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Reflectance variations in heat-treated ilvaite

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With 4 Figures

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Summary

Ilvaite, a black mixed-valence iron silicate, undergoes oxidation-dehydrogenation reaction when heated in air. Variations in the optical properties were investigated as function of the structural adjustments accompanying the process. Reflectance measurements were carried out in air on crystallographically oriented crystals heated at increasing temperatures (selected wavelengths of 471.1, 548.3, 586.6, and 652.3 nm). As expected on the basis of the strong structural anisotropy, sections parallel to the **c** axis (i.e. the chain axis) exhibit maximum bireflectance. The most relevant variation induced by heating affects the R_e value which appears to increase as consequence of the shortening of the M1-M1 contact along the **c** axis.

Introduction

Ilvaite, $\text{CaFe}_2^{2+}\text{Fe}^{3+}(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, is a black mixed-valence iron sorosilicate, typically occurring as a late forming mineral in Ca-Fe-Si skarn deposits (Burt, 1971).

The structure of ilvaite is based on iron octahedral ribbons, running parallel to the **c** axis. Seven-coordinated Ca^{2+} ions and Si_2O_7 groups interconnect the octahedral chains. At room temperature, ilvaite is monoclinic with space group $P2_1/a$ (Bartholomé et al., 1968) with Fe ions ordered on three crystallographically independent sites. One half of the Fe^{2+} ions occupies the M2 site, the other half the M11 site and the Fe^{3+} ions the M12 site. By increasing temperature, the structure undergoes a crystallographic phase transition to the orthorhombic symmetry $Pnam$, due to the complete disordering of Fe^{2+} and Fe^{3+} ions within the double-chain of M1-octahedra. This transition occurs within the range 60–70 °C (Ghose et al., 1984a, 1985; Robie et al., 1988). In the chemically pure synthetic ilvaite the transition occurs at 117 °C (Ghazi-Bayat et al., 1992).

A number of monoclinic structure refinements have been performed using both X-ray single crystal intensities (Finger et al., 1982; Takéuchi et al., 1983, 1993,

1994; Ghose et al., 1985, 1989; Finger and Hazen, 1987; Carrozzini, 1994; Bonazzi and Bindi, 1999) and neutron powder diffraction data (Ghose et al., 1984b). Accurate structural data over a wide temperature range were obtained and their relationship with thermophysical, magnetic, and electrical properties established (Yamanaka and Takéuchi, 1979; Nolet and Burns, 1979; Litterst and Amthauer, 1984; Ghazi-Bayat et al., 1987, 1989, 1992; Robie et al., 1988; Xuemin et al., 1988; Schmidbauer and Amthauer, 1998). The role of pressure (Evans and Amthauer, 1980; Finger and Hazen, 1987; Ghazi-Bayat et al., 1993), as well as the effects of the $\text{Mn}^{2+} \leftrightarrow \text{Fe}^{2+}$ and $\text{Al} \leftrightarrow \text{Fe}^{3+}$ substitutions, have been also examined (Ghazi-Bayat et al., 1989, 1992; Amthauer et al., 1997).

Robie et al. (1988) measured the unit-cell dimensions within the temperature range 25–800 °C and pointed out a dramatic change near 430 °C, where a and c parameters deviate from the linear trend of thermal expansion. According to these authors, this behaviour is probably related to the chemical reaction involving iron oxidation and hydrogen loss: $\text{CaFe}_2^{2+}\text{Fe}^{3+}(\text{Si}_2\text{O}_7)\text{O}(\text{OH}) \rightarrow \text{CaFe}_2^{2+}\text{Fe}_2^{3+}(\text{Si}_2\text{O}_7)\text{O}_2 + 1/2\text{H}_2$. The occurrence in ilvaite of the oxidation-dehydrogenation reaction induced by heat treatment in air was subsequently verified by Bonazzi and Bindi (1999), who examined the structural variations involved in this process. They found, in particular, that the oxidation-dehydrogenation reaction begins to develop at approximately 500–550 °C. The loss of hydrogen, estimated to be about 40% after the 700 °C annealing, causes a marked increase of the donor-acceptor interdistance, whereas the iron oxidation is made evident by the pronounced decrease of the $\langle \text{M1-O} \rangle$ octahedral distance. As a consequence of iron oxidation, changes in the Fe-Fe distances were also observed. The present work was undertaken to study the reflectance variations accompanying the structural adjustments induced by iron oxidation in ilvaite.

