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 $D_{o}$, 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$^{-1}$ cm$^{-1}$. An additional absorption band, near 24 000 cm$^{-1}$, together with the rising background toward the UV, tentatively assigned to the O → 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

**INTRODUCTION**

Euclase [BeAl$_2$SiO$_4$(OH)] is a nominally colorless monoclinic nesosilicate mineral (space group $P2_1/c$). It is an unusual gem, recognized for its ornamental qualities and of interest to gem and mineral collectors, though its perfect cleavage parallel to (010) makes it generally unsuitable for use in jewelry. The first specimen of euclase was found near Ouro Preto, brought to Europe in 1785 by Joseph Dombey and described and named by René-Just Haüy, from the Greek words “eu” and “klasis” meaning “well-breaking” (Atencio 2015). It is encountered as euhedral crystals in various hydrothermal contexts and granitic pegmatites (Cerny 2002; Atencio 2015). It is a breakdown product of beryl in low-temperature hydrothermal fluids, at high alumina activity, or associated in secondary assemblages with quartz and feldspar (Hazen et al. 1986). The Al-O distances range from 1.851 to 1.853 Å, with O-Al-O angles from 79.8 to 99.3° (Online Materials1 Fig. OM1a). The shortest octahedral O-O distance corresponds to the shared edge between Al octahedra. The average Al-O distance in euclase (1.902 Å, standard deviation of 0.050) is typical of octahedral Al$^{3+}$ in regular sites, as observed in beryl and grossular garnet (Cerny 2002; Simmons et al. 2012). Despite it often occurring as well-formed crystals, euclase has an inconspicuous appearance, forming small crystals, easily overlooked within pegmatic mineral assemblages. It is usually a breakdown product of beryl in low-temperature fluids, at high alumina activity, or associated in secondary assemblages with quartz and kaolinite (Cerny 2002).

The structure of euclase consists of distorted BeO$_4$(OH) tetrahedra and regular SiO$_4$ tetrahedra linked by corner-sharing along the c-axis. These tetrahedra are interconnected with slightly distorted AlO$_4$(OH) octahedra by corner sharing through hydroxyl groups, which form zigzag chains by edge sharing also along the c-axis (Hazen et al. 1986). The Al-O distances range from 1.851 to 1.983 Å with O-Al-O angles from 79.8 to 99.3° (Online Materials1 Fig. OM1a). The shortest octahedral O-O distance corresponds to the shared edge between Al octahedra. The average Al-O distance in euclase (1.902 Å, standard deviation of 0.050) is typical of octahedral Al$^{3+}$ in regular sites, as observed in beryl and grossular garnet (Cerny 2002; Simmons et al. 2012). Despite it often occurring as well-formed crystals, euclase has an inconspicuous appearance, forming small crystals, easily overlooked within pegmatic mineral assemblages. It is usually a breakdown product of beryl in low-temperature fluids, at high alumina activity, or associated in secondary assemblages with quartz and kaolinite (Cerny 2002).

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