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Mn^{3+} and the pink color of gem-quality euclase from northeast Brazil

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Abstract

Pink euclase of gem quality and centimeter size, presenting an unusual pink-orange coloration and a pink to orange pleochroism, was discovered near Livramento de Nossa Senhora, in Bahia State, Brazil. The origin of the pink coloration has been investigated using several spectroscopic techniques: UV-Vis-NIR spectroscopy, electron paramagnetic resonance (EPR), luminescence, and X-ray absorption near edge structure (XANES). The coloration is mainly due to the presence of Mn^{3+} substituted to octahedral Al^{3+} that causes an intense split band at about 18 500 and 21 000 cm^{-1}. The crystal field splitting D_q, crystal field stabilization energy (CFSE), and Racah parameter B for Mn^{3+} are 2055.5 cm^{-1}, 147 kJ/mol, and 886 cm^{-1}, respectively. The Mn^{3+} molar extinction coefficient varies as a function of polarization, between 23 and 55 $L.mol^{-1}\cdot cm^{-1}$. An additional absorption band, near 24 000 cm^{-1}, together with the rising background toward the UV, tentatively assigned to the $O \rightarrow Fe^{3+}$ OMCT, contributes to the pink-orange hue. The in-situ UV-Vis-NIR spectra on heating up to 500 °C show a color change toward an intense, stable pink color. CIE colorimetric parameters demonstrate that the color of the investigated euclase remains in the pink domain before and after heat treatment. In the absence of Mn^{2+}, shown by EPR and luminescence, the presence of Mn^{3+} evidences oxidative formation conditions due to contamination of the hydrothermal fluids by the surrounding host rock.

Keywords: Euclase, manganese, pink color, optical spectroscopy, crystal field, heat treatment, pleochroism, gems