

Mn³⁺ 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 Mn³⁺ substituted to octahedral Al³⁺ 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 Mn³⁺ are 2055.5 cm⁻¹, 147 kJ/mol, and 886 cm⁻¹, respectively. The Mn³⁺ 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 → Fe³⁺ 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 Mn²⁺, shown by EPR and luminescence, the presence of Mn³⁺ 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 [BeAlSiO₄(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; Simmons et al. 2012). Despite it often occurring as well-formed crystals, euclase has an inconspicuous appearance, forming small crystals, easily overlooked within pegmatitic mineral assemblages. It is usually a breakdown product of beryl in low-temperature (200–400 °C), acidic (pH 4–5) hydrothermal fluids, at high alumina activity, or associated in secondary assemblages with quartz and kaolinite (Cerny 2002).

The structure of euclase consists of distorted BeO₃(OH) tetrahedra and regular SiO₄ tetrahedra linked by corner-sharing along the *c*-axis. These tetrahedra are interconnected with slightly distorted AlO₅(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 Al³⁺ in regular sites, as observed in beryl and grossular with 6 Al–O distances at 1.91 and 1.92 Å, respectively. This average distance is also similar to that in moderately distorted sites in corundum (1.914 Å, standard deviation of 0.064) (Hazen et al. 1986). The smaller standard deviation shows that the octahedral Al site is slightly less distorted in euclase than in corundum. The zigzag chains can be described by an alternation of Al–Al pairs with $d(\text{Al–Al}) = 2.84$ and 2.94 Å. The shorter Al–Al distance is along the *r* direction, which forms a 10° angle with the *c*-axis (Online Materials¹ Fig. OM1b). Each O atom is threefold-coordinated, receiving a formal Pauling bond strength sum of 2.0.

Euclase is often colorless but may also be blue-, green-, and yellow-colored, sometimes presenting a color zoning. The sixfold-coordinated Al site may accommodate Cr or Fe impurities, responsible for the diversity of euclase colors. The green color arises from the presence of Cr³⁺ (Krambrock et al. 2008). Fe-substitution in the Al-site is the origin of a Fe²⁺–Fe³⁺ charge-transfer absorption band (IVCT), responsible for an intense blue color (Mattson and Rossman 1987). By contrast, pink euclase is very rare. A few small crystals of pale pink euclase, millimeter size, have been reported in the Borborema Pegmatitic Province, Brazil (Eeckhout et al. 2002; Cassedanne and Philippo 2015). Pale pink euclase has also been recently extracted for collector purposes at the Brumado pit, Bahia state, Brazil (<https://www.mindat.org/loc-192235.html>). However, the origin of this pink coloration is unknown.

Though Mn³⁺ has a limited stability field in aqueous solutions, as

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a result of a disproportionation into Mn^{2+} and Mn^{4+} , it is stabilized in about 30 minerals, either trapped during crystal growth or as a result of external irradiation (see, e.g., Laurs et al. 2003; Kurtz et al. 2020). It is an efficient coloring impurity in minerals (Burns 1993). As a $3d^4$ ion, Mn^{3+} is subject to a Jahn-Teller effect that stabilizes it in distorted sites. In the case of a substitution of Al^{3+} by Mn^{3+} , the octahedral site is expected to undergo a distortion because of the difference of ionic radii [$r(\text{Al}^{3+}) = 0.535 \text{ \AA}$ vs. $r(\text{Mn}^{3+}) = 0.645 \text{ \AA}$ (Burns 1993)].

This work reports the first investigation of euclase crystals, several centimeters large, with a pink-orange coloration (Online Materials¹ Fig. OM2). The samples were recently discovered in NE Brazil, near Livramento de Nossa Senhora, Bahia State, close to the Chapada Diamantina National Park. Their euhedral shape and their association with euhedral quartz indicate a formation in a hydrothermal context. Located at 70 km of the above-mentioned Brumado pit, the Livramento de Nossa Senhora deposit is known for its resources in gem-quality varieties of colored and colorless hydrothermal quartz (Reys 2017). The original euclase coloration, with a pink to orange pleochroism, originates from octahedral Mn^{3+} substituted to Al^{3+} . An additional contribution to pleochroism is due to a combination of a band at 24000 cm^{-1} and of a rising absorption edge, tentatively assigned to the $\text{O} \rightarrow \text{Fe}^{3+}$ oxygen to metal charge transfer (OMCT). Heating from 300 to 500°C in air during 3 h retains the initial intensity of the Mn^{3+} absorption bands and results in the annealing of the 24000 cm^{-1} contribution and a drastic decrease of the intensity of the OMCT. This induces a stable intense pink coloration. The presence of Mn^{3+} in the absence of Mn^{2+} is consistent with oxidizing formation conditions (Tarantola et al. 2019).

