CL emission mechanism of Pb-bearing carbonates

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Cathodoluminescence (CL) has been widely applied in earth science, extensively used in carbonate sedimentlogy. CL has the advantage to revealing optical features, which are invisible using transmitted light, such as growth zones of carbonate crystals. In general CL emission depends on various factors; impurities of trace elements, lattice defects and sample temperature. The CL of impurity activation such as transition metal ions has been much investigated for calcite-type carbonates, not for aragonite-type carbonates. Aragonite occasionally contains some amounts of Pb as an impurity. Therefore, we have conducted to clarify CL emission mechanism of Pb-bearing aragonite (tarnowitzite with compared to Pb-bearing calcite (plumbocalcite) by CL spectroscopy with temperature change.

Single crystals of tarnowitzite (Namibia and Morocco) and plumbocalcite (Namibia) were employed for CL measurements. Their color CL images were obtained with a cold-cathodo microscopy of the Luminoscope. CL spectra were measured by using a SEM-CL comprised of SEM combined with a grating monochromator at accelerating voltage of 15 kV and beam current of 0.1 nA in the wavelength-range of 300-800 nm. The sample temperature can be controlled in the range from −192 to 25 °C with a cryo- and heating-stage.

Color CL imaging shows a blue emission in tarnowitzite and a red emission in plumbocalcite. CL spectra of tarnowitzite have a intense broad band emission at around 390 nm in a blue region, whereas plumbocalcite exhibits two broad band emissions at around 320 nm in a UV region and at 620 nm in a red region. Two emissions in calcite CL are corresponding to Pb impurity center ($^3P_{0,1}\rightarrow{}^1S_0$) at 320 nm and Mn impurity center ($^4T_1\rightarrow{}^6S_1$). Blue emission derived from Pb ion activator in tarnowitzite depends on Pb content, suggesting a concentration quenching of CL above PbO 10 wt%. CL intensity of blue CL shows almost same between 25 to −70 °C, and subsequent sudden reduction below −90 °C, and gradual sensitizing above −150 °C. It is inexplicable by temperature-quenching theory, indicating that luminescence efficiency decreases with rising temperature due to an increase in non-radiative transitions. There, blue Pb activation in tarnowitzite should be characteristic in ns^2-type emission, which of process might be related to electron transfer among two or more energy levels.