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Optical absorption of electronic Fe-Ti charge-transfer transition in natural andalusite: The thermal stability of the charge-transfer band

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Abstract

Differently-colored natural Brazilian andalusite crystals heat-treated under reducing and oxidizing conditions were analyzed by optical spectroscopy. The intensity of a broad intense band at around 20500 cm^{-1} in the optical absorption spectra of all color zones of the sample is proportional to the product of Ti- and Fe-concentrations and herewith proves its attribution to electronic $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT transition. The band is strictly $\mathbf{E}\|\mathbf{c}$ -polarized, causing an intense red coloration of the samples in this polarization. The polarization of the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band in andalusite, $\mathbf{E}\|\mathbf{c}$, shows that the electronic charge-transfer process takes place in Al-O octahedral groups that share edges with neighbors on either side, forming chains parallel to the $\mathbf{c}$ -axis of the andalusite structure. Under thermal treatments in air, the first noticeable change is some intensification of the band at 800°C . However, at higher temperatures its intensity decreases until it vanishes at 1000°C in lightly-colored zones and 1100°C in darkly-colored ones. Under annealing in reducing conditions at 700°C and 800°C , the band also slightly increases and maintains its intensity at treatments at higher temperatures up to 1000°C .

These results demonstrate that weakening and disappearance of the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band in spectra of andalusite under annealing in air is caused by oxidization of Fe^{2+} to Fe^{3+} in IVCT $\text{Fe}^{2+}/\text{Ti}^{4+}$ -pairs. Some intensification of the band at 800°C is, most probably, due to thermally-induced diffusion of Fe^{2+} and Ti^{4+} in the structure that leads to aggregation of “isolated” Ti^{4+} and Fe^{2+} ions into $\text{Fe}^{2+}\text{-Ti}^{4+}$ -pairs. At higher temperatures, the competing process of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation overcomes such “coupling” and the band continues to decrease. The different thermal stability of the band in lightly- and darkly-colored zones of the samples evidence of some self-stabilization over an interaction of $\text{Fe}^{2+}/\text{Ti}^{4+}$ -pairs involved in IVCT process.

Key words: andalusite, optical absorption spectra, intervalence charge-transfer, redox behavior

Introduction

Electronic intervalence charge-transfer transitions (IVCT) of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}^{2+}/\text{Ti}^{4+}$ type are common phenomena in oxygen-based minerals, strongly influencing their color and pleochroism. As established by numerous investigations (e.g. Burns 1993 and the relevant references within), IVCT is intrinsic to structurally-adjacent transition metal ions of variable valence that form pairs or, occasionally, larger structural aggregates regarded in such cases as single quantum-mechanic systems (Sherman 1987a, b; Grodzicki and Amthauer 2000). At electromagnetic or thermal excitation, electronic transitions take place accompanied by a momentary change of valence or, in other words, an oscillation of valence between the two transition metal ions involved in the IVCT process. Such transitions are seen in optical absorption and, sometimes, in Mössbauer spectra of such minerals and compounds as distinct spectroscopic features.

As far as we are aware, just very few works were devoted to the investigation of the thermal stability of ion pairs involved in IVCT processes in crystal structures (Eigenmann and Günthard 1972, Eigenmann et al. 1972, Ignatov et al. 1990, Goreva et al. 2001). In synthetic Fe and Ti doped corundum, for instance, Eigenmann and Günthard (1972) and Eigenmann et al. (1972) gave strong evidence for the existence of biparticles $(\text{Fe}, \text{Ti})^{6+}$ involved in electronic charge-transfer processes, and for their high temperature redox behavior. For microinclusions of dumortierite in rose quartz, Goreva et al. (2001) also found that oxidation and reduction of iron ($\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$) in Fe-Ti IVCT centers are responsible for changes in dumortierite fiber color and absorption spectra. Very likely, a similar situation takes place, in Al_2SiO_5 polymorphs, kyanite, sillimanite and andalusite, in which structures adjacent AlO_6 -octahedra appropriate for the formation IVCT pairs are also present. In this paper, the results of optical absorption spectroscopy of natural Fe- and Ti-containing Brazilian andalusite, the thermal stability of its $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT absorption band, and the andalusite coloration are discussed.

