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## A Reflected Light Investigation of Ilvaite

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With 2 Figures

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### Summary

The reflectance of oriented crystal faces parallel (100) and (001) of ilvaite was measured in air and in oil at different wavelengths with linearly polarized light. Refractive indices and absorption constants were calculated from the reflectance values. In contrast to  $n_\beta$  and  $n_\gamma$ ,  $n_\alpha$  has a strong dispersion. For the calculation of  $n_\gamma$  the absorption constant can be neglected. According to the unit cell of *Belov* and *Mokeeva* (1954) with the lattice constants  $a_0 = 8.82$ ,  $b_0 = 13.07$ ,  $c_0 = 5.86$  Å,  $n_\alpha$  vibrates parallel to [001],  $n_\beta$  parallel to [100] and  $n_\gamma$  parallel to [010]. Ilvaite is optically negative.

### Zusammenfassung

#### *Auflichtuntersuchungen zur Optik des Ilvaits*

Auf orientiert geschliffenen (100) und (001) Kristallplatten von Ilvaite wurde das Reflexionsvermögen in Luft und in Öl mit linear polarisiertem Licht bei verschiedenen Wellenlängen gemessen. Aus den Reflexionswerten wurden die Brechungsindizes und Absorptionskonstanten berechnet.  $n_\alpha$  zeigt im Gegensatz zu  $n_\beta$  und  $n_\gamma$  eine auffallend starke Dispersion. Für die Berechnung von  $n_\gamma$  kann die Absorptionskonstante vernachlässigt werden. Nach der Aufstellung der Elementarzelle von *Belov* und *Mokeeva* (1954) mit den Gitterkonstanten  $a_0 = 8,82$ ,  $b_0 = 13,07$ ,  $c_0 = 5,86$  Å schwingt  $n_\alpha$  parallel [001],  $n_\beta$  parallel [100] und  $n_\gamma$  parallel [010]. Der Ilvaite ist optisch negativ.

The development of very sensitive microscope photometers in recent years (cf. e. g. *Piller*, 1977) facilitates the exact measurement of the reflectance of weakly reflecting minerals. Such measurements have proved useful for the determination of the refractive indices of highly refracting or strongly coloured transparent minerals in reflected light; *Beran* (1978, 1979) has also used these measurements for the determination of the chemical composition of trigonal carbonates (cf. also *Caye* and *Medenbach*, 1971; *Koritnig*, 1974; *Trojer*, 1955, 1962). Refractive indices of ilvaite determined by the measurements of reflectance showed values which differ distinctly from those given in the literature; in addition, there are differing data on

the orientation of the indicatrix and the optical character (cf. e. g. *Klockmanns Lehrbuch der Mineralogie*, 1978; *Tröger*, 1971; *Winchell* and *Winchell*, 1951).

The crystal structure of ilvaite was first determined by *Belov* and *Mokeeva* (1954). Recent refinement was done by *Beran* and *Bittner* (1974) and a neutron diffraction study was performed by *Haga* and *Takéuchi* (1976). The formula of ilvaite is  $\text{Ca}(\text{Fe}^{2+}, \text{Fe}^{3+})_2\text{Fe}^{2+}(\text{OH})\text{O}(\text{Si}_2\text{O}_7)$ . It consists in principal of isolated  $\text{Si}_2\text{O}_7$ -groups, which are linked with infinite double chains of edge-shared  $(\text{Fe}^{2+}, \text{Fe}^{3+})(\text{A})\text{O}_5\text{OH}$ -octahedra to a three-dimensional framework. In the octahedral vacancies of the framework  $\text{Fe}^{2+}(\text{B})$ -atoms are situated, in the seven fold coordinated vacant spaces there are Ca-atoms. Mössbauer-spectroscopy data on  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$ -charge transfer have recently been presented by *Nolet* and *Burns* (1979).

