

OPTICAL SPECTRA OF DI- AND TRIVALENT IRON IN CORUNDUM

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ABSTRACT

Polarized absorption spectra of natural yellow, green and blue sapphires containing iron in amounts of 0.X% by weight have been measured. The ratio of di- to trivalent iron was found to increase from yellow to blue specimens. The spectra were interpreted taking $B = 655 \text{ cm}^{-1}$ and $Dq = 1440 \text{ cm}^{-1}$ for Fe^{3+} and $Dq = 1330 \text{ cm}^{-1}$ for Fe^{2+} . The high Dq values are consistent with the site compression of these ions on aluminum sites. Anisotropy of the double band of Fe^{2+} is considerable with absorption for the ordinary ray highest. This leads to a blue color when viewed along c and a yellow-green one perpendicular to it if the ratio of di- to trivalent iron is about 0.07. Anisotropy of the bands of Fe^{3+} is small.

Oscillator strengths are between 10^{-5} and 10^{-4} for the spin forbidden bands of Fe^{3+} and higher than 10^{-3} for the double band of Fe^{2+} .

In synthetic blue corundums grown by the Verneuil process no trivalent iron can be detected in the absorption spectrum, but divalent iron and some trivalent titanium are clearly identified.

Yellow corundums from Ceylon contain very little iron and their absorption spectra consist mainly of an absorption edge in the near UV and two broad bands near 22000 and 28200 cm^{-1} . Their spectra are similar to that of a synthetic colorless crystal after irradiation with X rays.

INTRODUCTION

Colored varieties of natural corundum crystals are highly valued gemstones. The color of the extensively studied ruby has been shown to be due to trivalent chromium (see for instance Tanabe and Sugano, 1957; McClure, 1962; Harder, 1968), the blue shift of its absorption bands arising from the compression of this ion on the constricted aluminum sites (Orgel, 1957). Large quantities of ruby are synthesized in the Verneuil process. Synthetic blue corundums are obtained by adding both iron and titanium oxides to the starting material while yellow colors are produced by addition of nickel oxide and green ones by addition of vanadium oxide alone or in mixture with other oxides (Baumgärtel, 1962). Natural blue, green and yellow corundums do not contain transition metal ions other than iron in amounts sufficient for coloration (Harder, 1968) and the variation in color is thought to be due to the ratio between di- and trivalent iron decreasing from blue to yellow.

McClure (1962) has given polarized absorption spectra of all trivalent ions of the first transition row in corundum. However, his spectra of

trivalent iron were too weak to be assigned with certainty, and the oscillator strengths given are only a lower limit since concentrations were taken from chemical analysis and no account was taken of possible oxidation states other than three.

In the present study attempts have been made to determine the ratios of di- and trivalent iron in crystals of different color, to study the effect of ion compression on the Fe^{3+} and the even larger Fe^{2+} ion and to compare it with theoretical predictions, to obtain reliable spectra and Dq and B values for the spin forbidden bands of the Fe^{3+} ion and to measure band intensities and polarization ratios for the transitions of both di- and trivalent iron in the considerably distorted octahedral positions of the corundum lattice.

EXPERIMENTAL

Polarized absorption spectra were taken with a Zeiss PMQ II single beam spectrophotometer in the range 4000 to 30000 cm^{-1} using Polaroid polarizing foils (type HR for the near infrared and type HN 32 for visible and near UV regions). Most samples were cut and polished platelets, some faceted gemstones were also used for comparison. Impurity contents were taken from X-ray fluorescence analysis and are estimated to be accurate to within $\pm 25\%$ (Harder 1968), reproducibility being much higher. Band positions were determined by graphical separation in the case of band overlap and extrapolation of band centers from lower values of absorbance as indicated by the almost vertical lines in the figures. Oscillator strengths f were calculated assuming Gaussian band shape according to the formula

$$f = 4,6 \cdot 10^{-9} \cdot \epsilon \cdot \delta$$

with ϵ the molar extinction coefficient in $\text{cm}^2/\text{millimole}$ and δ the band width at half height in cm^{-1} . In the case of trivalent iron they are accurate to about $\pm 50\%$, the large error being due to uncertainties in the baseline, overlap of bands and the already mentioned uncertainty in the iron concentration. In the case of divalent iron the uncertainty is about twice as large because in almost all specimens most of the total iron was present in the trivalent state leading to large errors for the small difference between total and trivalent iron. In each case at least five different samples were compared and the deviations were usually much smaller than the errors given above. In synthetic specimens no trivalent iron could be detected in the optical spectra, but the accumulation of color in the outer parts of the crystals was an additional source of error.

