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Temperature quenching mechanism of cathodoluminescence in 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 (Reeder , 1987; Gillhaus et al, 2001), but of which each occupancy in Ca site (A site) and/or Mg site (B site) has not been precisely estimated. Furthermore, temperature effect on CL efficiency has not been discussed in spite of potentially important function to control CL emission mechanism, though the factors effected on dolomite CL such as luminescence centers have been extensively investigated. 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, where site occupancy for Mn^{2+} ions in dolomite lattice has been also evaluated.

Three dolomite samples from Binntal/VS, Swiss (D-17a), Arizona, USA (D-26a) and New Mexico, USA (D-28a) were selected for CL measurements after carbon-coating on their polished surfaces. These samples contain Mn^{2+} ions as an activator, but too low for divalent Fe as a quencher.

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 ^{o}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.

All samples exhibit a broad band in red region CL spectrum between 580 and 640 nm at room temperature. 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. Two emission components at around 1.84 and 2.15 eV. The former can be assigned to the emission derived from Mn ion impurity occupied at A site, the latter to the emission at B site. The component intensities decrease in two steps of temperature range between -190 to -100 and -50 to 150 ^{o}C with an increase in sample temperature. 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. By assuming the Mott-Seitz model, activation energy in temperature quenching process can be calculated by a Arrhenius plot using integrated intensity of each component as an emission efficiency. Each activation energy was determined as follows; 0.03 eV for A and B sites below -100 ^{o}C and 0.100 eV for A site and 0.097 eV for B site above -50 ^{o}C. The former corresponds to the value of CO_3 vibration, and the latter to Ca-O or Mg-O vibration. Judging from the similarity of the activation energy in the process of temperature quenching and lattice vibration energy, the temperature quenching energy might be transferred as a phonon to the specific lattice vibration through non-radiative transition.

Keywords: dolomite, cathodoluminescence, temperature quenching