

ELECTRONIC AND VIBRATIONAL ABSORPTION
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ABSTRACT

The optical and near-infrared absorption spectra of cordierite have been measured in polarized light. Electronic transitions in octahedrally coordinated Fe^{2+} give rise to the color and remarkable pleochroism of the mineral. A number of vibrational modes of molecular water are observed in the infrared spectrum.

Cordierite, $(\text{Mg, Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$, is a typical metamorphic mineral found in gneisses and schists. Because of its bluish-violet color, gemologists sometimes refer to it as water sapphire or iolite. Iron-bearing cordierites exhibit a pronounced pleochroism which is obvious even in unpolarized light. An interpretation of the absorption spectra in the visible and near-infrared regions is presented in this paper.

EXPERIMENTAL

The cordierite single crystals used in our experiments are from India. Chemical analysis gave 2.4 Fe^{2+} , 0.4 Fe^{3+} , and 0.1 weight percent Mn, conforming to an approximate formula $\text{Mg}_{1.8}\text{Fe}_{0.2}\text{Al}_4\text{Si}_5\text{O}_{18}$. In addition to the major constituents, characteristic lines of the following elements appeared in an emission spectrogram: Ca, Na, K, Ti, B, Li, In, Sn, Ni and Cr. The latter four metals are not recorded in other cordierite analyses (Deer, Howie and Zussman, 1962). About 1 to 2 percent water is accommodated in channels formed by the aluminosilicate framework. The density of the Indian cordierite is 2.587 g/cc. The optic sign is negative and the indices of refraction at 589.3 nm are $\alpha = 1.5370$, $\beta = 1.5440$, $\gamma = 1.5480$.

An X-ray diffractometer pattern confirmed the identification of the mineral and gave lattice parameters of $a = 9.72 \pm .02$, $b = 17.01 \pm .06$ and $c = 9.33 \pm .03$ Å. The space group is *Cccm*, orthorhombic, with four molecules per unit cell. Cordierite is pseudo-hexagonal with a crystal structure closely related to beryl. Indialite, a high-temperature cordierite, is truly hexagonal with $b = \sqrt{3}a$. Structure refinement of the low-temperature orthorhombic form (Gibbs, 1966) shows ordering of silicon and aluminum amongst the tetrahedral sites. The high-low inversion in cordierite is probably an order-disorder phenomenon, similar to that observed in the feldspar family. Miyashiro (1957) has characterized the structural states of cordierite by a distortion index Δ , derived from the 2θ values of the 311, 151, and 241 reflections. Our specimen gave $\Delta = 0.24^\circ$ close to low-cordierite value of 0.23° reported by Gibbs (1966).

The optical and near-infrared absorption spectrum of low-cordierite are shown in Figures 1-3. Polarization directions are labeled according to the previously-stated lattice parameters. A back-reflection Laue camera was used to orient the specimens, which were subsequently cut and polished into plates of several thicknesses (0.1 to 5.0 mm). Room-

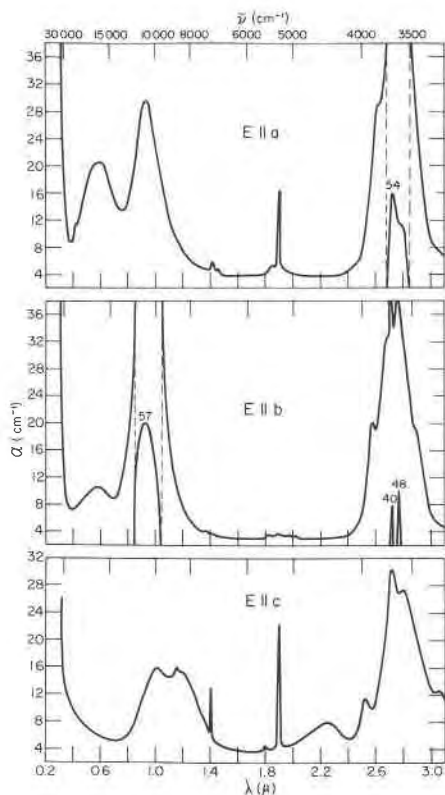


FIG. 1. Room-temperature absorption spectrum of cordierite in polarized light.

temperature absorption data for the 0.3 to 3.0 μ range (Fig. 1) were recorded on a Beckman DK-1 spectrophotometer with quartz prism optics. Improved resolution (Fig. 2) was obtained by cooling the sample to 77°K in a Cary 14 spectrometer equipped with a combined prism-grating system. A Glan-Thompson air gap prism was used as a polarizer, although almost identical results were achieved with stacked AgI plates. All peaks were checked on the unpolarized spectrum. Transmission data at longer wavelengths (2.5 to 6.0 μ) are shown in Figure 3; they were recorded on a Beckman IR-12 using AgI plate polarizers. The aqua-

marine spectra in Figure 4 were obtained with the Beckman DK-1 and Glan-Thompson prism.

