Quantitative evaluation of temperature effect on the cathodoluminescence of calcite:Mn

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Cathodoluminescence (CL), the emission of light caused by electron bombardment, has been widely applied in earth science, most extensively used in carbonate sedimentlogy. In such studies CL has the advantage that it can reveal features which are invisible using transmitted light, such as growth zones of calcite crystals. In general CL emission depends on various intervening factors; impurities of trace elements, lattice defects and sample temperature. The effect of sample temperature on the CL of calcite, however, has scarcely been investigated so far. This study provides quantitative estimation of the temperature effect on CL emission of the calcites having various concentrations of Mn(II) activator.

Six natural calcites with Mn content of 13, 129, 1260, 3520, 9170 and 66500 ppm, were used for CL measurements, labeled as CM13-CM66500. Scanning electron microscope combined with a grating monochromator was used to measure CL spectra ranging from 300 to 800 nm, where the operation condition is at 15kV and 0.03-1.0 nA. The sample temperature can be controlled in the range from -192 to 300 deg. C with a cryo- and heating-stage.

CL spectra of all samples exhibit almost similar pattern with a single broad peak at 620-650 nm, of which variation might be attributable to crystal field (Mn-ligands distance). The emission peak can be assigned to the electronic transition from the excited 4G to the ground state 6S. Only CM13 with a low Mn content gives a broad band peak at 370 nm in blue region, resulted from lattice defects. Gaussian curve fitting of CL spectral peak gives peak position, half maximum full-width (HMFW) and integrated intensity for each peak.

CL intensities of CM13 and CM129 with a low Mn content shows an increase with rising temperature up to -50 deg. C, but unchangeable at higher temperature, whereas the intensity of CM13 turns to an increase above 100 deg. C. This sensitized effect may be caused by an energy transfer from defect center to Mn(II) center. CM1260 and CM3520 with Mn content of several thousand ppm exhibit a similar behavior of their intensities on heating, where the intensities has not so much change over a wide range of temperature. This fact suggests that CL emission process has not any non-radiative transition for these samples. On the other hand CM9170 and CM66500 with a high Mn content are characterized by rapid decrease of their intensities with increasing temperature. Reducing rate is high up to -100 deg. C for CM9170 and up to -150 deg. C for CM66500. Such behavior is 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. Activation energy of 0.03 eV for CM9170 and 0.053 eV for CM66500 in temperature quenching process correspond to lattice vibration energy. It implies that the energy of non-radiative transition might be transferred to lattice as phonon.

The result leads that activator (Mn(II)) concentration considerably affects temperature quenching effect on CL of calcite. There are no other precedents except such calcite.