C11 show oscillatory CL zoning in which a bright rim corresponding to cristobalite and a dull core corresponding to amorphous silica minerals, identified by Raman spectroscopy, are observed. Amorphous silica minerals exhibit dark CL emissions, which are not observed in crystalline minerals (Stevens-Kalceff et al., 2000). This suggests that CL microscopy can be used to

identify amorphous and crystalline silica minerals and visualize their spatial distributions. A CL image of C-Ob shows the characteristic distribution of CL intensity, which is not observed in the other cristobalite samples. It shows oscillatory CL zoning on the rim (area A) and radial lath-shaped textures (area B) with bright CL superimposed on weak luminescence background (area C) (Figs. 1c and 1d). Raman spectroscopy proves the absence of other minerals such as quartz, tridymite, and amorphous SiO_2 in this area. No features corresponding to oscillatory zoning and lath-shaped CL textures are observed in optical microscopic and BSE images (Figs. 1a and 1b). The difference between the CL intensities of these CL textures might be related to the Al_2O_3 and K_2O contents. Bright lath-shaped areas have a high concentration of K_2O and Al_2O_3 impurity, 0.02 and 0.90 wt%, respectively; the K_2O and Al_2O_3 contents in the dark areas are at the most 0.11 and 0.76 wt%, respectively. According to Dennen et al. (1970), the ratio of Al between an aluminous phase and quartz can be used to determine the temperature of crystallization, because the Al content in quartz is linearly correlated to the temperature. This implies that the lath-shaped areas with bright emissions might have crystallized from rhyolitic magma at higher temperature than other dark areas. Thus, CL spectroscopy and microscopy provide detailed information on the thermal history during the crystallization of cristobalite, which is quite difficult to obtain using other analytical methods.

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