Experimental methods

A number of single crystals of ilvaite from the same sample (Torre di Rio, Rio Marina, Elba Island, Italy, no. E-3819, Mineralogical Museum of the University of Florence) used for the structural study (Bonazzi and Bindi, 1999) were selected for heat treatment and reflectance measurements.

Crystals were annealed in air for 48 hrs. at selected temperatures ranging from 450 °C to 700 °C, using a magnetic release furnace which allows rapid cooling to room temperature. Crystallographic orientation was determined by means of Weissenberg photographs. For each heating temperature, two crystals were embedded in resin to obtain two sections, cut parallel (\parallel) and perpendicular (\perp) to [001], respectively (according to $a > b > c$ unit cell choice). Specimens were accurately polished using diamond abrasives (grit size up to 0.25 μm). The reflectance was measured in air by means of a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor under a Zeiss Axioplan ore microscope. Filament temperature was approximately 3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6, and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. In order to obtain R% values for vibrations parallel to the crystallographic axes

Table 1. Average chemical composition (wt. %) together with their standard deviations, in parenthesis, for the ilvaite crystals treated at different temperatures

	RT \pm c (#18)	RT \parallel c (#18)	450 \pm c (#21)	450 \parallel c (#32)	550 \pm c (#18)	550 \parallel c (#30)	600 \pm c (#19)	600 \parallel c (#36)
SiO ₂	29.55 (0.25)	29.50 (0.28)	29.67 (0.17)	29.70 (0.19)	30.05 (0.23)	30.13 (0.16)	29.88 (0.20)	30.03 (0.13)
Al ₂ O ₃	0.36 (0.18)	0.32 (0.11)	0.62 (0.30)	0.40 (0.36)	0.29 (0.09)	0.24 (0.16)	0.22 (0.08)	0.43 (0.19)
FeO*	50.49 (0.42)	50.49 (0.41)	50.64 (0.43)	50.50 (0.85)	51.29 (0.41)	51.11 (0.57)	50.13 (0.47)	51.31 (0.36)
MnO	1.56 (0.38)	1.75 (0.48)	1.13 (0.12)	2.02 (0.78)	1.00 (0.05)	1.49 (0.52)	2.18 (0.22)	1.18 (0.19)
MgO	0.11 (0.05)	0.10 (0.04)	0.10 (0.02)	0.10 (0.03)	0.15 (0.02)	0.14 (0.04)	0.09 (0.04)	0.11 (0.02)
CaO	13.85 (0.08)	13.85 (0.09)	13.86 (0.06)	13.46 (0.19)	13.79 (0.08)	13.52 (0.10)	13.93 (0.08)	13.56 (0.16)
total	95.92	96.01	96.02	96.18	96.57	96.63	96.43	96.62
	625 \pm c (#21)	625 \parallel c (#37)	660 \pm c (#22)	660 \parallel c (#28)	675 \pm c (#20)	675 \parallel c (#16)	700 \pm c (#19)	700 \parallel c (#19)
SiO ₂	29.67 (0.18)	29.75 (0.15)	29.73 (0.24)	29.60 (0.26)	29.78 (0.37)	29.66 (0.43)	29.40 (0.34)	29.49 (0.35)
Al ₂ O ₃	0.28 (0.11)	0.56 (0.37)	0.05 (0.02)	0.32 (0.29)	0.20 (0.04)	0.27 (0.10)	0.21 (0.03)	0.23 (0.05)
FeO*	51.11 (0.26)	50.65 (0.90)	51.36 (0.38)	51.13 (0.41)	51.24 (0.24)	51.23 (0.38)	51.61 (0.32)	51.60 (0.35)
MnO	1.04 (0.13)	1.72 (0.46)	1.16 (0.07)	1.18 (0.22)	1.19 (0.11)	1.49 (0.24)	0.92 (0.06)	0.95 (0.07)
MgO	0.14 (0.02)	0.09 (0.02)	0.10 (0.01)	0.15 (0.05)	0.09 (0.02)	0.09 (0.02)	0.17 (0.02)	0.18 (0.02)
CaO	13.85 (0.06)	13.56 (0.13)	13.86 (0.11)	13.72 (0.14)	13.95 (0.10)	13.78 (0.12)	13.77 (0.09)	13.74 (0.09)
total	96.09	96.33	96.26	96.10	96.45	96.52	96.08	96.19