Experimental details

Samples preparation

Elongated prismatic gem-quality andalusite crystals from an unspecified location in Brazil were used for the investigations. Orientation was accomplished using perfectly-developed prismatic {110} crystal faces and checked by conoscopic observation with a polarizing microscope. Initially, a sample for optical absorption spectroscopic measurements was prepared as a rectangular prism of thickness 2.41 mm and 3.52 mm along crystallographic **b**- and **a**-direction, respectively, polished on four sides. In unpolarized transmitted light, the sample displayed a strange color, distributed as irregular intermittent darker and lighter zones (Rossman 2009). In **E**||**a**- and **E**||**b**-polarizations, the sample was homogeneously pale greenish-yellow, whereas in **E**||**c**-polarizations it acquired irregularly-distributed dark-red to very dark-brown-red color in the light and dark zones, respectively (Rossman 2009). This sample was used for measuring **E**||**a**- and **E**||**b**-polarized optical absorption spectra and determination of its composition by microprobe and plasma emission spectrometry (ICP) in four points: two dark and two light zones. However, the sample was too thick and dark to get a high-quality **E**||**c**-polarized spectrum in the visible range.

To measure a spectrum in **E**||**c**-polarization, the sample was thinned along the **a**-axis. During thinning, the color of the sample was curiously changed, acquiring more reddish tints. At a thickness of 0.79 mm, the light zones acquired red color whereas the dark ones still retained their grayish color. An **E**||**c**-spectrum of the light zone was measured at this thickness of the sample (Fig. 1a). Further, a fragment of it, having been thinned down to 0.28 mm, in the dark zones became red, whereas in the light ones it turned to pink. A high-quality **E**||**c**-spectrum of the dark zone (Fig. 1b) was acquired on this 0.28 mm thin sample.

Thermal treatments at oxidizing and reducing conditions were carried out on two fragments of a polished plate of thickness 0.49 mm cut off along the **c**-axis of a zoned andalusite crystal. The orientation of the plate was strictly parallel to **c**-axis and close to the **ac**-plain.

Spectroscopic measurements

Optical absorption spectra were measured at room temperature in the range 350-1800 nm (ca. $28570\text{-}5555\text{ cm}^{-1}$) with a single-beam microspectrophotometer constructed from a SpectraPro-275 triple grating monochromator, a highly-modified polarizing mineralogical microscope MIN-8 supplemented with Tomson-Glan polarizing prism, and an IBM PC. Two achromats $4.7\times$ served as objective and condenser. Changeable photoelectric multiplying tubes and cooled PbS-cell were used as photodetectors. A mechanical high-stabilized 300 Hz-chopper and lock-in amplifier were applied to improve the signal/noise ratio. The spectra were scanned with steps $\Delta\lambda=1\text{ nm}$, 2 nm and 5 nm in the range 330-450, 450-1000 and 1000-1750 nm, respectively. The spectral slit width did not exceed 1 nm in the whole range studied. The diameter of the measuring spot was not larger than $500\text{ }\mu\text{m}$. All spectra are normalized to 1.0 cm thickness. The resultant linear absorption coefficient was then plotted versus the wavenumber. To evaluate energy, peak intensity and half-widths of the bands, Peakfit 4.0 (Jandel Scientific) software was used to fit the spectra with Gaussian curves after they were converted to linear wavenumber scale. Band shapes were assumed to be Gaussian. The absorption background was fitted by a combination of Gaussian and Lorenz.

The orientation of the sample was controlled optically on the XY-stage of the microscope supplemented with a rotation table, using crossed polarizers.

Thermal treatment

Thermal treatment in oxidizing conditions was performed in air at temperatures from 500 to 1100°C in a horizontal tube furnace powered by an electronic device providing a temperature stabilization of $\pm 5^{\circ}\text{C}$. Thermal treatment in reducing conditions was carried out in a similar way in a gas flow of a mixture of Ar with 5% H_2 at temperatures from 700 to 1000°C in a horizontal tube furnace powered by an electronic device providing temperature stabilization of $\pm 1^{\circ}\text{C}$ (Table

1). Oxygen fugacity (f_{O_2}) was monitored by a zirconia-based solid electrolyte oxide sensor from Ceramic Oxide FabricatorsTM. The outputs of the temperature and oxygen fugacity were controlled with a sensor without interruption during the experiments and stored in a computer. In both temperature treatments, the annealing was carried out in 100°C steps in three stages. First, the furnace was warmed up to the desired temperature and stabilized. Then the sample was inserted into the furnace for 120 minutes. After that time it was moved out from the furnace and freely cooled on air down to the room temperature.