EXPERIMENTAL METHODS

The chemical composition was determined using a CAMECA SX-100 electron microprobe analysis (EMPA) at the Camparis platform, Sorbonne Université, Paris, France. The analyses were averaged over 100 analytical points. The standard minerals that were used for the analysis are diopside (SiK α), orthoclase (AlK α), MnTiO_3 (TiK α ; MnK α), Fe_2O_3 (FeK α), pure Ge (GeK α). A 25 kV, 10 nA beam current counting 5 s was used for the Al, Si, Ge elements. A 25 kV, 200 nA beam current counting 30 s was used for Ti, Mn, Fe elements. Corrections were made using the usual PAP procedure (CAMECA). BeO and H_2O , which cannot be quantified using the electron microprobe, have been obtained by differences.

The crystallographic parameters ($a = 4.6309$, $b = 14.3312$, $c = 4.7769 \text{ \AA}$, $\beta = 100.295^\circ$ in the $P2_1/c$ space group) were determined using a XCalibur S 4-circle diffractometer equipped with a Sapphire CCD detector. The euclase single crystal was oriented along the A and B orientations [crystal sections (001) and (010), respectively], using X-ray diffraction. Crystal thickness was determined by means of a digital Mitutoyo micrometer with an accuracy of $\pm 1 \text{ }\mu\text{m}$. The E/a , E/b , E/c , E/Lc , and E/lr polarization directions were recorded (Hälenius and Skogby 1996), using a Glan Taylor polarizer made of two calcite prisms. Optical absorption spectra of pristine euclase and the sample heated at 500°C and recovered at ambient temperature have been obtained in transmission mode in the $330\text{--}2000 \text{ nm}$ ($5000\text{--}30000 \text{ cm}^{-1}$) range with a resolution of 1 nm using a Perkin Elmer Lambda 1050 UV/Vis/NIR spectrometer (IMPMC, spectroscopy platform) with a $4 \times 4 \text{ mm}$ beam size. A He-cryostat under vacuum (around $3.4 \times 10^{-7} \text{ mbar}$) attached to the spectrometer was used to record low-temperature spectra (down to 10 K). The sample was not damaged on quenching to room temperature. In situ high-temperature optical spectra of the sample were recorded up to 500°C in air, with steps of 50°C lasting 30 min using a Linkam heating stage, which was held horizontal and combined with a Cassegrain-type microscope with a beam size of $20\text{--}150 \text{ }\mu\text{m}$ diameter (Chassé et al. 2015). Fits of the obtained spectra were carried out using the Fityk software (Wojdyr 2010), under the assumption of a Gaussian line shape for both $d\text{-}d$ absorption bands and the UV-absorption edge. Colorimetric Yxy coordinates were computerized from the measured unpolarized optical spectra using the CIE 1931 convention and the D_{65} illuminant (average midday

light in Western Europe) published by the CIE (Hunt 1991).

Electronic paramagnetic resonance (EPR) spectrum was recorded using a X-band Bruker EMX-plus spectrometer operating at 9.86 GHz . The spectrum of the powered sample was obtained from 0 to 4000 G at room temperature with a 100 kHz frequency modulation, $1.002 \times 10^2 \text{ mW}$ microwave power, and 1.00 T modulation amplitude. The magnetic field range was calibrated relative to a DPPH standard ($g = 2.0037 \pm 0.0002$).

X-ray absorption near edge structure (XANES) spectra at the Fe K -edge were measured on the LUCIA beamline at the SOLEIL synchrotron (Saint-Aubin, France) with a Si(311) monochromator (Vantelon et al. 2016). The storage ring was operating in top-up mode at an electron current of 450 mA and 2.57 GeV . Polarized XANES spectra were recorded on single crystals ($E//c$) at ambient temperature with fluorescence detection. The XANES spectra were recorded in the $7075\text{--}7300 \text{ eV}$ range with 0.1 eV steps for the pre-edge (0.2 eV steps for the other XANES regions) and a 150 ms counting time. XANES spectra were collected using the continuous fly-scan mode. A possible drift of the pre-edge features was checked to ensure the absence of irradiation effects with a good accuracy of the data.

