

## Cathodoluminescence of natural tridymites and cristobalites

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Cathodoluminescence (CL) has been widely applied in earth science, especially in sedimentology using siliceous rocks. Although CL of quartz has been extensively studied, there have been few investigations about CL of other silica minerals such as tridymite and cristobalite. CL emission depends on various intervening factors; impurities of trace element, lattice defects and sample temperature. Since tridymite and cristobalite have several polymorphs according to heating or cooling processes, CL spectral data of these minerals at various temperatures should be useful for a study of polymorphism of silica minerals. We measured CL spectra using SEM-CL in wide temperature, and quantitatively discuss temperature quenching effect here.

Tridymite in andesite and cristobalite in andesite, rhyolite and obsidian were selected for CL measurements. SEM-CL (JEOL: JSM-5410) combined with a grating monochromator (OXFORD: Mono CL2) was used to measure CL spectra ranging from 300 to 800 nm, where the operation condition is at 15 kV and 0.15-0.5 nA. CL image was obtained by using Nuclide: Luminoscope.

CL image of tridymite shows homogenous blue emission, on the other hand cristobalite gives blue and violet CL. CL spectra of both tridymite and cristobalite occurred in andesite at room temperature have CL peak at 480 nm in blue color region. This blue emission is attributed to recombination of self-trapped exciton (STE), E' center caused by oxygen deficient defects or substitutional incorporation of Al impurity into Si site. CL intensity of tridymite in blue region decreases with an increase of electron irradiation time. Reducing rate is higher in the order of quartz, tridymite and cristobalite. Such CL behavior vs. temperature has been reported in quartz as a short-lived blue luminescence.

Cristobalite in obsidian only shows a broad band spectral peak at around 700nm in red color region. This emission might be assigned to Fe (III) impurity center by judging from CL data for silicate so far reported.

Tridymite in andesite indicates a rapid decrease in CL spectral intensity in blue color region on heating. Cristobalite has almost a same manner as the case of tridymite. Such phenomena can be construed in terms of a temperature quenching theory based on an increase in the probability of non-radiative transition with rising of temperature. A least-square fitting of the Arrhenius plot by assuming Mott-Seitz model provides activation energies of 0.025 eV from -192 to -70 deg. C and 0.129 eV from -70 to 50 deg. C in temperature quenching process for tridymite. These activation energies are equivalent to the order of Si-O stretching vibration energy. Activation energies for cristobalite are 0.032 eV from -192 to -70 deg. C and 0.182 eV from -70 to 120 deg. C. The former value of activation energy corresponds to O-Si-O bending vibration energy, and the latter to Si-O stretching vibration energy. It implies that the energy of non-radiative transition in heating process might be transferred to vibration in lattice as phonon.