

Unusual temperature effect on cathodoluminescence of kaolin group minerals

Hirotugu Nishido[1]; Tasuku Okumura[1]; Kiyotaka Ninagawa[2]; Takabumi Sakamoto[3]

[1] Res. Inst. Nat. Sci., Okayama Univ. Sci.; [2] Applied Phys. Okayama Univ. of Science; [3] Faculty of Risk and Crisis Manage., Chiba Inst. of Sci.

During the last few years cathodoluminescence (CL) has been widely applied to the geosciences. However luminescence emission depends on many factors such as the presence of activators, lattice defects and sample temperature. Especially temperature effect on CL has not been extensively investigated so far. We have reported unusual thermal quenching of CL emission in kaolin group minerals (Okumura et al., 2003). In this study quantitative analysis of this mechanism has been attempted.

For CL measurement we employed two kaolin group minerals, kaolinite (JCSS-1101 from Kanpaku) and dickite (JCSS-1301 from Shokozan), which were offered as a standard reference sample by the Clay Science Society of Japan. Tablets (2 mm in diameter) of pressed powdered sample were fixed on sample holder with Ag conductive paste, and they were then coated with carbon.

CL spectra were obtained using a SEM (JEOL: JSM-5410) equipped with a grating monochromator (OXFORD: Mono CL2), and collected over the range from 300 to 800 nm with a photon-counting system by using PMT under the condition of a scanning beam mode at 15 kV and 0.1-0.5 nA. The sample stage can be controlled at various temperatures using liquid nitrogen and embedded heater from -192 to 220 deg. C.

Kaolinite and dickite show CL emission in the blue spectral region with a broad band peak at around 390 nm, which can be assigned to radiation induced defect centers (RID) presumed from EPR investigation (Goetze et al., 2002). On cooling the intensity of such blue CL was largely depressed, and could not be detected below -100 deg. C. A new broad peak in dickite, however, appeared at 450-500 nm, and its intensity was reached to the highest value at -192 deg. C. Such behavior and XDR examination confirm that this peak is attributable to defect center of impurity quartz.

Both minerals show almost same manner of the change in CL intensity against sample temperature. The intensity increased on heating above -50 deg. C, and up to its maximum at 60 deg. C, and then reduced with more heat. This behavior do not follow usual thermal CL reduction derived from a temperature quenching theory based on an increase in the probability of non-radiative transition with the rise of temperature. Since CL emission band generally has a Gaussian shape in energy unit, the wavelength data (nm) after sensitivity correction of PMT was converted to energy one (eV) for quantitative analysis. Gaussian curve fitting of CL spectral peak gives integrated intensity equivalent to emission efficiency for each peak at various temperatures. Arrhenius plot by assuming Mott-Seitz model results in an activation energy (E) in temperature quenching process, E: 0.39-0.43 eV in the increasing process of CL intensity from -50 to 40 deg. C and E: 0.43-0.49 eV in the diminishing process above 60 deg. C. The value of such energy is corresponding to that of O-H stretching vibration (3500-3700 cm⁻¹) characteristic of kaolin group minerals. It suggests that the energy of non-radiative transition of the electrons from excited state to ground state might be transferred to lattice as phonon in temperature quenching process above 60 deg. C. To the contrary, same amount of energy in temperature sensitizing process below 60 deg. C was induced by the lattice vibration. Such phenomena have not been reported so far.

References

Goetze, J., Ploetze, M., Goette, Th., Neuser, R.D., and Richter, D.K. (2002) Cathodoluminescence (CL) and electron paramagnetic resonance (EPR) studies of clay minerals, *Mineralogy and Petrology*, 76, 195-212.

Okumura, T., Nishido, H., Ninagawa, K., and Sakamoto, T. (2003) Temperature effect on cathodoluminescence of 1:1 layer silicates, *Euroclay2003*, Abstract.