RESULTS AND DISCUSSION

Chemical composition and redox state

The chemical composition is close to the stoichiometric formula with 33.22 vs. $35.14 \text{ wt\% Al}_2\text{O}_3$ and 43.09 vs. $41.41 \text{ wt\% SiO}_2$, respectively. Such a limited variability was already reported (Pignatelli et al. 2017). However, the sum $\Sigma(\text{Al}_2\text{O}_3 + \text{SiO}_2)$ remains close to the theoretical value, with 76.31 vs. $76.55 \text{ wt\%}$, respectively.

The minor and trace elements detected by EMPA are Fe, Mn, Ti, and Ge. The average Fe content is 992 ppm . It is similar to that in blue and colorless euclase from Northeast Brazil (Graziani and Guidi 1980; Guedes et al. 2006). The average Mn content is 73 ppm . A similar content, 150 ppm , has been found in pink beryls from Minas Gerais, Brazil (Blak et al. 1982). The average Ti content is 46 ppm . It should be pointed out that Mn and Ti are unusual in euclase and have not been detected in colorless or greenish-blue samples from other locations (Graziani and Guidi 1980; Pignatelli et al. 2017). Finally, the sample contains an unusual concentration of Ge, 142 ppm , more than one order of magnitude above the average concentration in pegmatites and quartz-topaz greisens (Bernstein 1985; Höll et al. 2007; Breiter et al. 2013). Trace elements found in euclase samples from other localities (Sharp 1961; Graziani and Guidi 1980; Hanson 1985), such as Na, K, Ca, Sc, Cu, or Sn, were not detected.

As for the other euclase crystals investigated (Dias et al. 2009), the powder EPR spectrum of our pink euclase does not present native paramagnetic radiation-induced defects. This spectrum (Online Materials¹ Fig. OM3) presents only a signal from Fe^{3+} , substituted in the slightly distorted Al^{3+} octahedral site, corresponding to the EPR spectra of single crystals of blue and colorless euclase (Guedes et al. 2006) in which some Fe^{3+} has been evidenced. The absence of the EPR signals of Mn^{2+} and Ti^{3+} indicates that Mn and Ti occur as Mn^{3+} and Ti^{4+} , respectively. Moreover, the luminescence of Mn^{2+} has been tested under UV lamp. No Mn^{2+} luminescence has been detected neither under short nor long wavelengths. The excitation with red (785 nm) or green laser (532 nm) did not show laser-induced luminescence. This confirms the absence of Mn^{2+} in the pink euclase investigated.

XANES spectra were recorded at the Fe K -edge. Special care was given to avoid radiation-induced artifacts on Fe-speciation (see “Experimental methods” section). They were compared to crystal-line references representing typical Fe-speciation: siderite (FeCO_3) for $^{\text{VI}}\text{Fe}^{2+}$, staurolite [$\text{Fe}_2\text{Al}_3\text{Si}_4\text{O}_{23}(\text{OH})$] for $^{\text{VI}}\text{Fe}^{2+}$, andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) for $^{\text{VI}}\text{Fe}^{3+}$, and Fe-berlinite (FePO_4) for $^{\text{IV}}\text{Fe}^{2+}$ (Online