DISCUSSION

Electronic transitions in divalent iron and vibrational transitions in molecular water give rise to the principal absorption bands in cordierite.

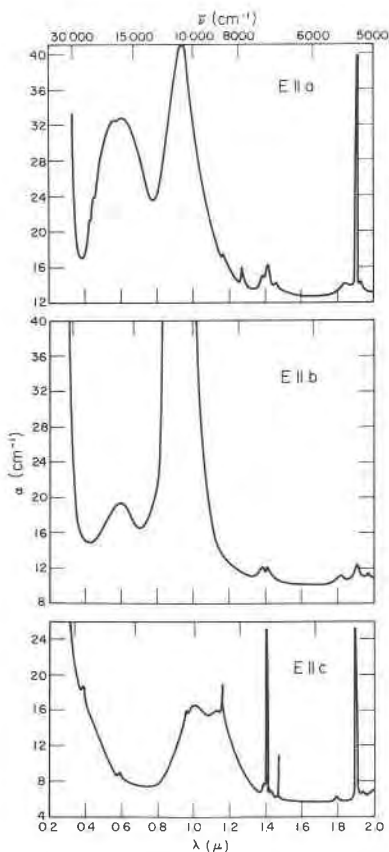


FIG. 2. Absorption spectrum of Indian cordierite at 77°K.

As shown in Figures 1 and 2, the visible portion of the spectrum is dominated by an absorption edge near 0.3μ and two broad peaks at longer wavelengths: 0.6 and 0.9μ for the direction of the electric vector $E||a$ and $E||b$, and 1.0 and 1.15μ for $E||c$. These spectra are attributed to Fe^{2+} and cause pleochroism; the colors are dark violet, medium blue-violet, and pale yellow for light polarized along a , b , and c , respectively.

The violet colors of *a* and *b* come from transmission between the absorption edge and the 0.6μ band. The latter is more intense for $E\parallel a$, giving it a deeper shade of violet. For $E\parallel c$, only the absorption edge contributes to the color. The edge absorbs the blue-violet portion of the spectrum, transmitting the complementary color, yellow.

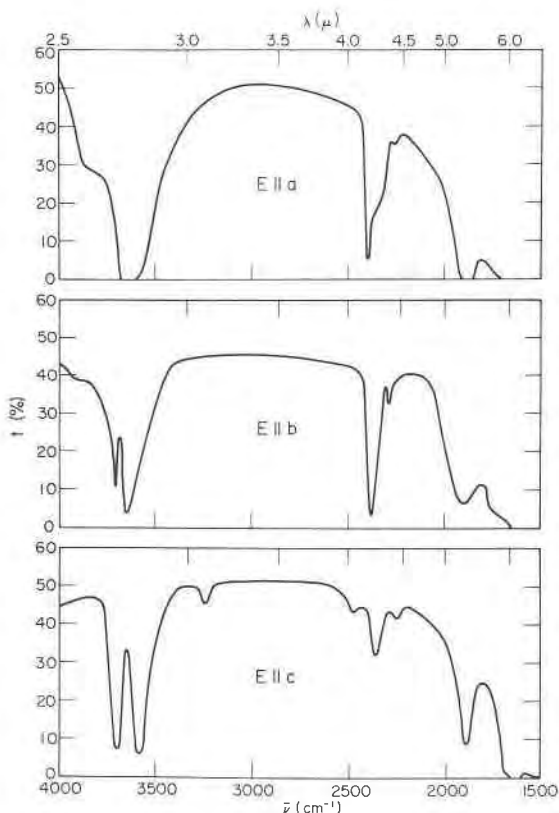


FIG. 3. Infrared transmission spectrum of cordierite. Sample thicknesses are 0.33 mm. for *a* and 0.16 mm. for *b* and *c*.

