Cathodoluminescence characterization of tridymite and cristobalite: Effects of electron irradiation and sample temperature

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ABSTRACT

Cathodoluminescence (CL) spectra of tridymite and cristobalite have broad peaks around 430 and 400 nm, respectively, both of which can be assigned to the \([\text{AlO}_2/\text{M}^+\text{]}\) defect. The CL intensities of these spectral peaks in the blue region decrease with prolonged exposure to electron irradiation, similar to the short-lived luminescence observed in quartz, although quartz shows a lower decrease in CL intensity compared to these minerals. Cristobalite has a higher CL intensity reduction rate during irradiation than does tridymite. Irradiation of these minerals at low temperatures results in a more rapid decay of CL emission, whereas that of quartz shows no apparent change in the rate of CL emission at similar temperatures. Confocal micro-Raman spectroscopy of the electron irradiated surface of these minerals reveals the amorphization caused by the interaction of the electron beam with the surface layer to a depth of several micrometers. This suggests that such structural destruction diminishes the activity of CL emission centers related to the \([\text{AlO}_2/\text{M}^+\text{]}\) defects by migration of monovalent cations associated with exchanged Al in the tetrahedral sites. Both samples present a considerable reduction of their CL intensities at higher temperature, suggesting a temperature quenching phenomenon. The activation energy in the quenching process was evaluated by a least-squares fitting of the Arrhenius plots, assuming the Mott-Seitz model. The result implies that the energy of non-radiative transition in this process might be transferred to lattice vibrations as phonons in two different manners. This might be related to different irradiation responses of the CL with a change in sample temperature.

Keywords: Tridymite, cristobalite, cathodoluminescence, electron irradiation, temperature quenching, Raman spectroscopy

INTRODUCTION

Cathodoluminescence (CL) is the emission of photons of ultraviolet (UV) to infrared (IR) wavelengths from a material stimulated by an incident electron beam. Its spectroscopy and microscopy provide useful information on the existence and distribution of defects and trace elements in materials, whereas it is quite difficult to obtain such vital information using other analytical methods. The CL features of materials are closely related not only to varieties of emission centers but also to their host chemical composition, crystal fields, and sample temperature. A better understanding of CL emission mechanisms and quantitative CL treatments would promote its application in the crystal chemistry of materials. Recently advanced applications of CL to minerals have been reported in various fields, e.g., detection and characterization of microdiamonds in ultrahigh-pressure metamorphic rocks (Ogasawara 2005), mineral chemistry of zoned alkali feldspars using the microbeam CL method combined with electron-probe microanalysis (Lee et al. 2007), and the pioneering approach of near-infrared CL to mineralogy (Barwood 2007).

The CL properties of silica minerals, especially quartz, opal, and amorphous SiO2 have been extensively investigated by many researchers to solve several fundamental problems in natural (Earth) science and material science, such as interpretation of diagenesis and provenance (e.g., Owen 1991; Götz et al. 2001; Goldstein and Rossi 2002), observation of growth fabric microstructures (e.g., Boiron et al. 1992), radiation halos (e.g., Owen 1988; Meunier et al. 1990; Komuro et al. 2002), and investigations on silica minerals in meteorites (e.g., Martian meteorites by Chennaoui-Aoudjehane et al. 2005). Although great scientific interest exists concerning the CL of silica minerals, very few investigations have been carried out on natural minerals such as tridymite and cristobalite. CL properties of the minerals of extraterrestrial origin, from the Moon and Mars, have been examined for the detection and identification of the minerals (Sippel 1971; Götz et al. 2001; Chennaoui-Aoudjehane et al. 2005; Chennaoui-Aoudjehane and Jambon 2007); however, their CL emission mechanisms and luminescence centers have not been discussed.

A change in CL properties can be detected in quartz as a result of bond breaking or impurity diffusion due to electron beam damage (Remond et al. 1992). At high beam currents, a remarkable reduction of CL intensity in the blue spectral region is recognized in quartz, interpreted as short-lived blue luminescence. The CL intensity of quartz during electron irradiation was also discussed in detail by Stevens-Kalceff and Phillips (1995) and Stevens-Kalceff et al. (2000). Their results indicate that the irradiation response depends on the type of luminescence center and sample temperature. Decreasing temperature leads to a drastic enhance-