RESULTS AND DISCUSSION

Trivalent iron. Polarized spectra of a slightly greenish yellow corundum containing about 0.4 percent Fe by weight are shown in Figure 1. Dichroism is small as seen from the difference spectrum (upper insert). Comparison with other specimens including purely yellow ones shows these bands to arise from the same ion, namely Fe^{3+} . The sharp bands at 22120 and 26570 cm^{-1} were assigned to the 4A_1 , ${}^4E(G)$ and ${}^4E(D)$ transitions respectively and a B value of 655 cm^{-1} was calculated from their positions taking C/B to be the free ion value of 4.73. The band at 9450

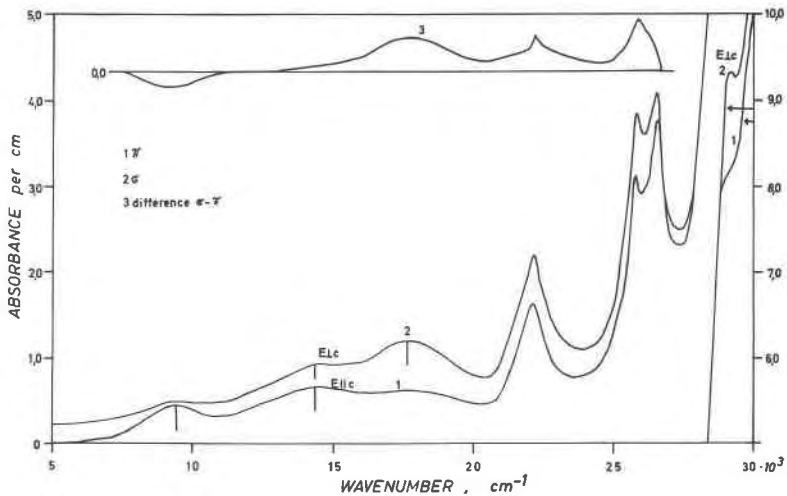


FIG. 1. Polarized spectra of Fe^{3+} in natural corundum from Umba, East Africa.

cm^{-1} is then identified as the ${}^4T_1(G)$ transition leading to a Dq value of 1440 cm^{-1} . The broad bands at 14350 cm^{-1} and 17600 cm^{-1} are thought to be split components of the ${}^4T_2(G)$ transition.¹ Band positions, half-widths, molar extinction coefficients and assignments are summarized in Table 1.

The ligand field strength has to be compared with data for other complexes of trivalent iron with oxygen. Dvir and Low (1960) give slightly different assignments for a similar spectrum of Fe^{3+} in beryl. Values of B and Dq are difficult to deduce from their data since one or two of their low energy bands may actually arise from small amounts of divalent iron. Dq values near 1270 cm^{-1} were obtained for a number of hexa-

TABLE 1. LIGAND FIELD BANDS OF Fe^{3+} IN CORUNDUM

| Transition (in cubic symmetry) | Position in cm^{-1} | Halfwidth in cm^{-1} | | ϵ in $\text{cm}^2/\text{millimole}$ | | $f \times 10^5$ | |
|----------------------------------|------------------------------|-------------------------------|-----------------|--|-----------------|-----------------|-----------------|
| | | $E \perp c$ | $E \parallel c$ | $E \perp c$ | $E \parallel c$ | $E \perp c$ | $E \parallel c$ |
| ${}^6A_1 \rightarrow {}^4T_1(G)$ | 9450 | 3000 | 2700 | 0.97 | 1.43 | 1.6 | 2.1 |
| ${}^4T_2(G)$ | { 14350 17600 | 4200 | 4400 | 2.2 | 5.0 | 5.0 | 4.8 |
| | | 3400 | 3600 | 3.0 | 1.9 | 5.5 | 3.8 |
| ${}^4A_1, {}^4E(G)$ | 22120 | 1700 | 1600 | 5.8 | 4.8 | 5.4 | 4.3 |
| ${}^4T_2(D)$ | 25680 | 970 | 970 | 8.6 | 7.1 | 4.6 | 3.8 |
| ${}^4E(D)$ | 26570 | 900 | 880 | 8.6 | 8.6 | 4.3 | 4.2 |
| ${}^4T_1(P)$ | 29000 | 1800 | 1800 | 14.7 | 12.5 | 14.5 | 12.4 |