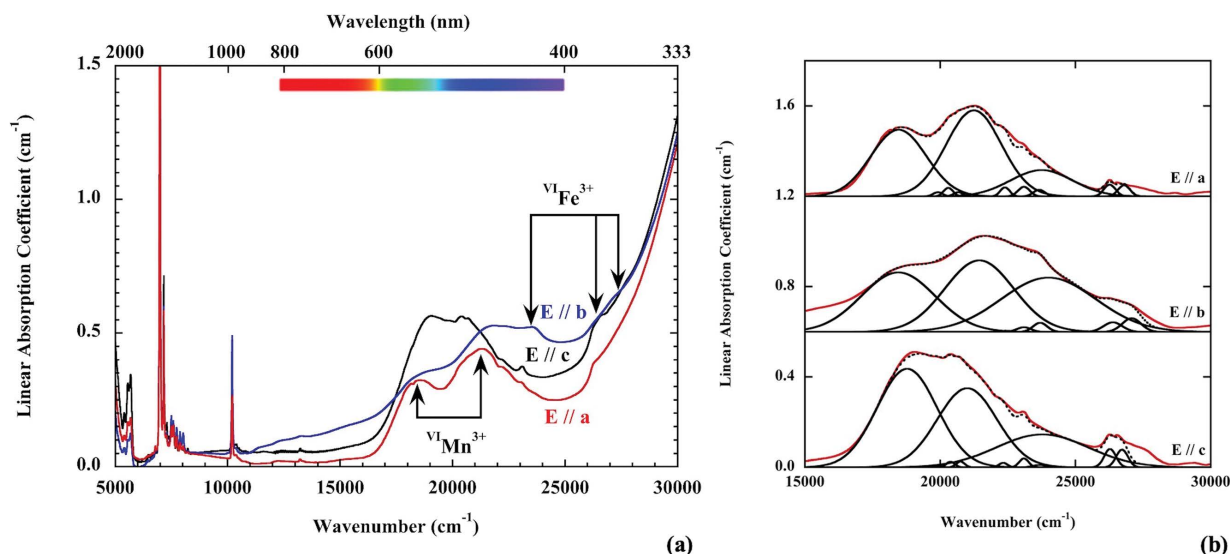


FIGURE 1. (a) Polarized optical spectra of pink-orange euclase along the *a*, *b*, and *c* axes. (b) Example of curve-resolved polarized optical spectrum of euclase along the *a*-axis. The red curve is the experimental spectrum after subtracting the tail of the Gaussian-shaped UV absorption edge at 45 000 cm^{-1} for the OMCT $\text{O} \rightarrow \text{Fe}^{3+}$. The black plain curves are the nine fitted Gaussian contributions: two major components (18 465 and 21 246 cm^{-1}), six minor components (19 916, 20 300, 20 668, 22 420, 23 100, and 23 665 cm^{-1}), and one component at 23 630 cm^{-1} . The black dotted curve is the sum of the fitted components. (Color online.)

Materials¹ Fig. OM4). The energy position and low intensity of the pre-edge shows the presence of only Fe^{3+} in octahedral coordination. XANES data indicate that the heating treatment at 500 °C does not change the redox state of iron, which remains in the ferric state.

Optical absorption spectra and the pink-orange pleochroism

The polarized spectra (E//*a*, E//*b*, E//*c*) present two narrow bands at 7000 and 10200 cm^{-1} corresponding to the first and second overtones of the OH stretching mode (Fig. 1). Curve fitted spectra in the visible range show two main bands corresponding to the ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$ transition of Mn^{3+} , with the splitting of the ${}^5\text{T}_{2g}$ level due to the low-symmetry field, in which Mn^{3+} is usually stabilized by a Jahn Teller effect (Burns 1993). The corresponding transitions will be referred to as ν_1 and ν_2 , respectively. The ν_1 band is located at 18 465, 18 453, and 18 780 cm^{-1} for E//*a*, E//*b*, and E//*c*, respectively. The ν_2 band occurs at 21 246, 21 449, and 21 000 cm^{-1} for E//*a*, E//*b*, and E//*c*, respectively. The characteristics of the ν_1 and ν_2 bands are given in Table 1. Weak bands near 20 000–23 000 cm^{-1} are related to Mn^{3+} spin-forbidden transitions. The small features at 23 680, 26 250, and 27 610 cm^{-1} are assigned to Fe^{3+} spin-forbidden transitions, from ${}^6\text{A}_1(\text{S})$ to ${}^4\text{E}$, ${}^4\text{A}_1(\text{G})$, ${}^4\text{T}_{2g}(\text{D})$, and ${}^4\text{E}_g(\text{D})$, respectively (Burns 1993; Vercamer et al. 2015). This is consistent with the presence of substitutional Fe^{3+} in the octahedral sites of Al^{3+} as shown by the EPR powder spectrum of our sample and XANES measurements (Online Materials¹ Figs. OM3 and OM4). The absence of crystal field transitions of Fe^{2+} , expected at 8000 and 11 600 cm^{-1} in euclase (Mattson and Rossman 1987), also indicates that iron only occurs as Fe^{3+} . The spectra show a strong UV absorption edge with a low-energy tail that rapidly falls off toward the visible range. It may arise from light scattering by optical heterogeneities (inclusions and fractures) and from the $\text{O} \rightarrow \text{Fe}^{3+}$ OMCT simulated by a Gaussian function centered at 40 000 cm^{-1} . This value is close to those determined in other studies on, e.g., planetary materials and glasses (Cloutis

et al. 2008; Vercamer et al. 2015).