 # = number of analyses for each crystal. *FeO as total iron, H₂O not determined

(R_a , R_b , R_c), replicate measurements were performed on different regions of the crystals, with particular care to choose optically homogeneous areas. Due to the very small deviation from the orthorhombic symmetry at room temperature, we considered ilvaite as orthorhombic over the whole range. The R_a and R_b values were determined on sections \perp [001], and R_c on sections \parallel [001].

Chemical compositions were determined by means of electron microprobe JEOL JXA 8600 equipped with four wavelength dispersive spectrometers, operating at 15 kV and 10 nA. In order to check the homogeneity of the crystals, replicate analyses on different spots were performed. Table 1 reports the average chemical data.

Results and discussion

Due to the short Fe-Fe distances, the mineral appears black in color (*Nolet and Burns, 1979*), with vitreous to submetallic luster. Although it appears as an essentially transparent mineral when about 10 to 20 μm thick, the mineral is partially opaque when observed with reflected light in thick polished sections. Even small ilvaite crystals are black, the intense absorption being associated with intervalence charge transfer between Fe^{2+} and Fe^{3+} in neighboring cation sites (*Amthauer and Rossman, 1984*). Reflectance is moderate, dull gray, without striking internal reflections. As expected on the basis of the strong structural anisotropy, sections \parallel c (i.e. the chain axis) show maximum bireflectance (from deep gray to bluish gray), while it is negligible in the sections \perp c . In Fig. 1 the spectral

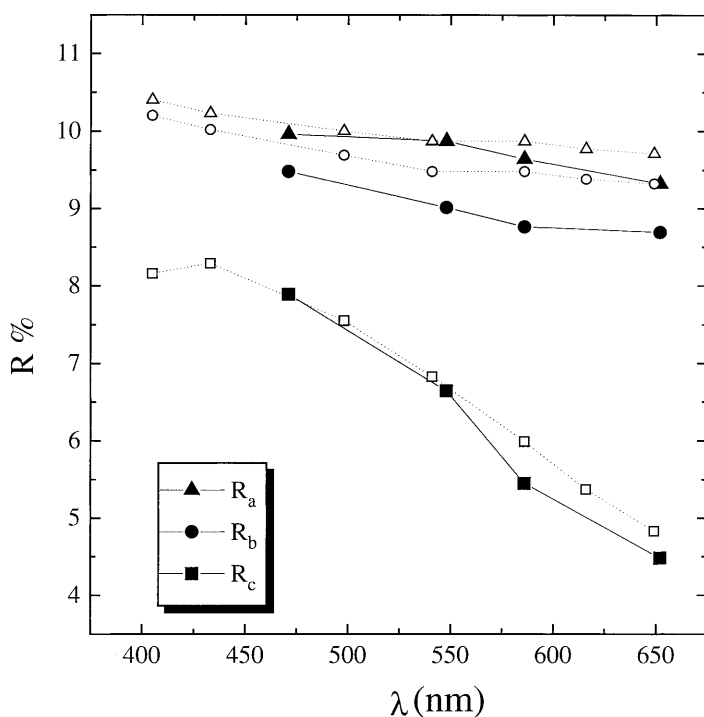


Fig. 1. Reflectance values for untreated ilvaite crystals (solid symbols) together with data (empty symbols) published by *Beran (1980)*