¹ Note added in proof: The latter band may also be due to simultaneous excitation to ${}^4T_1(G)$ of Fe^{3+} ion pairs.

coordinated Fe(III)-O complexes (Lehmann, to be published), practically identical to the value for Fe³⁺ in epidote (Burns and Strens, 1967). A compression factor of $1440/1270 = 1.13$ is obtained experimentally. A ratio of 1.16 is calculated using the $Dq \propto R^{-5}$ dependence (Orgel, 1957) and assuming R to be the mean value between the Fe(III)-O distance in Fe₂O₃ (2.01 Å) and Al-O distance in corundum (1.90 Å if the ion is displaced from its asymmetrical position (McClure, 1962)). This is a good agreement between theory and experiment, but it must be emphasized that allowing for a change of the C/B ratio from the free ion value results in slightly different values of Dq .

The oscillator strengths for the spin forbidden bands are rather high. Possibly the lack of a center of symmetry leads to higher intensities. Burns and Strens (1967) observed intense absorptions of Fe³⁺ in distorted octahedral sites in epidote whereas no enhancement of absorption was observed for tetrahedral chloro complexes of the isoelectronic divalent manganese (Lawson, 1967). Lohr and McClure (1967) have shown the intensities in divalent manganese complexes to increase if the cations are bridged by monoatomic anions such as Cl⁻ or O²⁻. These authors also observed increasing intensities of the spin forbidden bands with a shift of the absorption edge to lower energies. This effect is capable of explaining the high band intensities of Fe³⁺ in corundum since overlap between the higher spin forbidden bands and the low energy tail of the charge transfer band is considerable. However, no such correlation could be established for other Fe(III)-O complexes (Lehmann, to be published) whereas an increase of intensity was observed with decrease of B values (corresponding to a low energy shift of ⁴A₁, ⁴E and higher transitions and possibly indicating an increase of covalency). Evidently this problem needs further experimental and theoretical study.

Divalent iron. Figure 2 shows the polarized spectra of a crystal with about 0.7 percent iron. It appears blue when viewed along the c axis and yellowish-green perpendicular to it. The sharp bands at 22120, 25680 and 26570 cm⁻¹ are again strong indicating the presence of a large amount of trivalent iron. In addition two strong broad bands are seen in the region between 10000 and 20000 cm⁻¹. They are shown after subtraction of the absorption of trivalent iron in the upper insert. Anisotropy is rather strong with absorption highest for $E_{\perp}c$. The double band must be due to the split components of the excited ⁵E state. The ⁵T₂ ground state is split into ⁵A₁ and ⁵E under the action of the trigonal field and the polarization ratio shows the ⁵A₁ component to be lowest. The situation is reversed from that of Ti³⁺ in corundum where the ²E state lies below ²A₁ (McClure, 1962). The sign of this trigonal splitting seems to depend on the distribution of ion charges since Groth and Liebertz (1968) also ob-

