UDK 549.08

M.N. TARAN [1], M. KOCH-MÜLLER [2]

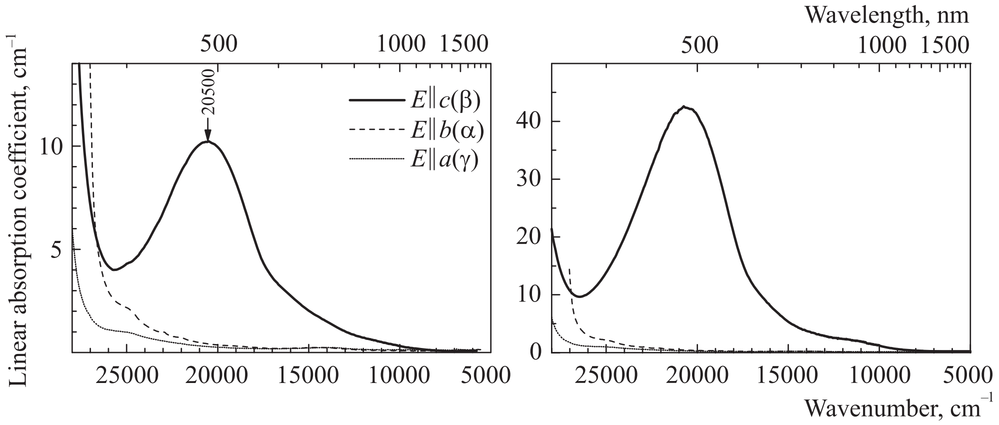
[1] Institute of Geochemistry, Mineralogy and Ore Formation, National Academy of Science of Ukraine
Palladin Ave., 34, 03680, Kyiv-142, Ukraine
[2] Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Section 3.3
Telegrafenberg, D 327, D-14473 Potsdam, Germany

# SPECTROSCOPY STUDIES OF NATURAL ANDALUSITE FROM BRAZIL

Elongated prismatic gem-quality zone-colored andalusite crystals from an unspecified location in Brazil were studied by polarized optical absorption and infrared FTIR spectroscopy. In unpolarized transmitted light, the sample displayed a strange hard-to-described color, distributed as irregular intermittent darker and lighter zones. Aside the main oxides, $SiO_2$ = 36.22 % and $Al_2O_3$ = 63.31 %, 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 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. As seen, the darker zones are obviously enriched in both Fe and Ti compared to the light ones.

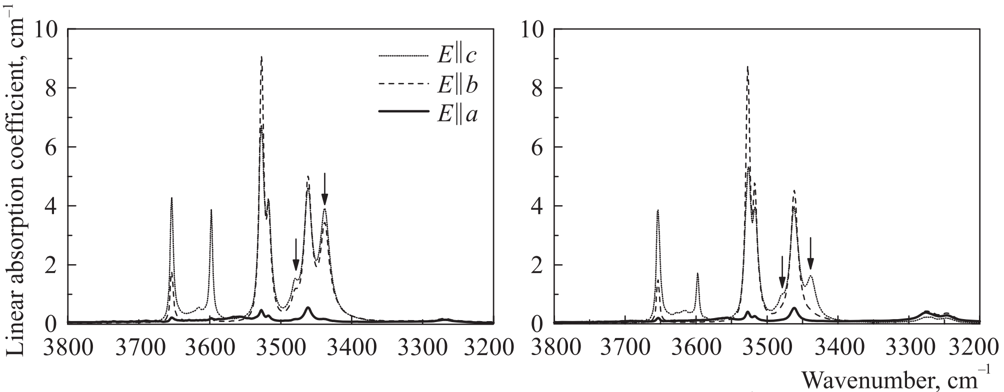
The main feature in polarized optical absorption spectra of the light and dark zones (Fig. 1, *a*, *b*, respectively) appears in $E||c$-polarization as a broad and intense absorption band with a maximum at around 20500 $cm^{-1}$, which together with the high-energy edge causes a dusk red color at $E||c$. By energy, width, polarization and some other properties this band is attributed to electronic $Fe^{2+}/Ti^{4+}$ intervalence charge-transfer (IVCT) transition. The Fe- and Ti-contents of variously-colored zones of the andalusite sample studied (see Table) well quantitatively proves this assignment [3].