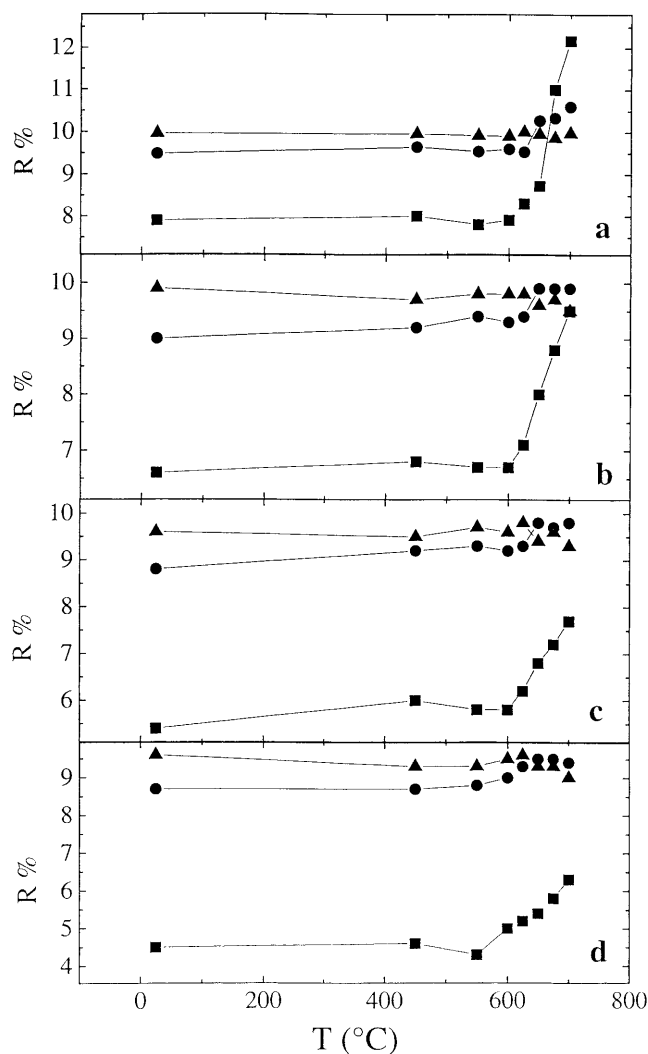


Fig. 2. Reflectance values for 471.1 (a), 548.3 (b), 586.6 (c), and 652.3 (d) nm wavelengths plotted against the heating temperature. Symbols as in Fig. 1

reflectance curves for untreated ilvaite are given, compared with those determined by *Beran* (1980) on ilvaite crystals from Rio Marina, Elba, Italy. No pronounced differences are observed in the reflectance values, as expected on the basis of the close similarity in the chemical composition of the two samples. The strong decrease of the R_c value (7.9–4.5%) with the increase of the wavelength accounts for the observed bluish hue; on the other hand, R_a and R_b show higher values (10.0–9.6% and 9.5–8.7%, respectively) which, however, are only slightly dispersed. Figure 2 shows the variation of the reflectance values as function of heating temperature. For all the four wavelengths R_a and R_b remain substantially unvaried up to 600 °C; after this treatment, slight variations occur leading $R_b > R_a$ at the end of the iron oxidation process. The most relevant variation affects the R_c value, which becomes higher than the others for $\lambda = 471.1$ nm (Fig. 2a). It is well known that higher values of reflectance are observed for pure ilvaite, and therefore small

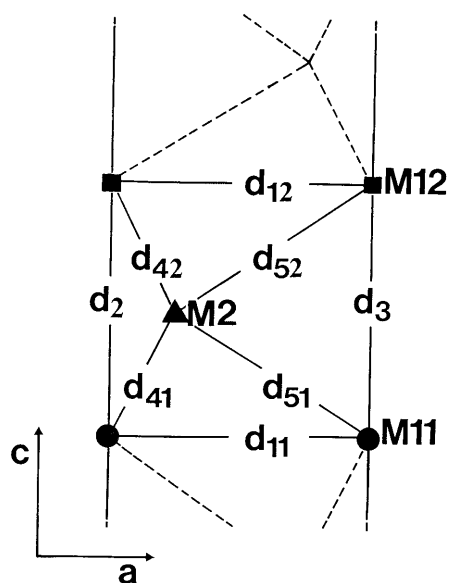


Fig. 3. Schematic representation of the Fe-Fe distances within the double octahedral chain of ilvaite (monoclinic phase). In the orthorhombic phase d_{11} - d_{12} , d_{41} - d_{42} , and d_{51} - d_{52} pairs are equivalent

