

# Activator concentration effect on temperature quenching phenomenon of cathodoluminescence in calcite

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Cathodoluminescence (CL), the emission of light following electron bombardment, has been widely applied in earth science, most extensively used in carbonate sedimentology. 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. In this study we provide quantitative estimates of the temperature quenching effect on CL emission of the calcites having various concentrations of Mn (II) activator.

Six natural calcites, of which Mn concentrations were 13, 129, 1260, 3520, 9170 and 66500 ppm, were used for CL measurement, and are labeled as C1-C6 in order of Mn content. The contents of rare earth elements and Fe are not so high enough for affecting CL emission as activator and quencher, respectively. Scanning electron microscope (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 0.03-1.0 nA. The sample temperature can be controlled in the range from -192 to 220 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  $6S$ . Since CL emission band generally has a Gaussian shape in energy unit, the wavelength data measured here were converted to energy (eV) data for quantitative analysis. Gaussian curve fitting of CL spectral peak gives peak position, half maximum full-width (HMFV) and integrated intensity for each peak. In all samples peak position shifts to high energy side linearly with temperature, also HMFV becomes progressively greater as the temperature is raised. It suggests that temperature effect on the transition process of electrons from excited state to ground state is almost independent of Mn concentration.

CL intensity of C1 and C2 with low Mn content shows an increase with rising temperature up to -50 deg. C, but unchangeable at higher temperature, whereas the intensity of C1 turns to an increase above 100 deg. C. C3 and C4 with Mn content of several thousand ppm exhibit a similar behavior of their intensity on heating, where the intensity has not so large alteration over a wide range of temperature. On the other hand C5 and C6 with high Mn content are characterized by rapid decrease of their intensity with increasing temperature. Reducing rate is high up to -100 deg. C for C5 and up to -150 deg. C for C6, but steady at higher temperature. Such behavior can be explained by a temperature quenching theory based on an increase in the probability of non-radiative transition with the rise of temperature. A least-square fitting of the Arrhenius plot by assuming Mott-Seitz model provides an activation energy of 0.04 eV for C5 and 0.05 eV for C6 in temperature quenching process. These values of activation energy 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 ion) concentration affects temperature quenching effect on CL of calcite considerably. There are no other precedents except such calcite.