Results

Composition of the sample

Aside the main oxides, $SiO_2 = 36.22$ wt. % and $Al_2O_3 = 63.31$ wt. %, in all differently-colored zones the microprobe analyses revealed an admixture of iron of around 0.35 wt. % when calculated as FeO and traces of titanium. Concentrations of all other elements typical for natural andalusite, Cr, V and Mn, were found to be lower than the detection limits.

The results of the Fe and Ti quantification by ICP-MS in four points are shown in Table 2. As seen, the darker zones are obviously enriched in both Fe and Ti compared to the light ones¹.

Optical absorption spectroscopy

Polarized spectra of the natural andalusite, measured in the light and dark zones (point 3 and 4, respectively (Table 1)), are shown in Figs. 1, **a** and **b** respectively. The spectra obtained closely resemble the spectra of natural andalusite from Brazil that were published by Faye and Harris (1969). As seen from the Figure, in the near UV-range in $E||a$ - and $E||b$ -polarization they consist of a high-energy absorption edge ($E||b > E||a$) with a superimposed weak shoulder at around 25000 cm^{-1} . Together with a weak, relatively-broad band at $\sim 14000\text{ cm}^{-1}$ ($E||a \approx E||b$), this causes slightly different coloration in polarized transmitted light: light-yellow-green at $E||a$ and

¹ Distinct marks of material evaporation produced by ICP on the polished surface of the sample were further used as targets for repeating spectroscopic measurements in the chosen areas after a series of subsequent annealing experiments.

light-greenish-yellow at $\mathbf{E}||\mathbf{b}$. Furthermore, the $\mathbf{E}||\mathbf{b}$ -spectrum is complicated by weak and narrow peaks at ca. 22000 cm^{-1} and 22900 cm^{-1} , which are almost unperceivable in $\mathbf{E}||\mathbf{a}$ -polarization. Note that due to the scale chosen, these two latter absorptions are not seen in Figure 1.

The main feature of the $\mathbf{E}||\mathbf{c}$ -spectrum is a broad and intense absorption band with a maximum at around 20500 cm^{-1} , which together with the high-energy edge causes a dusk red color in this polarization. The hard-to-describe color of andalusite in ordinary unpolarized light is, thus, a blend of this dusk red color with the light yellow-green and the greenish-yellow colors of $\mathbf{E}||\mathbf{a}$ - and $\mathbf{E}||\mathbf{b}$ -polarizations. In a thick enough sample, the band at 20500 cm^{-1} ($\mathbf{E}||\mathbf{c}$) covers almost the entire visible range and the observed grayish color of the sample (Rossman 2009) is, therefore, a blend of this dusk reddish radiation passed through the sample in $\mathbf{E}||\mathbf{c}$ -polarization with bright, weakly-colored radiation passed through the sample in $\mathbf{E}||\mathbf{a}$ - or/and $\mathbf{E}||\mathbf{b}$ -polarization. In thin samples, a reddish coloration appears due to the red color of the $\mathbf{E}||\mathbf{c}$ -beam mixed with the greenish, nearly-colorless $\mathbf{E}||\mathbf{a}$ - and $\mathbf{E}||\mathbf{b}$ -polarized light. Due to the variable intensity of the broad absorption band at $\sim 20500\text{ cm}^{-1}$ in $\mathbf{E}||\mathbf{c}$ -polarization, the observed color zonation of the sample is thus caused by an irregular distribution of this red color. As seen from Fig. 1b, the intensity in the dark zone (point 4) is about four times higher than in the light zone in point 3 (Fig. 1a), whilst the spectra in $\mathbf{E}||\mathbf{a}$ - and $\mathbf{E}||\mathbf{b}$ -polarization practically do not vary from zone to zone. Note that in the $\mathbf{E}||\mathbf{c}$ -polarized spectrum of the dark zone, there is also a distinct absorption feature at around 11100 cm^{-1} superimposing the low-energy wing of the broad intense band at $\sim 20500\text{ cm}^{-1}$ (Fig.1b).

