

# Colour-change Beryl from Brazil

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作者透過描述一顆來自巴西的變色綠柱石的化學及光譜特性及測試結果，描述該樣本的馬克西西型綠柱石色心及鐵鎂吸收帶。而該顆綠柱石的變色現象可能是因輻射處理及其後的漂色處理於日光下引至的色心非故意地做成。

## Abstract

The chemical and spectroscopic properties of a colour-change beryl from Brazil are given. The test sample reveals radiation induced Maxixe-type colour centres as well as iron- and manganese-related absorption bands. The phenomenal colour change was probably unintentionally produced by irradiation and subsequent bleaching of part of the radiation induced colour centres in daylight.

Phenomenal gemstones showing special optical properties such as chatoyancy or asterism are always of interest to gemmologists. Colour change between daylight and incandescent light is one of these extraordinary optical features. It was first described in chrysoberyl (alexandrite) in the 19<sup>th</sup> century, but later also in other gem

minerals such as sapphire, spinel, garnet, fluorite, tourmaline, diaspore, and kyanite (see, e.g. Gübelin and Schmetzer, 1982; Hänni, 1983). So a faceted beryl which revealed a colour change from daylight to incandescent light was submitted by a gem collector for examination to evaluate the cause of colour of this unusual gemstone.

The faceted beryl of 4.51 ct in weight (Fig. 1 a,b) was bought at the Munich mineral fair some years ago and was thought to have come, originally, from Minas Gerais, Brazil. The beryl showed a light yellowish green colouration in daylight with a distinct colour change to a somewhat more intense pink in incandescent light. Pleochroism was weak in daylight and incandescent light (daylight: light yellowish green parallel to *c*, light green perpendicular to *c*; incandescent light: light yellowish pink parallel to *c*, light pink perpendicular to *c*). Its gemmological properties such as a specific gravity of 2.71 and refractive indices of 1.572 - 1.580 of the optically uniaxial crystal were typical of beryl. Chemical examination by energy-dispersive X-ray fluorescence (EDXRF) showed traces of transition metal elements such as manganese and iron (0.02 wt. % MnO, 0.25 wt.% Fe<sub>2</sub>O<sub>3</sub>) to be present in the gemstone.



The stone's polarized absorption spectrum revealed absorption maxima at 555 and 426 nm in the spectrum parallel to the *c*-axis and maxima at 688, 642, 625, 555 and 370 nm in the spectrum perpendicular to the *c*-axis (Fig. 2). In addition, a continuously increasing absorption from about 500 nm to the ultraviolet was observed for rays both parallel and perpendicular to *c*.

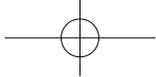
The weak absorption bands at 426 nm (parallel to *c*) and at 370 nm (perpendicular to *c*) are frequently observed in beryl and commonly assigned to trivalent iron (see, e.g., Wood and Nassau, 1968). The absorption bands at 688, 642, and 625 nm in the spectrum perpendicular to the *c*-axis are the strongest absorption bands of Maxixe-type colour centres (Nassau et al., 1976; Rink et al., 1990; Mathew et al., 1998, 2000). These colour centres are radiation induced  $\text{CO}_3^-$  radicals, which can be produced by the irradiation of  $\text{CO}_3^{2-}$ -bearing natural beryls from numerous localities. The Maxixe-type colour centres are unstable and fade upon exposure to light.

The continuously increasing absorption from about 500 nm to the ultraviolet is assigned to radiation induced yellow colour centres, which can be produced from iron-bearing beryls, which are more or less colourless. These colour centres reveal higher thermal stability than Maxixe-type colour centres, but are bleached upon heat treatment at about 400 °C (Rink et al., 1990; Mathew et al., 1998, 2000).

The absorption bands at 555 nm in the spectrum parallel and perpendicular to the

*c*-axis are assigned to manganese-related colour centres. Manganese-bearing natural and synthetic beryls including the new mineral pezzottaite, a cesium-rich member of the beryl family, reveal two different basic types of absorption spectra (Table 1). Although there are some variations in the positions of the absorption maxima given by different authors, two types of manganese-related absorption spectra are clearly distinguished, i.e. the spectra of the pink or orange pink morganite and pezzottaite and the spectra of natural and synthetic red beryl.

