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Emission mechanism of cathodoluminescence in smithsonite

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Cathodoluminescence (CL) has been widely applied in mineralogical investigation, especially for carbonates. CL of carbonates is characterized by various types of emission centers such as impurity and defect centers. Smithsonite ($ZnCO_3$) has emission centers of divalent Mn ion as activator and divalent Fe ion as quencher (Gotte and Richter, 2004). However, the defect center in smithsonite has not been investigated so far, since its emission is not so often found in carbonates. We have detected blue CL emission in smithsonite, suggesting structural defect center. In this study, we have assigned emission bands in CL spectra including defect center and clarified the mechanism of the CL in smithsonite in a wide temperature range.

Three crystals of smithsonite from San Antonio, Mexico (S-08, S-11) and Slaiman, Uzbekistan (S-17) were selected for CL measurements after carbon-coating on their polished surfaces. SEM-CL analysis was conducted using an SEM (JEOL: JSM-5410) combined with a grating monochromator (Oxford: Mono CL2) to measure CL spectra ranging from 300 to 800 nm in 1 nm steps at accelerating voltage of 15 kV and beam current of 1.0 nA. The CL emitted from the samples was collected by a photon counting method with a photomultiplier tube, and converted to digital data. All spectra were corrected for total instrumental response determined using a calibrated standard lamp. The sample temperature can be controlled in the range from -190 to 50 degree C with flowing liquid nitrogen and using an embedded heater in a cryostage (Oxford: C1003). CL color imaging was carried out with Luminoscope (ELM-3 R) consisting a cooled CCD camera by excitation voltage at10kV and beam current of 0.5 mA.

CL spectra of S-11 at room temperature show a board band at around 650 nm in red region, which can be assigned to the electronic transition from excited state of 4G to ground state of 6S corresponding to divalent Mn activator substituted for Zn ion. S-08 has a broad band at around 400 nm in blue region in its CL spectrum. Its emission might be caused by the defect center in smithsonite lattice. S-17 has also emission peaks at around 650nm in red region and 400nm in blue region. The deconvolution of the spectra in an energy unit using a Gaussian fit reveals that a red emission has two components peaked at 1.61 and 1.82 eV and a blue emission consists of two components at 3.28 and 3.82 eV. Therefore, there are at least two deferent defect centers in smithsonite, suggesting different crystal fields between them. The intensity of a blue emission decreases with an increase of sample temperature as explained by a temperature quenching theory based on an increase in the probability of non-radiative transition with the rise of temperature (Mott-Seitz model). Activation energy in each temperature quenching process can be calculated by an Arrhenius plot using integrated intensity of each component as a luminescent efficiency. It results in activation energy of 0.027 eV for component centered at 3.28 eV. This energy value corresponds to the energy of O-Zn-O bending vibration (0.024 eV: Frost et al, 2008), suggesting energy-transfer from the radiation to lattice vibration as photon. However, the intensity of a red emission is not affected by the change of sample temperature. These facts indicate that the temperature quenching mechanism might depend on the types of emission centers related to impurity or structural defect.

Keywords: smithsonite, cathodoluminescence, emission mechanism