Optical spectroscopy study of variously colored gem-quality topazes from Ouro Preto, Minas Gerais, Brazil

Abstract

Variously colored gem-quality topazes from Ouro Preto, Minas Gerais, Brazil, were studied by optical absorption spectroscopy and photoluminescence methods. In the near infrared range ($\lambda \approx 750$–$2500$ nm) the absorption spectra display an identical pattern of narrow intense absorption lines caused by overtones and combination vibrations of OH groups, which do not relate to the coloration of the topazes studied. Their colors were found to be caused by combination of three sets of absorption features, (1), (2), and (3) in the visible and near-UV range, which are due to different color centers. (1) denotes a pair of broad split bands with maxima $\approx 18,000$ and $25,000$ cm$^{-1}$ caused by electronic spin-allowed $dd$ transitions of Cr$^{3+}$ ions. They cause a light rose to deep violet color and characteristic pleochroism of Cr$^{3+}$-containing topazes. Photoluminescence evidences of at least three different types of Cr$^{3+}$ complexes which, most probably, differ by ligand surroundings, $O_4F_2$, $O_4F(OH)$ and $O_4(OH)$ (2) Corresponds to the intense weakly polarized UV absorption edge. Two different parts, the thermally stable one, caused by ligand-to-metal charge transfer, and the thermally unstable one, caused by some defect center(s), contribute to the edge. (3) denotes a system of two broad unstructured bands with maxima around $19,000$ cm$^{-1}$ ($X > Y = Z$) and $24,000$ cm$^{-1}$ ($Y = Z \gg X$). They cause the unique orange color and characteristic pleochroism of Brazilian Imperial topazes. Combinations of (1) and (3) absorption features cause various yellow-rose colors of the samples. Investigations of natural irradiated and thermally treated topazes show that the color centers (1) and (3) transform to each other at annealing and X- or gamma irradiation. The color of natural orange-red Imperial topazes is assumed to be caused by Cr$^{4+}$, stabilized by other impurity ions and/or defect irradiation EPR centers. At $T = 300$ K Cr$^{4+}$ reduces to Cr$^{3+}$, the color of Imperial topazes changes to pale rose, caused by spin-allowed bands of Cr$^{3+}$. In artificially irradiated crystals the (3)-center, Cr$^{4+}$, may be induced according to the reaction $2\text{Cr}^{3+} \rightarrow \text{Cr}^{4+} + \text{Cr}^{2+}$, which involves chromium pairs in adjacent Al sites of the structure. Such artificially induced color is unstable at room temperature and in daylight. The processes of the decay of (3)-centers may be described as a recombination $\text{Cr}^{4+} \rightarrow \text{Cr}^{2+}$ that results in vanishing of the (3)-bands accompanied by the appearance or increase in Cr$^{3+}$ $dd$ bands, the original orange color turning to a pale rose.

Keywords

Topaz · Chromium · Optical absorption spectra · Luminescence · Radiation centers

Introduction

Topaz, $\text{Al}_2(\text{F,OH})_2\text{SiO}_4$, is a typical mineral whose color is caused rather by irradiation-induced color centers than by electronic $dd$ transitions of transition metal ions. In nature, topaz is frequently found as large gem-quality
crystals of various colors, which often can be changed by irradiation and/or thermal treatment. Color centers of different types and in different combinations occur in natural topazes so that almost all color varieties can be found. Large dimensions, high crystal quality, attractive colors, and relatively low prices make natural and treated topazes a very popular gemstone.

The color of natural topazes has been the subject of many spectroscopic investigations (see Schott et al. 2003 and the literature cited therein). However, a convincing interpretation of the color varieties is still open, except for the pink color of chromium-bearing topazes, where the color is proved to be caused by electronic dd transitions of Cr$^{3+}$. Unique orange-red Brazilian topazes, also frequently called Imperial topaz (e.g., Rolff 1971; Kievenko et al. 1982) are one of the most prized natural topazes. Until now, only a few publications have been devoted to spectroscopic studies of this topaz variety (Dickinson and Moore 1967; Petrov 1977, 1978; Petrov et al. 1977, Platonov et al. 1984). The color of these special topazes can be enhanced by irradiation and bleached by annealing. A recent EPR study of orange-red Imperial topaz by Schott et al. (2003) revealed two electron centers, both having thermal behavior similar to that of the optical absorption bands responsible for the color. In this work we studied differently colored topazes from Ouro Preto, Brazil, by optical absorption and photoluminescence measurements. The aim was to elucidate further the nature of color in topazes.

**Characterization of the topazes investigated**

The topazes were up to a few cm long, and about 1 cm thick, of high crystal quality with well-developed prismatic habit. Five differently colored samples were selected for investigation. From the Saramenha deposit (e.g., Sauer et al., 1996) a light violet topaz, K1, an orange-red topaz, K3, and two yellowish rose topazes, K2 and K4, were taken and from the Rodrigo Silva deposit a colorless topaz, K5. A deep violet chromium-bearing topaz from Kamenka River (Ural/Russia) previously studied by Taran et al. (1994) was also included in the investigation for reference. Each crystal was cut in an oriented rectangular parallelepiped. They were ground and polished so that polarized optical absorption spectra could be measured along the principal axes of the optical indicatrix, $X||a$, $Y||b$ and $Z||c$. The orientation within an error of $\pm 5^\circ$ was accomplished according to the external forms of the crystals and controlled by conoscopic observation under a polarization microscope. Thickness of the samples was measured by a micrometer screw, and varies from 1.5 to 3 mm.

**Results and discussion**

The microprobe compositions of the Brazilian topazes show that they are all rather pure materials: the content of each impurity metal oxide does not exceed 0.0 wt% (Table 1), which is near the detectable limit of the electron microprobe. Nevertheless, the lower concentration of transition metals as Ti and Cr in the colorless topaz K5, when compared with the colored samples K1–K4, seems evident. The Ural topaz shows a relatively high concentration of chromium, 0.36 wt% Cr$_2$O$_3$, nearly one order of magnitude higher than the Brazilian topazes K1–K5.

The fluorine content in all Brazilian topazes is about 12 wt%. This is much lower than the theoretical value of 20.6 wt% of pure Al$_2$F$_5$SiO$_4$ and shows significant F$\rightarrow$OH substitution.

The optical absorption spectra of the studied topazes are significantly different in the visible range, 330–750 nm.