Unpolarized optical spectra of the pink euclase in the A and B orientations, crystal section (001) and (010), respectively, are presented in Figure 2. The difference in position of the main Mn^{3+} bands is the origin of the orange to pink pleochroism (Online Materials¹ Fig. OM5).

The simultaneous pink and orange hues lead to the typical pink-orange coloration of euclase. The orange hue is related to the rising slope in the UV domain combined with an additional absorption at 24 000 cm^{-1} . The combination of the two transmission windows in the red and violet domains results in the pink coloration. As these two transmission windows are wider in the B orientation than in the A orientation, the pink coloration is more intense in the B orientation, leading to the observed pleochroism.

To quantify the color and pleochroism of the investigated euclase, the chromatic coordinates were calculated using unpolarized optical spectra to describe the color as observed with the naked eye (Fig. 3). The coordinates are overlaid onto the Commission Internationale de l'Eclairage (CIE) 1931 color space template and give the chromaticity (hue and saturation) of the color. The horse-shoe shape defines all visible colors. In its center, the white reference point enables the assessment of the color saturation, especially for thin samples. The colorimetric coordinates of euclase in the A and B orientations indicate a variation of color from orange to pink

TABLE 1. Position (ν), molar extinction coefficient (ϵ), width ($\omega_{1/2}$), and splitting magnitude of resolved Mn^{3+} spin-allowed transitions in polarized spectra of the pink euclase

Parameters	E// <i>a</i>	E// <i>b</i>	E// <i>c</i>	E⊥ <i>c</i>	E// <i>r</i>
ν_1 (cm^{-1})	18465	18453	18780	18804	18963
ϵ ($\text{L}/\text{mol} \cdot \text{cm}^{-1}$)	25.84	23.01	38.21	34.52	55.53
$\omega_{1/2}$ (cm^{-1})	2400	3200	2600	2400	2500
ν_2 (cm^{-1})	21246	21449	21000	21085	21000
ϵ ($\text{L}/\text{mol} \cdot \text{cm}^{-1}$)	33.11	27.28	30.66	29.17	28.47
$\omega_{1/2}$ (cm^{-1})	2400	3000	2600	2400	2400
Splitting (cm^{-1})	2781	2996	2220	2281	2097

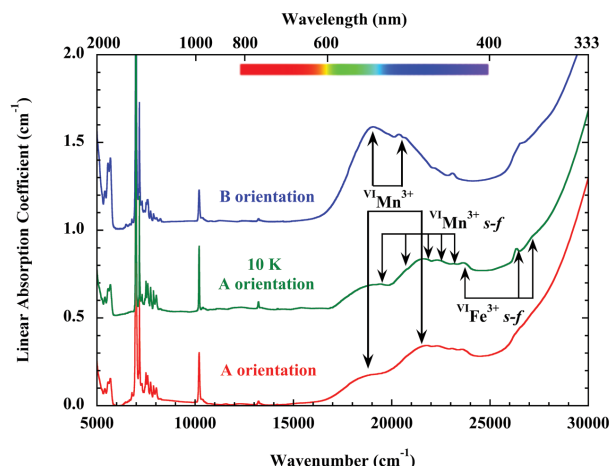


FIGURE 2. Unpolarized optical spectra of pink-orange euclase in the A and B orientations [crystal sections (001) and (010), respectively] and at 10 K in the A orientation with ($s-f$) the spin-forbidden transitions of Mn^{3+} and Fe^{3+} in octahedral site. (Color online.)

resulting from the pleochroism of the crystal. Comparison with another pleochroic Mn^{3+} -bearing mineral, pezzottaite (Rossmann 2021) (Fig. 3), shows a distinct pleochroism from pink-orange to pinkish purple, illustrating the original coloration of pink-orange euclase.