Thermal behavior of the $Fe^{2+}/Ti^{4+}$ IVCT band is essentially different under oxidizing and reducing conditions. At oxidizing conditions, the thermal behavior of the band is also different in the light and dark zones. Thus, the band is stable at temperatures lower than ca. 700 °C. At higher temperatures the 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 slightly increases and maintains its intensity when treated at higher temperatures up to 1000 °C. These results demonstrate undoubtedly that the weakening and disappearance of the $Fe^{2+}/Ti^{4+}$ IVCT band in spectra of andalusite under annealing in air is caused by oxidization of $Fe^{2+}$ to $Fe^{3+}$ in IVCT $Fe^{2+}/Ti^{4+}$-pairs. The different thermal stability of the band in lightly- and darkly-colored zones of the samples evidence a certain self-stabilization effect over an interaction between $Fe^{2+}/Ti^{4+}$-pairs involved in IVCT process.



*a* *b*

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



*a* *b*

***Fig. 2.*** Polarized FTIR spectra of natural andalusite: *a* — lightly-colored zone; *b* — darkly-colored zone

**ICP content of iron and titanium measured in four points of differently-colored zones of the andalusite crystal studied, ppm**

| Element | Zones | | | |
|---|---|---|---|---|
| | Light, point 1 | Dark, point 2 | Light, point 3 | Dark, point 4 |
| Ti | 13 | 31 | 13 | 37 |
| Fe | 2206 | 2390 | 2038 | 2772 |

Polarized FTIR spectra in the range 3200—3650 cm$^{-1}$ of light and dark zones are shown in Fig. 2, *a*, *b*, respectively. They consist of a series of sharp absorption lines $E\|b \approx E\|a >> E\|c$ attributed by Burt et al. [1] to stretching OH-vibrations. The spectra measured on different zones show distinct differences: the harp lines at 3481 cm$^{-1}$ and 3437 cm$^{-1}$ (denoted by arrows), which in the light zones are distinct in $E\|a$ and $E\|b$ polarizations, in the $E\|b$-polarized spectrum of the dark zone are absent. On the whole, the integrated absorbance in the spectral range in question, 3800 cm$^{-1}$ — 3200 cm$^{-1}$, is somewhat higher in the light zone than in the dark one.

Using a calibration proposed by Burt et al. [1], one can evaluate the respective water content (in ppm by weight) as ~95 and ~76. The infrared hydroxyl absorption lines transform under annealing at T > ca. 800 °C. At higher temperatures the intensities of the split doublet at 3527 $cm^{-1}$, 3517 $cm^{-1}$ and, to a somewhat lesser extent, the line 3438 $cm^{-1}$ continually decreases whilst that of the line at 3462 $cm^{-1}$ significantly increases in all three polarizations, $E||a$, $E||b$ and $E||c$, probably, at the expense of the former three bands. Under annealing at 1100 °C during 2 hours these processes facilitate, especially, the doublet at 3527 $cm^{-1}$ and 3517 $cm^{-1}$ drastically decreased. Further heating at 1100 °C leads to a continual decrease of all absorption lines in the range 3800—3200 $cm^{-1}$. The line at 3437 $cm^{-1}$, though significantly decreased, still has a distinct $E||b$-polarized component in the light zone and none at all in the dark one.