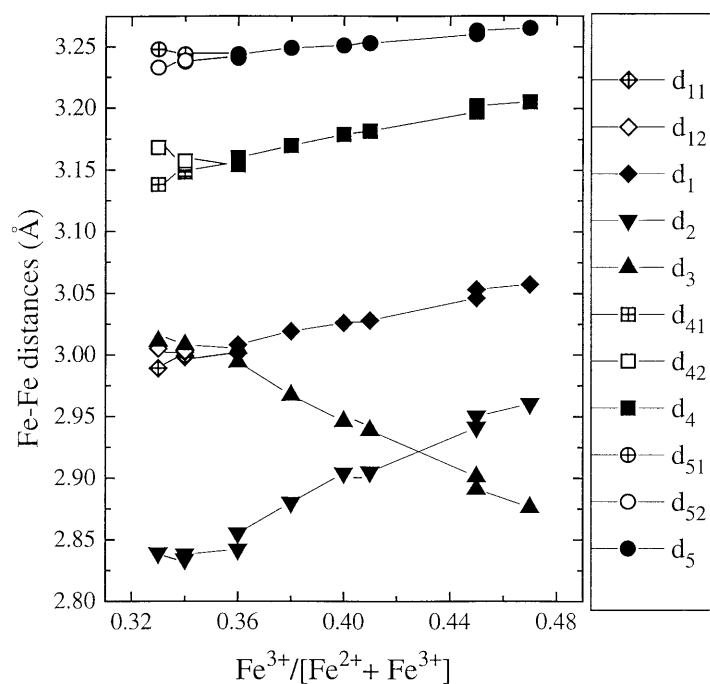


Fig. 4. Fe-Fe distances plotted against the $[Fe^{3+}/(Fe^{2+} + Fe^{3+})]$ ratio

variations could be also due to differences in chemical composition. However, the crystals employed differ from each other very slightly (Table 1) and no dependence on chemical differences was found.

After heating at 750 °C, due to the decomposition of ilvaite, crystals resulted in a minute intergrowth consisting of hematite and hedenbergite. According to *Robie*

Table 2. Fe-Fe distances (Å) in heat-treated ilvaite

	RT	400	450		500	550	600	615	625	660	675	700
d ₁₁	2.989	2.998	2.999									
				d ₁	3.001	3.008	3.019	3.026	3.028	3.046	3.053	3.057
d ₁₂	3.005	3.002	3.003									
d ₂	2.839	2.834	2.838		2.842	2.855	2.880	2.904	2.905	2.941	2.950	2.960
d ₃	3.011	3.008	3.008		3.005	2.994	2.967	2.946	2.939	2.901	2.891	2.876
d ₄₁	3.138	3.148	3.150									
				d ₄	3.154	3.160	3.170	3.179	3.182	3.197	3.202	3.205
d ₄₂	3.168	3.155	3.157									
d ₅₁	3.248	3.244	3.244									
				d ₅	3.241	3.244	3.249	3.251	3.253	3.260	3.263	3.265
d ₅₂	3.233	3.238	3.239									

Distances are computed using the atomic coordinates reported by *Bonazzi and Bindi* (1999). Labels as in Fig. 3

et al. (1988), who studied the thermal expansion of ilvaite heated in vacuum, incongruent melting occurs at 750 °C, probably involving the decomposition: $\text{CaFe}_3\text{Si}_2\text{O}_7\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{CaSi}_2\text{O}_5$ (liquid). On the other hand, fully oxidized decomposition products are formed by heating ilvaite in air. As reported by *Dietrich* (1972), the breakdown of ilvaite to hematite and clinopyroxene begins to develop at 785 °C, and at 1175 °C the sample is completely melted.