The broad bands described in the previous paragraph are due to rearrangements in the $3d^6$ electron configuration of iron. Fe^{2+} has a 5D ground state with four unpaired electrons. When placed in an undistorted octahedral environment, the 5D state of the free ion divides into a 5T_2 ground state and a 5E excited state. Transitions between these two states give rise to intense absorption near 1μ in many iron compounds. The breadth of the absorption band results from the Franck-Condon

principle, since the electronic excitation is accompanied by vibrational excitation. Transitions to crystal-field states derived from the lower excited states of the free Fe^{2+} ion (3H , 1I , etc.) are spin-forbidden and therefore weak.

In cordierite, the iron ion is coordinated to six oxygens forming a

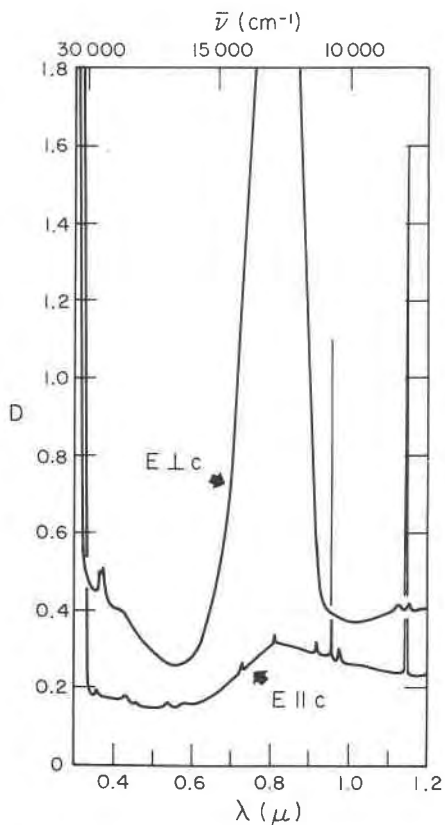


FIG. 4. Optical density of Brazilian aquamarine, thickness 5 mm. Sharp line spectra are caused by water.

deformed octahedron with orthorhombic symmetry. The orthorhombic distortion splits the 5E excited state into two A states, resulting in two absorption bands near 1μ . The observed energy separations of the A states are about 6000 cm^{-1} for the a and b directions, and about 1000 cm^{-1} for c . Comparable results for other high-spin salts of Fe^{2+} and isoelectronic Co^{3+} have been reported by Cotton and Meyers (1960). The dynamic Jahn-Teller effect provides an alternative explanation of

the splitting. However, comparison of the Fe^{2+} spectra in beryl (Fig. 4) with those in cordierite suggests that dynamic effects are unimportant. Beryl has a trigonal crystalline field, and the 5E state does not divide in such an environment. In the absence of a dynamic Jahn-Teller effect, we predict a single absorption peak, as observed. Grum-Grzhimailo and co-workers (1962) have observed similar spectra in several beryl specimens.

Many of the infrared absorption bands in cordierite (Figs. 1–3) are caused by vibrational transitions in trapped water molecules. Figure 5 shows the three fundamental vibration modes of H_2O ; ν_1 and ν_3 are symmetric and antisymmetric stretching modes, and ν_2 is a bending mode of lower frequency. All three fundamentals are infrared active, leading

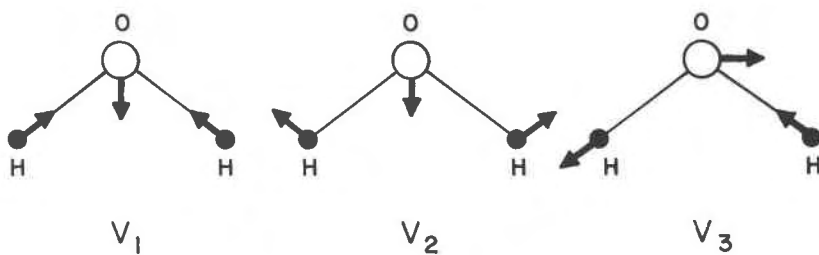


FIG. 5. Principal H_2O vibration modes. Arrows indicating displacement directions are not drawn to scale.

to intense absorption near 2.7μ (ν_1 and ν_3) and 6μ (ν_2). Vibrational transitions are customarily designated by the upper level quantum numbers (ν_1 , ν_2 , ν_3), since all transitions originate in the ground state (0, 0, 0). Tentative assignments of the cordierite spectra are made by comparison with the water vapor spectrum (Herzberg, 1945). Table 1 lists the observed wave numbers for the various fundamental, overtone, and combination bands. Though the agreement is generally good, the cordierite values are consistently smaller for higher levels, perhaps due to increased anharmonicity. Note that the bending mode (ν_2) has increased in frequency while the stretching frequencies (ν_1 and ν_3) have decreased, in going from the gaseous to the solid state. This is as expected, for the surrounding atoms make deformation more difficult while at the same time weakening the O–H bond strength. Observation of transitions involving the bending mode ν_2 affords conclusive evidence for the existence of molecular H_2O .