Crystal chemistry of Mn^{3+}

The ν_1 and ν_2 transitions of Mn^{3+} in euclase, at around 18 500 and 21 000 cm^{-1} , occur at similar positions as in grossular (17 302 and 19 504 cm^{-1} ; Geiger et al. 1999), beryl (17 900 and 20 000 cm^{-1} ; Czaja et al. 2018) or corundum (18 750 and 20 600 cm^{-1} ; McClure 1962). The splittings of the upper ${}^5\text{T}_{2g}$ term, related to site distortion, remain smaller in these minerals, 1850 to 2500 cm^{-1} , relative to the larger values observed in other minerals such as viridine and piemontite, 14 100 and 12 000 cm^{-1} , respectively (Burns 1993).

The five Mn^{3+} spin-forbidden transitions are well-resolved at 10 K (Fig. 2). According to the d^4 Tanabe-Sugano diagram, the transition at 19 500 cm^{-1} corresponds to the octahedral Mn^{3+} field-

independent transition ${}^5\text{B}_1(\text{D}) \rightarrow {}^3\text{E}(\text{H})$. The other transitions at 20 700, 21 125, 22 375, and 23 125 cm^{-1} also arise from transitions to field independent levels derived from the ${}^3\text{H}$, ${}^3\text{F}$, and ${}^3\text{G}$ states of octahedral Mn^{3+} , as observed in kyanite (Wildner et al. 2013), red beryl (Czaja et al. 2018; Fridrichová et al. 2018), or elbaite tourmaline (Kurtz et al. 2020).

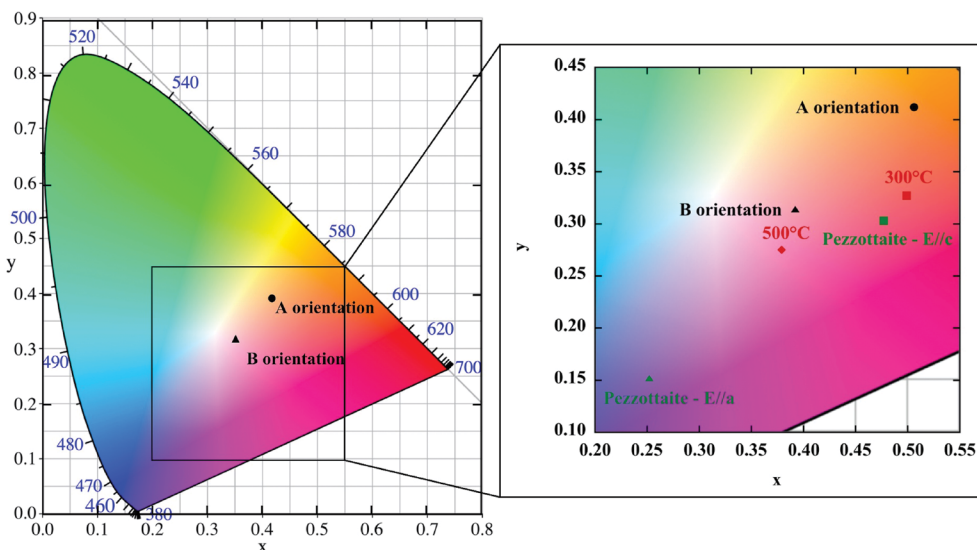
Using the barycenter calculation method, D_q parameter is calculated to be 2055 cm^{-1} . This value is among the highest recorded in Mn^{3+} -bearing minerals. The spin-forbidden, field independent ${}^5\text{B}_1(\text{D}) \rightarrow {}^3\text{E}(\text{H})$ transition at 19 500 cm^{-1} provides a way to calculate the Racah parameter $B = 886 \text{ cm}^{-1}$. This value is intermediate between that in corundum, 965 cm^{-1} (McClure 1962), and in beryl, 818–835 cm^{-1} (Czaja et al. 2018; Fridrichová et al. 2018), showing a variation in the covalent contribution of the Mn^{3+} -O bond in these minerals.

The crystal field stabilization energy (CFSE) for Mn^{3+} ions increases with the distortion of the site (Burns 1993; Hälenius 2004). The small CFSE value in euclase, 147 kJ/mol, is similar to the 130–152 kJ/mol values found for octahedral Mn^{3+} in beryl, corundum, garnet, or diopside, showing a slight distortion of the Mn^{3+} site (McClure 1962; Hälenius 2004; Czaja et al. 2018). Higher CFSE values of 185–200 kJ/mol reflect more distorted sites in andalusite, epidote, and tetragonal garnets (Abs-Wurmbach et al. 1981; Hälenius and Skogby 1996; Hälenius 2004).