In the spectrum of our sample, the intense absorption maximum of morganite in the 480 nm range, with polarization perpendicular to the *c*-axis, is not observed and thus the spectrum is closer to that of red beryl. There are, however, some differences that have to be mentioned. In the spectrum of the colour changing beryl from Brazil, the absorption maximum in the spectrum parallel to the *c*-axis is observed at about 555 nm which is close to the position of the absorption maximum of red beryl. Our sample, however, did not reveal the typical shift of the position of the absorption maximum to about 540 nm in the spectrum, with polarization perpendicular to the *c*-axis, as reported by various authors (again, see Table 1). These differences might be due to radiation-induced manganese-related colour centres as mentioned by Solntsev (1981), who described the production of specific absorption bands with maxima at 525 nm (polarization  $\parallel c$ ) and at 485 nm (polarization  $\perp c$ ).



In summary, the spectrum of our sample consists of three different types of absorption bands which are assigned to a) Maxixe-type colour centres, b) iron-related, probably radiation-induced yellow colour centres and c) manganese-related transition metal absorption bands. Most probably, the sample is an irradiated, originally colourless or very light pink beryl (morganite). After bleaching part of the radiation-induced colour centres, especially part of the Maxixe-type colour centres in daylight, the sample showed an absorption spectrum with a manganese-related absorption maximum in the greenish-yellow of the visible range and two areas with higher transparency in the red and blue-green range. This type of absorption spectrum, probably unintentionally produced, is a typical feature of colour-change gemstones and is observed in many gem materials which reveal a distinct colour change between daylight and incandescent light.

At present, a high percentage of pink to orange-pink beryls (morganites) in the trade are treated by electron irradiation in Brazil or elsewhere in order to improve the natural colour, especially in order to increase the colour intensity of originally very light coloured specimens. It should be possible to detect at least some of the treated stones by careful examination of polarized absorption spectra in the visible and ultraviolet range (Schmetzer, unpublished data).

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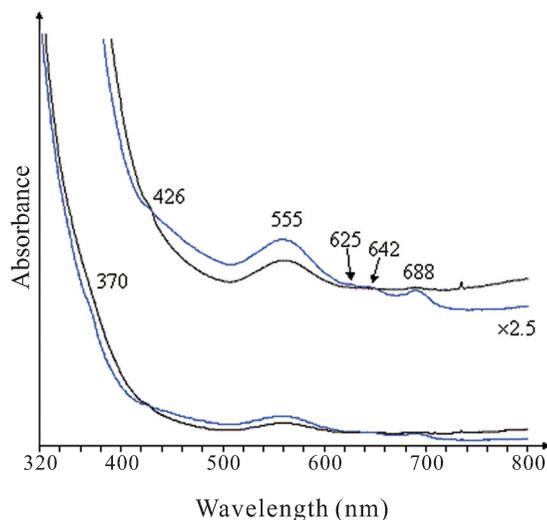


Fig. 1a



Fig. 1b

**Fig. 1 a, b** This faceted beryl of 4.51 ct in weight, size 13.0 x 7.8 mm, showed a distinct colour change from light green in daylight (a) to a somewhat more intense pink in incandescent light (b).



**Fig. 2** The polarized absorption spectrum (black  $\parallel$  c, blue  $\perp$  c) of the colour changing beryl from Brazil showed numerous absorption bands which are assigned to Maxixe-type colour centres, to manganese d-d transitions and to iron-related yellow colour centres (details see text).

**Table 1** Summary of spectroscopic properties of manganese-bearing natural and synthetic beryls.

Mineral name (variety)	Absorption maxima (nm)	Polarization	Intensity	References
Pink to orange pink beryl (morganite), pezzotaite	820 560 540 480	$\perp$ c $\parallel$ c $\perp$ c $\perp$ c	  560 > 540 480 > 540	Wood and Nassau (1968) Schmetzer et al. (1974a) Platonov et al. (1989) Laurs et al. (2003)
Natural red beryl, synthetic manganese-bearing red beryl	560 540 525* 490 485*	$\parallel$ c $\perp$ c $\parallel$ c $\perp$ c $\perp$ c	560 $\approx$ 540  shoulder	Nassau and Wood (1968) Schmetzer et al. (1974b) Solntsev (1981) Shigley et al. (1984) Platonov et al. (1989) Shigley et al. (2001) Laurs et al. (2003)

\* radiation-induced manganese-related colour centres