Reflectance measurements have been performed in linearly-polarized light on two plates of ilvaite crystals which have been polished in sections parallel to (100) and (001), in air and in oil ( $n = 1.518$ ). The orientation of the crystal plates which have been cut with an accuracy of  $\pm 2^\circ$  was checked by the precession method. The indices refer to the unit cell of *Belov* and *Mokeeva* (1954), with the lattice constants  $a_0 = 8.82$ ,  $b_0 = 13.07$ ,  $c_0 = 5.86$  Å and the space group *Pbnm* (cf. Table 1). Measurements have been performed with the

Table 1. *Data on the Ilvaite Used for Reflected Light Investigation*

Locality of sample: Rio Marina, Elba, Italy

Chemical composition (average values of 20 microprobe point analyses in weight%; the standard deviations are given in round brackets):  $\text{SiO}_2 - 28.9(0.7)$ ,  $\text{Al}_2\text{O}_3 - 0.4(0.1)$ ,  $\text{FeO} - 51.9(0.9)$  (total iron reported as FeO),  $\text{MnO} - 0.6(0.1)$ ,  $\text{MgO} - 0.3(0.1)$ ,  $\text{CaO} - 13.6(0.4)$

Lattice constants (cf. *Beran* and *Bittner*, 1974):  $a_0 = 8.800(3)$ ,  $b_0 = 13.019(4)$ ,  $c_0 = 5.852(3)$  Å

Space group: *Pbnm*,  $Z = 4$   $\text{CaFe}_2^+ \text{Fe}^{3+}\text{Si}_2\text{O}_8\text{OH}$

reflected light microscope Orthoplan-Pol and the microscope photometer MPV 2, using as objectives tension-free planachromates, respectively immersion contrast planachromates,  $20\times$  magnification and a numerical aperture of 0.40. The diameter of the circular measuring area was 0,1 mm. The reflectance standard used was a glass prism 1.9 (R9) of Leitz (standard number 697). The preparation of polished sections was performed on diamond-impregnated plastic laps and diamond polishing pastes on nylon cloth (cf. *Taggart*, 1977). The ilvaite crystals used for the investigations have been analysed by electron microprobe and checked for homogeneity (cf. Table 1).

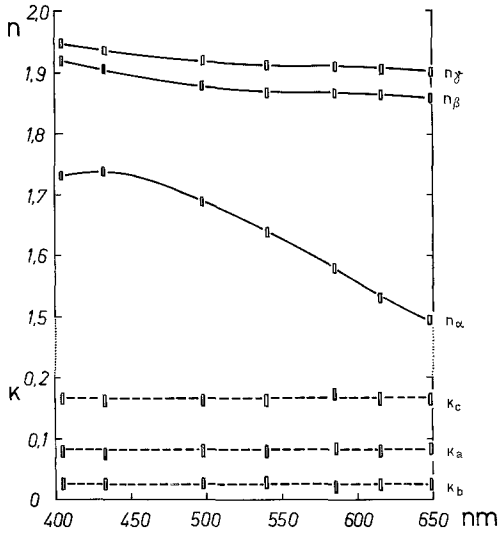


Fig. 1. Dispersion curves for the refractive indices  $n$  and absorption constants  $\kappa$  of ilvaite. Continuous lines – refractive indices calculated from reflectance values in air and in oil ( $n = 1.518$ ); dashed lines – absorption constants calculated from reflectance values in air and in oil ( $n = 1.518$ ). The subscripts  $a b c$  allocated to  $\kappa$  are indicators for the orientation (unit cell according to *Belov and Mokeeva, 1954* with lattice constants  $a_0 = 8.82$ ,  $b_0 = 13.07$ ,  $c_0 = 5.86 \text{ \AA}$  and space group  $Pbmm$ )

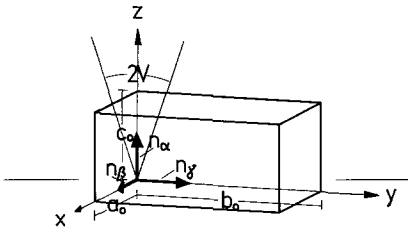


Fig. 2. Position of the main refractive indices and of the optic axes in relation to the unit cell of ilvaite (unit cell according to *Belov and Mokeeva, 1954* with lattice constants  $a_0 = 8.82$ ,  $b_0 = 13.07$ ,  $c_0 = 5.86 \text{ \AA}$  and space group  $Pbmm$ )

On the (100) face measurements with the vibration direction of the linearly polarized light parallel to [001] and parallel to [010] have been performed, and on (001) measurements with the vibration direction of the linearly polarized light parallel to [100] and [010]. Interference filters for wavelengths of 405(21), 433(18), 498(18), 541(18), 586(21), 616(20) and 649(22) nm have been used. The band widths of the filters employed are given in round brackets. The results are summarized in Fig. 1. Continuous lines refer to refractive indices which have been calculated from reflectance

values in air and in oil ( $n = 1.518$ ; cf. Table 2). The absorption constants  $\kappa$  (kappa) which have to be considered in this context are shown as dashed lines. For the formulae used for these calculations compare e. g. *Rinne and Berek*, 1953, p. 331; *Galopin and Henry*, 1972, p. 265. The maximum calculated refractive index  $n_\gamma$  vibrates parallel to [010], the smallest refractive index  $n_\alpha$  parallel to [001] and  $n_\beta$  parallel to [100] (cf. Fig. 2). Corresponding orientation was determined by *Capdecemme* (1946).