The EPR data show the absence of Mn^{2+} . Thus, the molar extinction coefficient ϵ was directly calculated from the intensity of the Mn^{3+} absorption bands. The value of ϵ (Mn^{3+}) (Table 1) is similar to that found in hydrogarnets (5–50 $\text{L/mol}^{-1}\text{cm}^{-1}$; Hälenius 2004). As the removal of the center of symmetry relaxes the Laporte selection rule, ϵ increases with the distortion of the Mn^{3+} site (Smith et al. 1982); the values observed in euclase in the directions $E//a$, $E//b$, $E//c$, $E\perp c$ (23–8 $\text{L/mol}^{-1}\text{cm}^{-1}$) confirm a moderate distortion. The higher molar extinction coefficient value ($\sim 51 \text{ L/mol}^{-1}\text{cm}^{-1}$) in the r direction may be explained by a coupled substitution of Mn^{3+} in both octahedral adjacent Al^{3+} sites inducing a stronger distortion of the sites.

After isochronal heating from 300 to 500 $^{\circ}\text{C}$, the color changes to pure pink (Fig. 4). This modification of the color is also

FIGURE 3. Colorimetric representation of the pleochroism (in black) and the heat treatment effects (in red) of the pink euclase in the CIE color space chromaticity diagram (calculated from 380 to 780 nm optical spectra system Yxy with D_{65}) by comparison with the chromaticity values (in green) of pezzottaite (after the data of Rossmann 2021). (Color online.)



visible using the chromatic coordinates between 300 °C (pink-orange) and 500 °C (pure pink) (Fig. 3). The fit of the polarized optical spectra recorded at ambient temperature on the pristine sample indicates the presence of a Gaussian component around 24 000 cm^{-1} (Fig. 1). This component disappears after heating at 500 °C (Fig. 5). At the same time, the rising background toward the UV domain falls down. As a consequence, the transmission window between 23 000 and 25 000 cm^{-1} is enlarged, the orange hue disappears and the color of the crystal turns pure pink. This 24 000 cm^{-1} band, with a larger width than the ν_1 and ν_2 bands whatever the polarization, shows an intensification in the $E//b$ direction (Table 1). As no signal related to paramagnetic defect centers can be observed on the EPR spectrum, this thermally unstable band may be tentatively attributed to diamagnetic defects.

IMPLICATIONS

The absence of Mn^{2+} in the euclase investigated precludes a radiation-enhanced Mn-oxidation, often observed in other Mn^{3+} -bearing minerals and easily annealed at 350 °C giving colorless minerals (Laurs et al. 2003; Kurtz et al. 2020). Therefore, a stable pink color due to the presence of Mn^{3+} implies oxidative formation conditions. The euclase crystals occur in a hydrothermal vein hosted in a schist. Local oxidizing conditions are reflected by the presence of abundant large green andalusite (viridine) crystals in the schist (Online Materials¹ Fig. OM6), a well-known Mn^{3+} mineral (Hålenius 1978; Smith et al. 1982; Schnellrath 1989; Abs-Wurmbach et al. 1981). At a regional scale, epidote group minerals, hosting Mn^{3+} , and sericite are associated with plagioclase in the basement that includes the Brumado pluton (Teixeira et al. 2010). In the Brumado pluton, the Pedra Preta magnesite deposit also shows the presence of epidote, together with lepidolite (Bodenlos 1954). The Brumado pit has been recently reported to host pink euclase (<https://www.mindat.org/loc-192235.html>). As shown for the conditions of formation of gems in Rhodope (Tarantola et al. 2019), this may lead to the preservation of an oxidizing environment during the migration of the fluids in the São Francisco craton. A low-fluid/rock ratio during the whole geodynamic evolution and a Fe-