The curve-fitting procedure applied to the $\mathbf{E}||\mathbf{c}$ -polarized spectrum of the light zone (point 3) reveals that aside from the main band at 20500 cm^{-1} , at least two weaker Gaussian components at around 14450 cm^{-1} and 24900 cm^{-1} are necessary for a satisfactory fitting (Fig. 2a). These bands are close in energy and width to those seen in the initial $\mathbf{E}||\mathbf{a}$ - and $\mathbf{E}||\mathbf{b}$ -spectra

(cf. Fig. 1), In the $\mathbf{E}||\mathbf{c}$ -polarized spectrum of the dark zone, an additional weak Gaussian at $\sim 12000\text{ cm}^{-1}$ is necessary for a satisfactory fitting (Fig. 2b).

The thermal behavior of the color center, causing the band at $\sim 20500\text{ cm}^{-1}$ ($\mathbf{E}||\mathbf{c}$), is essentially different under oxidizing and reducing conditions. At oxidizing conditions, the thermal behavior of the band is different in the light and dark zones of the sample (Fig. 3). Plots of the relative linear intensity of the band in question derived by the curve-fitting procedure (cf. Fig. 2) vs. annealing temperature in air are shown in Figs. 4 **a**, **b** for the light and the dark zone, respectively. As seen, the band is stable at temperatures lower than ca. 700°C : annealing of the initial sample for tens of hours at 500°C and 600°C does not induce any perceivable changes in the spectra. Only annealing at 700°C produces a distinct decrease of the band intensity at points 3 and 4 (Fig. 4). Very remarkably, in both points further annealing at 800°C causes a relatively weak but distinct intensification of the 20500 cm^{-1} band. Heating at 900°C induces a further decrease: in the light zone the band decreases to nearly one third of its initial intensity, while in the dark zone it decreases much less, only $\sim 90\%$ of the initial value. During heating at 1000°C in the light zone, the band completely vanishes, and the material becomes colorless. In the dark zone, it still retains up to 22% of its intensity. In this zone the material still has a relatively weak but quite distinct reddish coloration. As was observed in the dark zone of the sample annealed at 1000°C , a long subsequent annealing at lower temperature, 800°C , does not affect the intensity of the residual band in any noticeable way. However, further annealing at 1100°C removes it completely in the dark zone, and the whole sample becomes perfectly transparent and colorless. Note that in the light zone, the intensity of the high-energy absorption edge slightly increases with annealing, but in the dark one it remains practically unchanged (cf. Fig. 3, a and b).

In contrast to the results of the oxidizing treatment, in spectra of heat-treated andalusite at reducing conditions, the band at $\sim 20500\text{ cm}^{-1}$ ($\mathbf{E}||\mathbf{c}$) slightly increases with heating to 700 and 800°C . During further annealing at 900 and 1000°C for 2 hours, its intensity remains practically unchanged (Fig. 5). This behavior is consistent for both the light- and dark-colored zones.

Discussion

MacDonald and Merriam (1938) investigated the composition of pegmatitic andalusite from Fresno County, California. In their thin sections, there was alternation of light and dark material of pleochroic colors similar to what is seen in our sample. By wet analysis, the compositions of the lightest and darkest varieties differ mostly in the Fe content (wt %): $\text{Fe}_2\text{O}_3 = 0.51$ and 2.44 , and $\text{FeO} = 0.62$ and 0.42 , respectively. Ti, however, was not detected, and is thus below the detectable limit. On this basis, the authors concluded that the differences in the optical properties between the light and dark varieties are caused by the variations in Fe^{3+} content.