Intensity differences for the three polarization directions suggest preferred orientation of the trapped water molecules. Combination bands in the $1\text{--}2\mu$ range (Figs. 1, 2) are observed with greatest intensity for

$E||c$ and are extremely weak for b . Such modes are excited by an electric vector parallel to the line joining the hydrogen atoms of the H_2O molecule. We therefore conclude that many of the molecules lie in the (010) plane with the H-H direction parallel to c . Similar polarization phenomena are observed in beryl (Fig. 4) and have been described by Wickersheim and Buchanan (1959).

Preferred orientation might result from hydrogen bonding between the water molecule and the aluminosilicate framework, with protons bonding the oxygen of the water molecule to two oxygens in the hexagonal rings. If the two oxygens belong to different rings, the water molecule

TABLE 1. COMPARISON OF H_2O VIBRATION BANDS IN GASEOUS STATE WITH THOSE OBSERVED IN CORDIERITE

Vibration state			Water vapor	Cordierite
v_1	v_2	v_3	(cm^{-1})	(cm^{-1})
0	1	0	1595	1650
0	2	0	3151	3240
1	0	0	3652	3580
0	0	1	3756	3680
0	1	1	5332	5260
0	2	1	6874	6800
1	0	1	7252	7110
1	1	1	8807	8620
2	0	1	10613	10380

will be oriented along c , in agreement with the interpretation of the infrared data. Which oxygens are bonded to the water molecule? Refinement of the cordierite structure (Gibbs, 1966) has shown that two of the six cations forming the hexagonal ring are aluminum and four silicon. Pauling's electrostatic valence rule is not satisfied for the ring oxygens bonded to Al. Protons are attracted to these sites, as indicated schematically in Figure 6. There are several nearly equivalent positions for the water molecule, most of which lie in or near the (010) plane.

Three other peaks in the infrared spectrum deserve comment. According to Scholze (1960), the fundamental Si-OH vibration lies near 1000 cm^{-1} , outside the range of our experiments. The Al-OH fundamental probably lies at a slightly lower frequency. We observe absorption at 1900 cm^{-1} (Fig. 3), possibly an overtone of the Si-OH fundamental, and at 4450 cm^{-1} (Fig. 1) a broad combination band of Si-OH and O-H. The spectra near 2400 cm^{-1} (Fig. 3) probably originate from yet a dif-

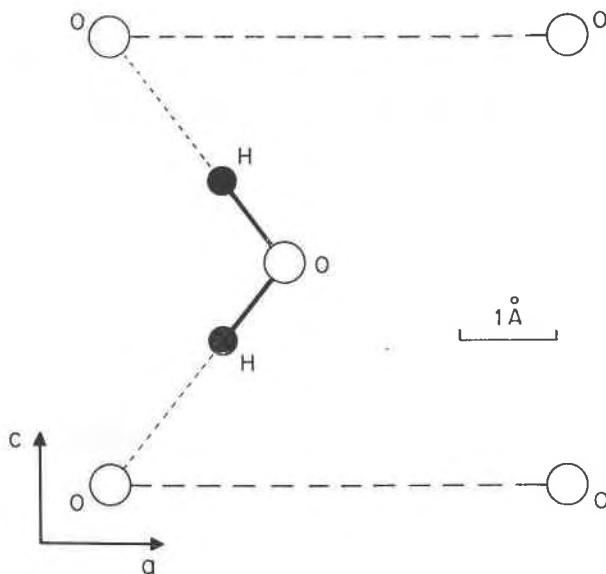


FIG. 6. Possible orientation of trapped H_2O molecule in cordierite. Dotted lines denote hydrogen bonding and dashed lines hexagonal ring layers.

ferent source, trapped carbon dioxide. The antisymmetric stretching mode of CO_2 leads to strong absorption in this region.

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