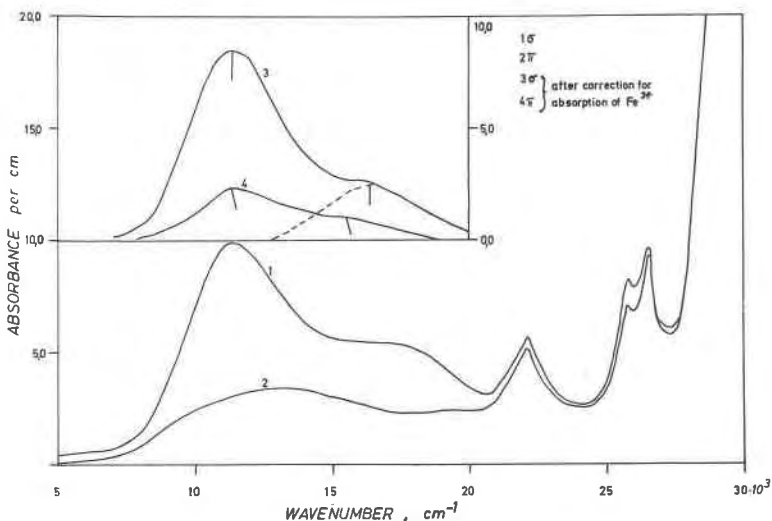


FIG. 2. Polarized spectra of a pleochroic corundum from Khao Ploi Waen, Thailand, containing both di- and trivalent iron.

served dichroism in LiNbO_3 doped with Cr^{3+} (having the same structure as corundum) to be reversed from that in ruby.

Band positions, molar extinction coefficients, halfwidths and oscillator strengths are listed in Table 2. Oscillator strength of the band at 11400 cm^{-1} was taken to be 0.002 for polarization perpendicular to the c axis and was determined from a dark blue sample containing little trivalent iron and measured with unpolarized light along the optical axis. It is rather high for an octahedral complex, but the corresponding band of Fe^{2+} in octahedral interstitials in quartz has about the same oscillator strength (Lehmann, 1967). Due to this high intensity a ratio of about 0.1 between di- and trivalent iron is sufficient to give a corundum the blue color of divalent iron.

The splitting of the excited state into two bands must arise from the

TABLE 2. DOUBLE BAND OF Fe^{2+} IN CORUNDUM

| | Band 1 | | Band 2 | |
|--|-------------|-----------------|-------------|-----------------|
| | $E \perp c$ | $E \parallel c$ | $E \perp c$ | $E \parallel c$ |
| polarization | | | | |
| position in 1000 cm^{-1} | 11.4 | 11.4 | 16.4 | 15.6 |
| halfwidth in 1000 cm^{-1} | 4.1 | 3.4 | 3.8 | 4.7 |
| ϵ in $\text{cm}^2/\text{millimole}$ | 106 | 28 | 31 | 11 |
| $f \times 10^3$ | 2.0 | 0.5 | 0.5 | 0.2 |

Jahn-Teller effect since a purely trigonal field does not split E states. The separation of the two split components is one of the largest reported so far as seen from Table 3. On the other hand, in all cases reported so far the excited 5E state of Fe^{2+} showed a splitting into two separate bands of comparable intensity. We believe that for this reason alone the possibility of an intervalence transition between Fe^{2+} and Fe^{3+} as in prussian blue (Robin, 1962) as the source of the second band can be excluded with certainty.

Dq can be calculated according to the formula:

$$10Dq = (\nu_1 + \nu_2)/2 - 2\nu/3 = (11400 + 16400)/2 - 2\nu/3.$$

(ν = band position)

If the trigonal splitting parameter ν is estimated to be 900 cm^{-1} a value of 1330 cm^{-1} is obtained for Dq of Fe^{2+} in corundum. Dq values for other

TABLE 3. SPLITTING OF THE EXCITED 5E STATE OF Fe^{2+} IN DIFFERENT CRYSTALS

| Crystal | Site | Symmetry | Literature |
|------------------|---------------------------------|-------------------------|----------------------------|
| MgO | octahedral (O_h) | 1980 cm^{-1} | Shankland, 1968 |
| α -quartz | dist. octahedr. (C_{2v}) | 3400 cm^{-1} | Lehmann, 1967 |
| corundum | dist. octahedr. (C_3) | 5000 cm^{-1} | this work |
| gillespite | square planar (appr. D_{4h}) | 11350 cm^{-1} | Burns <i>et al.</i> , 1966 |

Fe(III)-O complexes range from 910 cm^{-1} in glass (Bates, 1962, p. 231) and 1083 cm^{-1} in MgO (Shankland, 1968) to about 1180 cm^{-1} in quartz (Lehmann, 1967). The value for Fe^{2+} in MgO is best suited for a comparison since the difference in ionic radii for Fe^{2+} and Mg^{2+} is small and the symmetry is cubic. A compression factor of 1.24 is calculated for Fe^{2+} in Al_2O_3 and MgO. The experimental ratio of $1330/1083 = 1.23$ is in good agreement with the predicted value and can be regarded as ultimate proof for substitutional incorporation of Fe^{2+} in the corundum lattice.