A correlation between the trend observed in reflectivity and the heated induced structural variations previously observed (*Bonazzi and Bindi*, 1999) can be attempted. In order to make the data comparable, we used for this study crystals of ilvaite similar in chemical composition and size to that previously used for the structural study. The annealing procedure was the same as well. According to *Bonazzi and Bindi* (1999), the strong increase of the $[\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})]$ ratio takes place after the 550° heat treatment, as indicated by the marked decrease of the $\langle \text{M1-O} \rangle$ distance, from 2.076 Å (550 °C) to 2.057 Å (700 °C). Accordingly, the most appreciable variations in the optical behaviour are observed in the same temperature range. Figure 3 shows the Fe-Fe contacts in the octahedral ribbon of ilvaite. The corresponding values obtained after each treatment are reported in Table 2. As a consequence of a greater electrostatic cation repulsion, the Fe-Fe distances increase with the $[\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})]$ ratio, (Fig. 4). Nevertheless, as expected for a not purely ionic compound, the M1-M1 (d₃) contact, which is directed parallel to the *c* axis, strongly decreases with increasing heating temperature. Therefore, the observed increase of reflectance for vibrations parallel to the *c* axis appears to be related to the shortening of the Fe-Fe distance (d₃) along this direction. A greater orbital overlapping, indeed, likely modifies the energy of the level into which electrons may be excited by absorption of electromagnetic radiation.

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References

- Amthauer G, Rossman GR* (1984) Mixed valence of iron in minerals with cation clusters. *Phys Chem Mineral* 11: 37–51
- Amthauer G, Ghazi-Bayat G, Lottermoser W, Redhammer G* (1997) Fe²⁺, Fe³⁺ – order, disorder and phase transition in synthetic Al-bearing ilvaite. *Terra Nova [Abstr Suppl 1]* 9: 427
- Bartholomé P, Duchesne JC, Van der Plas L* (1968) Sur une forme monoclinique de l'ilvaite. *Ann Soc Géol Belgique* 90: 779–788
- Beran A* (1980) A reflected light investigation of ilvaite. *Tschermaks Mineral Petrogr Mitt* 27: 225–230
- Bonazzi P, Bindi L* (1999) Structural adjustments induced by heat treatment in ilvaite. *Am Mineral* 84: 1604–1612
- Burt DM* (1971) The facies of some Ca-Fe-Si skarns in Japan. *Carn Inst Wash Yearbook* 70: 185–188
- Carrozzini B* (1994) Crystal structure refinements of ilvaite: new relationships between chemical composition and crystallographic parameters. *Eur J Mineral* 6: 465–479
- Dietrich V* (1972) Ilvait, Ferroantigorit und Greenalith als Begleiter oxidisch-sulfidischer Vererzungen in den Oberhalbsteiner Serpentiniten. *Schweiz Mineral Petrogr Mitt* 52: 57–74
- Evans BJ, Amthauer G* (1980) The electronic structure of ilvaite and the pressure and temperature dependence of its ⁵⁷Fe Mössbauer spectrum. *J Phys Chem Sol* 41: 985–1001
- Finger LW, Hazen RM* (1987) Crystal structure of monoclinic ilvaite and the nature of the monoclinic-orthorhombic transition at high pressure. *Z Krist* 179: 415–430
- Finger LW, Hazen RM, Hughes JM* (1982) Crystal structure of monoclinic ilvaite. *Carn Inst Wash Yearbook* 81: 386–388
- Ghazi-Bayat B, Amthauer G, Schürmann K, Hellner E* (1987) Synthesis and characterization of the mixed valent iron silicate ilvaite, CaFe₃[Si₂O₇/O/(OH)]. *Mineral Petrol* 37: 97–108
- Ghazi-Bayat B, Amthauer G, Hellner E* (1989) Synthesis and characterization of Mn-bearing ilvaite CaFe_{2-x}Mn_xFe³⁺[Si₂O₇/O/(OH)]. *Mineral Petrol* 40: 101–109
- Ghazi-Bayat B, Behruzi M, Litterst FJ, Lottermoser W, Amthauer G* (1992) Crystallographic phase transition and valence fluctuation in synthetic Mn-bearing ilvaite CaFe_{2-x}Mn_x²⁺Fe³⁺[Si₂O₇/O/(OH)]. *Phys Chem Mineral* 18: 491–496
- Ghazi-Bayat B, Amthauer G, Ahsbahs H* (1993) High pressure X-ray diffraction study of ilvaite CaFe₂²⁺Fe³⁺[Si₂O₇/O/(OH)]. *Phys Chem Mineral* 20: 402–406
- Ghose S, Hewat AW, Marezio M, Dang NV, Robie RA, Evans HT* (1984a) Electron and spin ordering and associated phase transitions in ilvaite, a mixed valence iron silicate. *Trans Am Geophys Union* 65: 289
- Ghose S, Hewat AW, Marezio M* (1984b) A neutron powder diffraction study of the crystal and magnetic structures of ilvaite from 305 K to 5 K – a mixed valence iron silicate with an electronic transition. *Phys Chem Mineral* 11: 67–74
- Ghose S, Sen Gupta PK, Schlemper EO* (1985) Electron ordering in ilvaite, a mixed-valence iron silicate: crystal structure refinement at 138 K. *Am Mineral* 70: 1248–1252
- Ghose S, Tsukimura K, Hatch DM* (1989) Phase transitions in ilvaite, a mixed-valence iron silicate. II. A single crystal X-ray diffraction study and Landau theory of the monoclinic to orthorhombic phase transition induced by charge delocalization. *Phys Chem Mineral* 16: 483–496