From the data obtained it is obvious that there are several types of OH-groups in the andalusite structure and that the red color of andalusite, caused by the electronic $Fe^{2+}/Ti^{4+}$ IVCT transition between $Fe^{2+}$ and $Ti^{4+}$ in the adjacent octahedra sites, relates to a certain type of these hydroxyl groups. The main difference between the spectra of the light and dark zones, differing in intensity of $Fe^{2+}/Ti^{4+}$ IVCT absorption band, consists, as mentioned above, of the presence or absence of the $E||b$-polarized components of the two distinct lines at 3481 $cm^{-1}$ and 3437 $cm^{-1}$. This can only be, if some portion of hydroxyls, causing these absorption lines, is differently oriented in the two zones. Therefore, one can discriminate between at least three types of OH-groups in the structure: first, those, which cause all other absorption lines, aside the lines at 3481 $cm^{-1}$ and 3437 $cm^{-1}$. Their predominant orientation in the both zones is O—H-vector lying in the *ab*-plane since all absorption lines are strong in $E||a$- and $E||b$-polarization, but very weak in $E||c$ one. Theoretical calculation of critical points, potential for protonation in andalusite, and polarization properties of the infrared absorption lines in question suggests that these may be O1 and O2 [1]. Second, there are two types of hydroxyl groups, both causing the lines at 3481 $cm^{-1}$ and 3437 $cm^{-1}$, which are differently oriented in the structure of the two zones: those in the light zones having O—H-vector again laying within the *ab*-plane similarly to all others (see above), and those in the dark zones, which O—H-vector is strictly aligned along *a*-axis of the structure.

Our data clearly show that in the dark zones, enriched by Fe and Ti, a part of OH groups, causing the absorption lines at 3481 $cm^{-1}$ and 3437 $cm^{-1}$, both strictly $E||a$-polarized, should neighbor $Fe^{2+}$-$Ti^{4+}$-pairs or other combinations of these ions. Their O—H-vector aligns parallel to *a*-axis thus causing zero intensity of the lines in question at $E||b$ and $E||c$. Most probably, this is due to a redistribution of electronic density along the bond between $Fe^{2+}$ and $Ti^{4+}$ ions in IVCT pairs or complexes, which concentration in the dark zones are estimated to be nearly four times higher than in the light zones (cf. Figs. 1, *a*, *b*). Summarizing, we can assume that in the light zones a major part of OH-groups is related to isolated iron ions, most probably, $Fe^{2+}$, which charge balance at $Al^{3+}$ to $Fe^{2+}$ substitution maintains by $O^{2-} \rightarrow OH$ substitution, probably, on neighboring O1 and O2. Note, that the total amount of OH, evaluated from the FTIR spectra, ~95 wt. ppm of water (see above) or 1717 mole ppm of protons, is commensurable with the amount of $Fe^{2+}$: in light zones the total concentration of iron is nearly 2000 ppm (see Table), from which, according to Meisel et al. [2], the $Fe^{2+}/Fe^{3+}$ ratio is of the order of one, i. e. around 1000 wt. ppm, or 2785 mole ppm of $Fe^{2+}$. It is also essential that Meisel et al. (1990) assume "…that $Fe^{2+}$ content in andalusite is limited — e. g. by the presence of $Ti^{4+}$ or other cations providing the charge compensation…". Therefore, it may as well be provided by protons incorporating into neighboring oxygen sites.

As we assumed, in the dark zones the $Fe^{2+}/Ti^{4+}$ IVCT pairs, formed by ferrous and titanium ions substituting $Al^{3+}$ in adjacent octahedral sites of the structure are self-stabilized due to an interaction between them. Also, there may be complexes like $Fe^{2+}$-$Ti^{4+}$-$Fe^{2+}$ or more complicate Fe- and Ti-aggregates elongated along *c*-axis, which thermally are more stable than isolated $Fe^{2+}/Ti^{4+}$ pairs. For charge balance a part of the OH-groups in the dark zones, which are seen in the spectra as the strictly $E\|a$-polarized lines at 3481 $cm^{-1}$ and 3437 $cm^{-1}$ (see above), is adjacent to such $Fe^{2+}$- and $Ti^{4+}$-aggregates.

REFERENCES

1. *Burt J.B., Ross N.L., Gibbs G.V., Rossman G.R., Rosso K.M.* Potential protonation sites in the Al2SiO5 polymorphs based on polarized FTIR spectroscopy and properties of the electron density distribution // Phys Cnem Minerals. — 2007. — **34**. — P. 295—306.
2. *Meisel W., Schnellrath J., Griesbach P., Gutlich P.* The state of iron in andalusite // Hyperfine Interactions. — 1990. — **57**. — P. 2261—2268.
3. *Taran M.N., Koch-Müller M.* Optical absorption of electronic Fe—Ti charge-transfer transition in natural andalusite: the thermal stability of the charge-transfer band // Phys. Chem. Minerals. — 2011. — **38**. — P. 215—222.