In a synthetic blue corundum grown by the Verneuil process the broad bands of Fe^{2+} were clearly resolved, but no trivalent iron could be detected in the absorption spectrum. There was evidence for the bands of trivalent titanium at 18450 and 20300 cm^{-1} (McClure, 1962) and an additional band at 24500 cm^{-1} was probably due to V^{3+} . Baumgärtel (1962) believes the blue color to be due to titanium, but our measurements clearly show that titanium only has a minor effect on the color especially since doping with titanium alone gives a pink hue. Its chief role is to shift the equilibrium between di- and trivalent iron to the divalent state by supplying Ti^{4+} for charge compensation since doping

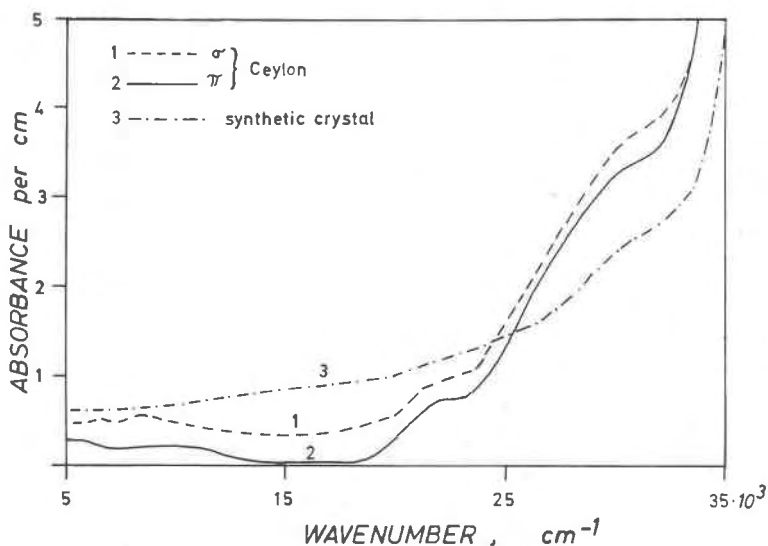


FIG. 3. Absorption spectra of natural yellow corundum from Ceylon and a synthetic colorless corundum after X ray irradiation.

with iron oxide alone results in a yellow-green color raising from a large proportion of trivalent iron (Fischer and Schlee, 1955, p. 229).

Yellow Corundum from Ceylon. A yellow corundum from Ceylon containing only 0.005 percent iron showed a completely different absorption spectrum as seen in Figure 3. It consists mainly of two broad bands near 22000 and 28200 cm^{-1} and an absorption edge in the near UV region. Dichroism is very small. The spectrum is very similar to that of a colorless synthetic crystal after X-ray irradiation (Curve 3 of Figure 3). The only difference is the steady rise in absorption between 10000 and 18000 cm^{-1} in the latter giving it an unattractive brown color.

This experiment shows the yellow color in the natural corundum to arise from irradiation color centers. In the natural crystal they are completely stable at room temperature while the synthetic one bleaches completely within a few days even in the dark. Additional experiments are planned for the near future to elucidate the structure of these color centers.

CONCLUSION

Polarized absorption spectra and X-ray fluorescence analyses of blue, green and yellow corundums showed the blue color to be caused by intense absorption of divalent iron substituting for aluminum in the corundum lattice. Trivalent iron alone leads to a yellow color while green

hues are caused by absorption of both di- and trivalent iron with the ratio of di- to trivalent iron in the range of a few percent. Even in most natural blue corundums the amount of trivalent iron exceeds that of divalent, normally by a factor between five and ten. The high ligand field strengths observed agree well with the compression of these two ions on aluminum sites.

The roles of titanium and iron in synthetic blue corundums grown by the Verneuil process are discussed and tetravalent titanium is suggested to act as charge compensator for the divalent iron.

In yellow corundums from Ceylon with very low concentrations of transition metal ions the color is caused by irradiation color centers probably not associated with transition metal ions.

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