

Temperature quenching effect on the cathodoluminescence of calcite

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Cathodoluminescence (CL), the emission of light following electron bombardment has been widely applied in earth sciences, 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 Mn (II) activated calcite.

The sample used for CL spectral measurement is Mn-bearing calcite (Mn: 9710 ppm) from Dalnegorsk, Russia. All measurements were made with a CL scanning electron microscopy (CL-SEM), which comprises a SEM (Jeol: JSM-5410) combined with an integral monochromator (Oxford: Mono CL2). The sample stage can be controlled at various temperatures using liquid nitrogen and embedded heater. CL spectra were collected over the wavelength range from 350 to 800 nm with a photon-counting system employed by PMT under the conditions of a scanning electron beam of energy 15 kV and current 0.05 nA.

CL spectral measurements from 81 K to 298 K exhibit a single broad emission peak at 620 - 640 nm, which can be assigned to d-d transition of Mn (II) ion as an activator. An increase in sample temperature leads to the reduction of CL intensity due to a temperature quenching caused by an increase in the probability of non-radiative transition with the rise of temperature. Its tendency is remarkable at temperature range from 81 K to 183 K.

The temperature quenching effect on CL emission efficiency was evaluated by assuming the configuration model based on the Frank-Condon principle. Since the CL emission bands generally have a Gaussian space in energy unit, the wavelength L (nm) data were converted to energy E (eV) where the CL intensities were multiplied by $L \times L$ due to transformed unit. The CL emission efficiency (A) was obtained from integrated intensities after a Gaussian peak fitting of the corrected intensities. The plot of the value of $\ln(1/A-1)$ against $1/T$ (T : Absolute temperature) shows a linear relationship to each other between 81 K and 163 K. We obtained an activation energy of 0.04 eV by least-square curve fitting of the Arrhenius plot. Relatively low activation energy results in the pronounced effect of temperature quenching on CL intensity at low temperature range.

Mean full width half maxima of the Gaussian fitted peaks became progressively greater as the temperature is raised; 0.17 eV at 81 K, 0.22 eV at 298 K. Its broadening of spectral peaks is attributed to spreaded amplitude of energy level at elevated temperatures.

An increase in sample temperature shifted the CL emission positions of the Gaussian fitted peaks toward the side of lower energy; 1.93 eV at 81 K, 1.98 eV at 298 K. Walker et al. (1989) reported a similar shift of the CL peaks on heating for calcite; 15500 cm^{-1} (1.92 eV) at 77 K, 15800 cm^{-1} (1.96 eV) at room temperature. It is not clear for this reason, while it might be related to crystal field altered by the change of sample temperature.

-References-

Walker, G., Abumere, O.E. and Kamaluddin, B. (1989) Mineralogical Magazine, 53, 201 - 211.