

Effects of Mn activator and site occupancy on cathodoluminescence of dolomite

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Cathodoluminescence (CL) has been widely applied in mineralogical and petrological investigations, especially for carbonates. Dolomite commonly red CL emission related to an impurity center of divalent Mn in Ca-site and Mg-site (Sommer, 1972; Walker et al, 1989). Furthermore, temperature effect on CL efficiency has not been discussed in spite of potentially important function to control CL emission mechanism. In this study we have clarified luminescent mechanism of dolomite in a wide range of temperature using a SEM-CL, and confirmed a temperature quenching of its emissions. The quenching process has been quantitatively evaluated by CL spectral deconvolution method assuming the Mott-Seitz model.

Five dolomite samples from Hase, Japan (D01), Nakase, Japan (D02), Raura, Peru (D03), Binntal, Switzerland (D04), Arizona, USA (D05) 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 with a temperature controlled stage from -190 to 250 °C. The dispersed CL was collected by a photon counting method using a photomultiplier tube (R2228) and converted to digital data. All CL spectra were corrected for the total instrumental response.

CL spectra of all samples at room temperature exhibit almost similar pattern with a broad band at 525-800 nm in a red region. The spectral peaks are sharpened and enhanced at lower temperature due to reduction of thermal lattice vibration and an increase in luminescent efficiency, suggesting high spectral resolution of the emission bands at low temperature. Therefore, a Gaussian fitting was conducted to quantitatively deconvolute spectral data obtained at low temperature in an energy unit. The results confirmed that CL of all samples consist of two emission components at around 1.84 eV (Mg-site) and 2.15 eV (Ca-site) in red region, of which variation might be attributable to crystal field (Mn-ligands distance). In general, luminescence efficiency of the material decreases with a rise in temperature due to an increase in non-radiative transitions. This phenomenon has been recognized in several minerals such as quartz, cristobalite and tridymite as temperature quenching. Furthermore, an increasing temperature makes a shift of the emission peak to a higher wavelength side. The emission intensity varies depending on the samples with different concentrations of activator (Mn²⁺) and quencher (Fe²⁺), and site occupancy of the Mn²⁺ ion between two cation sites in dolomite structure. The facts suggest that the behavior of the emission intensity with changes in temperature is not explained on the basis of a temperature quenching theory based on an increase in the probability of non-radiative transition with the rise of temperature (Mott-Seitz model). Probably activator (Mn²⁺) concentration affects temperature quenching effect on CL of dolomite considerably.