For the standard wavelength 589 nm the following refractive indices can be given:  $n_\alpha = 1.575$ ,  $n_\beta = 1.870$ ,  $n_\gamma = 1.913$ . In view of the fact that reflectance values measured in oil are very low (cf. Table 2), there results a degree of error of  $\pm 5$  relative %. The degree of error for reflectance values measured in air is  $\pm 0.5$  relative %. Correspondingly the medium standard deviation of the calculated refractive indices is  $\pm 0.007$ . In assessing the quality of these deductions it is important that the reflectance values of ilvaite are close to the reflectance values of the standard used in this work. Because of the low values of the absorption constants and of the refractive indices a relatively small error of these values can be expected (cf. *Piller and Gehlen*, 1964; *Embrey and Criddle*, 1978). The half optic axial angle  $V$  around  $n_\gamma$  has been calculated from the refractive indices (at 589 nm, following the formula for non-absorbing crystals, cf. e. g. *Rinne and Berek*, 1953, p. 202) and amounts  $71.75^\circ$ . This shows that ilvaite is an optically biaxial *negative* mineral with an optic axial angle  $2V$  of about  $36.5^\circ$  (optic axial plane (100); cf. Fig. 2).

As Fig. 1 clearly shows, the absorption constants do not reveal any dispersion within the standard deviation of about  $\pm 0.01$ . In view of the small value of  $\kappa_\beta$  one would obtain from the reflectance values measured only in air practically identical values for  $n_\gamma$ . The influence of absorption constants is most pronounced in the calculation of the  $n_\alpha$ -values. The exceptionally strong dispersion of  $n_\alpha$  is also remarkable, and it shows anomalous behavior in the short wavelength field. Ilvaite accordingly has a strong dispersion of the birefringence and a relatively strong dispersion of the optic axial angle.

IR-spectroscopic investigations (*Hanisch*, 1967; *Beran and Bittner*, 1974) show that the optic behavior of ilvaite in the near IR area continues in a similar manner. In oriented polished crystal plates the strongest absorption can be observed parallel to [010], parallel to [001] there is the weakest absorption. Parallel to [100] there is a stronger absorption than parallel to [001] and a weaker absorption than parallel to [010]. ( $\text{Fe}^{2+}, \text{Fe}^{3+}$ ) $\text{O}_5\text{OH}$ -octahedra double chains which are arranged in the crystal structure of ilvaite in the direction of [001], may assist in explaining high reflectance values measured (respectively high refractive indices calculated) on (001). It is in this direction that the strongest retardation of the light should be expected (cf. *Nolet and Burns*, 1979).

Table 2. *Reflectance Data on Ilvaite*

wavelength (nm)	<i>Vjalsov</i> (1973)			<i>Picot and</i> <i>Johan (1977)</i>		present study			present study ( $n_{oil} = 1.518$ )		
	$R_g$	$R_m$	$R_p$	$R'_g$	$R'_p$	$R_g$	$R_m$	$R_p$	$im_{R_g}$	$im_{R_m}$	$im_{R_p}$
405						10.40	10.20	8.16	1.55	1.52	1.21
420				10.3	8.6						
433						10.23	10.02	8.29	1.50	1.47	1.22
460	9.7	9.0	8.3	10.1	8.2						
498						10.00	9.69	7.55	1.42	1.39	1.11
500	9.7	8.5	7.9	9.9	7.6						
540	9.7	8.9	7.8	9.8	7.0						
541						9.87	9.48	6.83	1.37	1.33	0.99
580	9.7	8.6	7.4	9.8	6.3						
586						9.87	9.48	5.99	1.35	1.30	0.82
616						9.77	9.38	5.37	1.32	1.27	0.73
620	9.6	8.6	7.0	9.8	5.5						
649						9.71	9.32	4.83	1.29	1.24	0.64
660	9.6	8.6	6.4	9.8	5.0						
700	9.6	8.6	6.0	9.6	5.4						

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