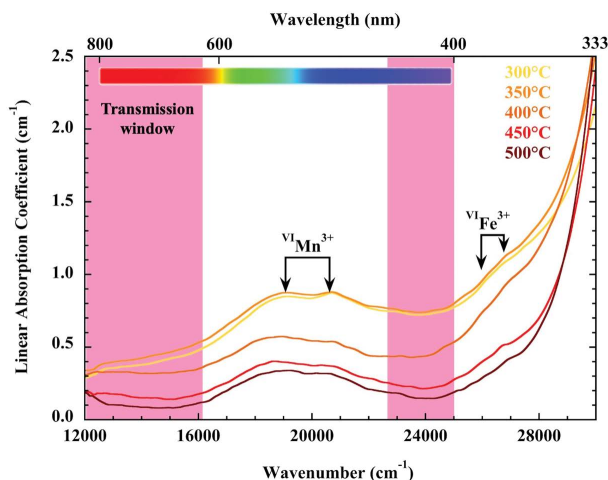


FIGURE 4. Optical microspectroscopic study of the isochronal in situ measurements between 300 and 500 °C of pink euclase in the B orientation. (Color online.)

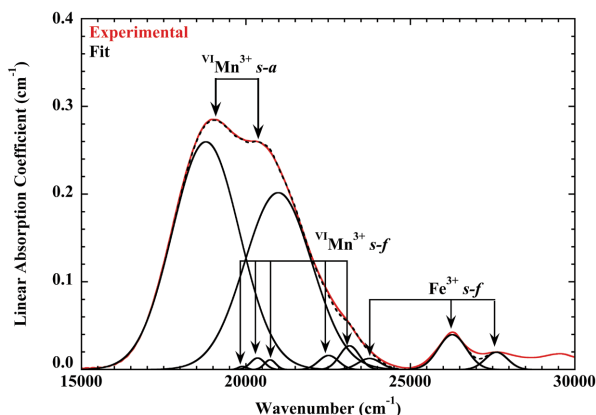


FIGURE 5. Curve resolved unpolarized optical spectrum at ambient temperature of euclase in the B direction after heat treatment (500 °C). The red curve is the experimental spectrum after subtracting a Gaussian baseline for the UV domain for the OMCT O → Fe^{3+} . The black curves are the fitted Gaussian contributions: two major components for the Mn^{3+} spin-allowed ($s-a$) transitions (18 784 cm^{-1} ; 20 983 cm^{-1}) and five minor components for Mn^{3+} spin-forbidden ($s-f$) transitions (19 900, 20 356, 20 737, 22 515, and 23 151 cm^{-1}) and three minor components for Fe^{3+} spin-forbidden ($s-f$) transitions (23 758, 26 276, and 27 615 cm^{-1}). The black dotted curve is the sum of the fitted components. (Color online.)

poor character of the hydrothermal fluid is necessary to buffer the oxygen activity to high levels and create adequate oxidizing conditions. These parameters have been invoked to explain the formation of Mn^{3+} bearing gems (Tarantola et al. 2019), among which is pink tourmaline (Laurs et al. 1998). In the present case, this will preserve the presence of Mn^{3+} during the contamination of hydrothermal fluids by the surrounding rocks, as suggested by the high-Ge content of the sample.

Indeed, the pink euclase investigated presents an unusual high-Ge concentration, 142 ppm. Germanium has also been detected in blue and colorless euclase from Minas Gerais, Brazil (Graziani and Guidi 1980) and, locally, a concentration of 97–105 ppm Ge was found in andalusite from Paramirim das Crioulas, located 20 km from Livramento de Nossa Senhora (Schnellrath 1989). This may indicate contamination of the hydrothermal fluids, by analogy with Colombian euclase, which presents also high-Ge contents (230–530 ppm; Pignatelli et al. 2017), an indirect indication of the contamination of the hydrothermal fluids by the surrounding host rock. An implication of these peculiar formation conditions is that redox conditions appear to govern the color of euclase. EPR and luminescence indicate the absence of Mn^{2+} . As shown by XANES, pink euclase contains iron only in the ferric form. By contrast, in blue euclase, the presence of Fe^{2+} , involved in a characteristic Fe^{2+} – Fe^{3+} IVCT in this mineral, indicates more reducing conditions. This makes euclase color an interesting indicator of the formation conditions.

Among pink-colored gemstones (topaz, tourmaline, garnets, beryls, etc.), the newly discovered pink-orange euclase presents an unusual hue and pleochroism that make it particularly attractive for collectors. The heat-treatment modifies the color from pink-orange to a stable pure pink coloration. In tourmaline, heating treatment results in the loss of almost all absorption features, leading to a colorless mineral. By contrast, in euclase, the Mn^{3+}

absorption bands are still observed in heated samples resulting in a stable pure pink coloration.

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