First, the broad $\mathbf{E} \parallel \mathbf{c}$ -polarized band at 20500 cm^{-1} in the andalusite spectrum was attributed to $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ IVCT (Faye and Harris 1969), but further such bands in spectra of many terrestrial oxygen-based minerals, including that in andalusite (Smith and Strens 1976; Smith 1977), were re-assigned to $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT type. In andalusite, the temperature behavior of this band (Smith 1977) is in agreement with its attribution to electronic $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT transition (cf. Taran and Langer 1998). Judging from the Fe- and Ti-contents of variously-colored zones of the andalusite sample studied (Table 2), this assignment is well proved quantitatively. The dark zones in the band in question are much more intense than the light ones, and are considerably enriched with Ti^{4+} and, especially, with Fe^{2+} . Concentration of Fe^{2+} - Ti^{4+} -pairs involved in the IVCT process is believed to be proportional to the product of the Fe- and Ti-concentrations (Smith and Strens 1976; Mattson and Rossman 1988). When the products of Fe- and Ti-concentrations in point 3 and 4 of the andalusite studied (Table 2) are compared with the intensity of the band in $\mathbf{E} \parallel \mathbf{c}$ -spectra measured in the vicinities of these two points (Fig.1), the ratio of the linear intensities is ~ 4.0 , while a ratio of the $\text{Fe} \times \text{Ti}$ -products in them is ~ 3.9 . This is a good quantitative confirmation of the band's assignment to electronic $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT transition. Assuming that all titanium atoms neighbor Fe^{2+} and, thus, all are involved into IVCT processes, the molar absorptivity of the band at 20500 cm^{-1} in $\mathbf{E} \parallel \mathbf{c}$ -polarized spectrum (Fig. 1), can be evaluated using the expression

$$\varepsilon = k_{\alpha} \cdot V_{\text{el}} \cdot N_L / 1000 \cdot n \cdot Z,$$

where k_{α} is the linear absorption coefficient equal to $\log(I_0/I)/t$ at the band maximum determined from the curve-fitting analysis, with thickness t in cm, V_{el} the unit-cell volume in $[\text{cm}^3]$, N_L Avogadro's number, n the number of donor-acceptor contacts pfu, and Z the number of formula units per unit cell (Platonov et al. 2000). This calculation gives $\varepsilon \approx 7000 \text{ mol}^{-1}\text{cm}^{-1}$, which is much higher than that estimated by Mattson and Rossman (1988) for stoichiometric Fe, Ti-bearing minerals, but commensurable with the molar absorptivity of $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT bands in blue and red varieties of Fe, Ti-bearing dumortierite (Platonov et al. 2000). Strict polarization of the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band in andalusite, $\mathbf{E} \parallel \mathbf{c}$, demonstrates that the electronic charge-transfer process takes place in Al-O octahedral groups that share edges with neighbors on either side, forming chains parallel to the $\mathbf{c}$ -axis of the andalusite structure.

A weak broad band appearing in all three polarizations at around 14500 cm^{-1} (Figs. 1, 2), as well as a relatively broad shoulder at 25000 cm^{-1} and a couple of weak narrow peaks at ca. 22000 cm^{-1} and 22900 cm^{-1} , were all attributed by Faye and Harris (1969) to spin-forbidden dd -transitions of $^{\text{VI}}\text{Fe}^{3+}$ substituting Al^{3+} . However, this assignment looks now rather questionable when compared with spectra of $^{\text{VI}}\text{Fe}^{3+}$ -bearing minerals such as grossular, andradite, epidote, chrysoberyl etc. (e.g. Burns 1993 and relevant references within, Taran and Langer 2000). The broader feature at ca. 25000 cm^{-1} is probably caused by spin-forbidden transition of Fe^{3+} (very likely, $^6A_{1g} \rightarrow ^4A_{1g}, ^4E_g$), whereas the sharp peaks at $\sim 22000 \text{ cm}^{-1}$ and $\sim 22900 \text{ cm}^{-1}$ ($\mathbf{E} \parallel \mathbf{b} > \mathbf{E} \parallel \mathbf{a}$, Fig. 1) are more likely due to spin-allowed transitions of Fe^{2+} .

