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The nature of unusual luminescence in natural calcite $CaCO_3$

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Abstract

The unusual luminescence of particular varieties of natural pink calcite ($CaCO_3$) samples was studied by laser-induced time-resolved luminescence spectroscopy at different temperatures. The luminescence is characterized by intense blue emission under shortwave UV lamp excitation with an extremely long decay time, accompanied by pink-orange luminescence under longwave UV excitation. Our investigation included optical absorption, natural thermostimulated luminescence (NTL) and Laser-Induced Breakdown Spectroscopy (LIBS) studies. Two luminescence centers were detected: (1) a narrow violet band, with $\lambda_{max} = 412$ nm, $\Delta = 45$ nm, two decay components of $\tau_1 = 5$ ns and $\tau_2 = 7.2$ ms, accompanied by very long afterglow, and an orange emission band with $\lambda_{max} = 595$ nm, $\Delta = 90$ nm, and $\tau = 5$ ns. Both luminescence centers are thermally unstable with the blue emission disappearing after heating at 500 °C, and the orange emission disappearing after heating at different temperatures starting from 230 °C, although sometimes it is stable up to 500 °C in different samples. Both centers have spectral-kinetic properties very unusual for mineral luminescence, which in combination with extremely low impurity concentrations prevent their identification with specific impurity related emission. The most likely explanation of these observations may be the presence of radiation-induced luminescence centers. The long violet afterglow is evidently connected with trapped charge carrier liberation, with their subsequent migration through the valence band and ultimate recombination with a radiation-induced center responsible for the unusual violet luminescence.

Keywords: Calcite, time-resolved luminescence, radiation-induced luminescence centers