- Litterst FJ, Amthauer G* (1984) Electron delocalization in ilvaite, a reinterpretation of its ^{57}Fe Mössbauer spectrum. *Phys Chem Mineral* 10: 250–255
- Nolet DA, Burns RG* (1979) Ilvaite: a study of temperature dependent electron delocalization by the Mössbauer effect. *Phys Chem Mineral* 4: 221–234
- Robie RA, Evans HT Jr, Hemingway BS* (1988) Thermophysical properties of ilvaite $\text{CaFe}_2^{2+}\text{Fe}^{3+}\text{Si}_2\text{O}_7\text{O}(\text{OH})$; heat capacity from 7 to 920 K and thermal expansion between 298 and 856 K. *Phys Chem Mineral* 15: 390–397
- Schmidbauer E, Amthauer G* (1998) Study of the electrical charge transport in ilvaite using impedance spectroscopy and thermopower data. *Phys Chem Mineral* 25: 522–533
- Takéuchi Y, Haga N, Bunno M* (1983) X-ray study on polymorphism of ilvaite, $\text{HCaFe}_2^{2+}\text{Fe}^{3+}\text{O}_2[\text{Si}_2\text{O}_7]$. *Z Krist* 163: 267–283
- Takéuchi Y, Sawada H, Taniguchi H* (1993) The ilvaite problem. *Proc Inst Natural Sci, Nihon Univ* 28: 39–43
- Takéuchi Y, Sawada H, Taniguchi H, Uno R, Tabira Y* (1994) Submicroscopic twinning and chemical inhomogeneity of ilvaite, a mixed-valence iron sorosilicate $\text{HCaFe}_2^{2+}\text{Fe}^{3+}\text{Si}_2\text{O}_9$. *Z Krist* 209: 861–869
- Xuemin K, Ghose S, Dunlap BD* (1988) Phase transition in ilvaite, a mixed-valence iron silicate. I. A ^{57}Fe Mössbauer study of magnetic order and spin frustration. *Phys Chem Mineral* 16: 55–60
- Yamanaka T, Takéuchi Y* (1979) Mössbauer spectra and magnetic features of ilvaites. *Phys Chem Mineral* 4: 149–159

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