Taking into account that Brazilian andalusites with similar iron contents to those studied here have $\text{Fe}^{2+}/\text{Fe}^{3+}$ on the order of one (Meisel et al. 1990) and that the oscillator strengths of electronic spin-allowed transitions are a few orders of magnitude higher than those of spin-forbidden ones (e.g. Burns 1993), it seems quite reasonable to assign the weak broad band at 11900 cm^{-1} to electronic spin-allowed dd -transition $^5T_{2g} \rightarrow ^5E_g$ of $^{\text{VI}}\text{Fe}^{2+}$. This band is distinct in the $\mathbf{E} \parallel \mathbf{c}$ -spectrum of the dark zones of the sample that are relatively enriched with iron (cf. Fig.

1, **a** and **b**). The energy of the band is noticeably higher than that of the spin-allowed bands of $^{IV}\text{Fe}^{2+}$ in Mg, Fe^{2+} -silicates (e.g. Burns 1993). This may be due to the fact that in the andalusite structure, Fe^{2+} substitutes for Al^{3+} in octahedral sites that are smaller than those in the Mg, Fe^{2+} -silicates, where they substitute for larger Mg^{2+} (octahedral ionic radius of Al^{3+} and Mg^{2+} is 0.535 Å and 0.72 Å, respectively). Because the crystal field should be stronger in the smaller octahedral site, this can explain the higher energy of the spin-allowed band of $^{VI}\text{Fe}^{2+}$ in the andalusite spectrum compared to these bands in spectra of iron-magnesium silicates (cf. e.g. Burns 1993).

The weak, very broad band at $\sim 14000\text{ cm}^{-1}$ ($\mathbf{E}||\mathbf{c} \gg \mathbf{E}||\mathbf{b} \approx \mathbf{E}||\mathbf{a}$) which, according to the curve-fitting analysis is more intense in the dark than in the light zone (Fig. 2), can be assigned to $\text{Fe}^{2+}/\text{Fe}^{3+}$ IVCT.

The long-timed annealing in air at 500 and 600°C induced no effect on the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band (see Result). This is consistent with observation of Rozenson and Heller-Kallai (1980) who detected no change in Mössbauer spectra of natural andalusite from Hondo Canyon, New Mexico, of Fe_2O_3 content 2.09 % on heating during 21 days at 600°C. Note, however, that in the andalusite sample, studied by those authors, no Mössbauer spectroscopic features, which can be assigned to Fe^{2+} , were revealed, whereas in our samples should be a certain amount of Fe^{2+} , at least those, involved in $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT pairs (see also Meisel et al. 1990, who revealed some Fe^{2+} features in Mössbauer spectra of Brazilian andalusite similar to ours).

The results of thermal treatments in oxidizing and reducing conditions at 700°C and higher temperatures (see Results) inevitably prove that the thermal bleaching of andalusite, caused by the decrease down to disappearance of the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band at annealing in air, is due to oxidization of Fe^{2+} in the $\text{Fe}^{2+}\text{-Ti}^{4+}$ IVCT pairs. A similar conclusion was reached by Eigenmann and Günthard (1972) and Eigenmann et al. (1972), who used redox treatments in O_2 and H_2 gas flow at 1600°C of synthetic Fe- and Ti-doped sapphires. This authors admitted

existence of bi-particles $(\text{Fe}, \text{Ti})^{6+}$ in the corundum structure. Also, they concluded that the Fe-Ti interaction is very probably strong in the reduce state $(\text{Fe}, \text{Ti})^{6+}$, but weak or lifted in the oxidized state $(\text{Fe}^{3+}, \text{Ti}^{4+})$. We assume that a similar situation may exist in andalusite, which structure consists of chains of AlO_6 -octahedra arranged parallel to the c-axis with pairs of octahedra sharing a common edge.

The most interesting aspect is that the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band obviously behaves differently at oxidation conditions in dark and light zones, displaying a noticeably higher thermal stability in the former than in the latter. Because the dark and light zone's material differs mostly by different concentrations of iron and titanium and therefore by different intensity of the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band at 20500 cm^{-1} (see Result section and also Table 1), we consider this circumstance as an evidence of a self stabilizing effect of $\text{Fe}^{2+}\text{-Ti}^{4+}$ pairs involved in IVCT process. The nature of such phenomenon is unclear, but it seems that some kind of interaction exists between $\text{Fe}^{2+}\text{-Ti}^{4+}$ pairs, increasing with concentration of the pairs and increasing their stability against thermally-induced oxidation. It could be of a similar nature, but of relatively longer distance action, as the interaction between iron and titanium cations in $(\text{Fe}, \text{Ti})^{6+}$ -bi-particles in the corundum structure (Eigenmann and Günthard 1972, Eigenmann et al. 1972).

Also interesting is the dependence of intensity of the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band on the annealing temperature at oxidizing conditions, namely, its remarkable enhancement at heating at 800°C . This effect is stronger in the light than in the dark zone (Fig. 4). As this is the very first observation of this kind on minerals, we presumably explain it by thermally-induced diffusion of Fe^{2+} and Ti^{4+} in the andalusite structure. If, as we assume (see above), $\text{Fe}^{2+}\text{-Ti}^{4+}$ IVCT pairs are more preferable and more stable structural units than “isolated” Fe^{2+} and Ti^{4+} cations, this may facilitate aggregation of the latter into $\text{Fe}^{2+}\text{-Ti}^{4+}$ -pairs and, therefore, the intensification of the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band at 20500 cm^{-1} . At 900°C and higher temperatures the oxidation process $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, competing with such Fe^{2+} , Ti^{4+} -aggregation, causes the diminishing down to complete disappearance of $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band and turning up the zoned colored sample to a

homogeneously colorless state. It is remarkable that at reducing conditions the intensity of the IVCT band also increases (mostly at 800°C, see Fig. 5) which again is partly due to Fe^{2+} , Ti^{4+} -aggregation. But now, due to low oxygen fugacity (Tab. 1), the process of aggregation is not competed by $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation. As a result, the intensity of the band retains or even slightly increases under annealing at temperatures up to 1000°C. It should be noted that together with the Fe^{2+} , Ti^{4+} -aggregation the intensification of the IVCT-band on thermal treatment in reducing atmosphere may partly be due also to reduction of some of the original Fe^{3+} cations, neighbouring Ti^{4+} , to Fe^{2+} .

To finish, it should be emphasized that by our preliminary observations the established redox behaviors of the $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT band in andalusite studied are closely related to hydroxyl-bearing defects and their transformations at annealing in oxidation and reducing conditions. However, this is not a subject of the present study and needs further detailed investigations.

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Captions for Figures

Fig. 1. Polarized optical absorption spectra of natural andalusite: **a** – lightly-colored zone (point 3, Tab. 2); **b** – darkly-colored zone (point 4).

Fig. 2. Results of the curve fitting procedure of **E||c**-polarized spectra of natural andalusite: **a** – a lightly-colored zone; **b** – a darkly-colored zone.

Fig. 3. Effect of thermal annealing at oxidation conditions on air to **E||c**-polarized spectra of andalusite: **a** – a lightly-colored zone; **b** – a darkly-colored zone.

Fig. 4. Dependence of linear intensity of the **E||c**-polarized $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT absorption band at 20500 cm^{-1} in spectra of andalusite on temperature of the thermal annealing at oxidation conditions: **a** – lightly-colored zone; **b** – darkly-colored zone. Intensity of the band is normalized to its initial value in natural sample. At each temperature the sample was annealed during 2 h.

Fig. 5. Dependence of linear intensity of the **E||c**-polarized $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT absorption band at 20500 cm^{-1} in spectra of the dark-zone of andalusite on temperature of the thermal annealing at reducing conditions. The dependence of the band intensity in the lightly-colored zone (is not shown) is very close to that in the darkly-colored one. Intensity of the band is normalized to its initial value in natural sample. At each temperature the sample was annealed during 2 h.

Table 1. Reducing experiments on andalusite

Temperature, °C	Oxygen fugacity, log (f_{O_2} /bars)	Duration
700	-18	2 h
800	-18	2 h
900	-17	2 h
1000	-16	2h

Table 2. ICP content of iron and titanium measured in four points of differently-colored zones of the andalusite crystal studied.

	point 1, light zone	point 2, dark zone	point 3, light zone	point 4 dark zone
Ti, ppm	13	31	13	37
Fe, ppm	2206	2390	2038	2772

Fig. 1. Polarized optical absorption spectra of natural andalusite: **a** – lightly-colored zone (point 3, Tab. 2); **b** – darkly-colored zone (point 4).

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