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An FTIR study of tetrahedrally coordinated ferrous iron in the spinel-hercynite solid solution

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ABSTRACT

Room-temperature FTIR spectra of ten chemically and structurally well-characterized synthetic spinel-hercynite solid solution single crystals containing between 4 and 98 mol% hercynite component show that absorption in the range 2500–7000 cm^{-1} is linearly correlated ($R^2 = 0.995$) with $^{IV}Fe^{2+}$ concentration. The integral molar absorption coefficient for this absorption equals $1.49 \cdot 10^8$ cm/mol. In addition, the structure of the absorption envelope in this spectral region remains unchanged throughout the entire composition range. These two findings are consistent with assignments to a spin-allowed electronic *d-d* transition ($^5E \rightarrow {}^5T_2$) in $^{IV}Fe^{2+}$, split by the dynamic Jahn-Teller effect, and demonstrate that next-nearest interactions in Fe clusters have little or no effect on this absorption feature at ambient conditions.

INTRODUCTION

The optical absorption spectra of ferrous and ferric iron in spinel solid solution crystals have received renewed attention in recent publications (Andreozzi et al. 2001; Rossman and Taran 2001; Taran and Langer 2001; Hålenius et al. 2002). In these studies a variety of electronic processes have been suggested as causes for observed absorption bands. These include spin-allowed and spin-forbidden single-ion *d-d* transitions in ferrous and ferric ions, and intervalence charge transfers (IVCT) in pairs or clusters of ferrous and ferric iron at octahedral sites as well as exchange-coupled pair (ECP) transitions involving Fe^{3+}-Fe^{3+} and Fe^{2+}-Fe^{3+} clusters.

A prominent absorption band peaking at ~5000 cm^{-1} in spectra of iron-bearing spinel minerals has been assigned to the spin-allowed electronic *d-d* transition $^5E \rightarrow {}^5T_2$ in ferrous iron at tetrahedral sites (e.g., Slack 1964; Gaffney 1973; Mao and Bell 1975; Dickson and Smith 1976). In a re-examination of spectra of Fe^{2+}-bearing spinels, Slack et al. (1966) demonstrated that this absorption band is split due to the dynamic Jahn-Teller effect and that additional phonon-assisted transitions above 3770 cm^{-1} create a fine-structure, which becomes distinct at low temperatures. A splitting of the $^{IV}Fe^{2+}$ $^5E \rightarrow {}^5T_2$ transition in spectra of spinels with low Fe concentrations was recently also reported by Rossman and Taran (2001) and Taran and Langer (2001). Rossman and Taran (2001) suggested two alternative causes for the band split. Apart from the explanation presented by Slack et al. (1966), i.e., a dynamic Jahn-Teller effect, they considered next-nearest interactions due to local clustering of Fe^{2+} as a potential alternative. Due to a limited degree of Fe^{2+} substitution as well as the lack of Fe^{2+}-ordering data from, e.g., single crystal structure refinements, the data presented by Rossman and Taran (2001) was inconclusive.

In the present paper we have investigated a series of crystal chemically well-characterized synthetic single crystals on the join spinel (Sp)-hercynite (He), covering the range He_4-He_{98}, with the aim of exploring how the NIR/IR-absorption band system in the range 2500–7000 cm^{-1} depends on Fe site and valency distribution and thus also exploring the suggestion made by Rossman and Taran (2001).

SAMPLES

The sample synthesis as well as the crystal chemical character of the single crystals used in the present FTIR study is described in Andreozzi and Lucchesi (2002) and in a UV/VIS-absorption and Mössbauer spectroscopy study of the same samples (Hålenius et al. 2002).

In summary, single crystals along the spinel–hercynite join were synthesized by means of a flux-growth method using Al_2O_3, MgO, and Fe_2O_3 powders as nutrients mixed with a flux compound, $Na_2B_4O_7$. The mixture was reacted in a Pt/Au-crucible under a continuous flow of CO_2:H_2 mixture at constant ratios resulting in O atom fugacities ranging from 10^{-11} to 10^{-17} bars at temperatures from 1200 to 900 °C. Up to 200 mg of high-quality spinel crystals about 0.2–0.5 mm in size were recovered from each experiment. Some of these crystals were selected for structure refinement through single-crystal XRD (Andreozzi and Lucchesi 2002) and others for optical absorption spectroscopy (Hålenius et al. 2002). Most of the remaining material was powdered and used for Mössbauer spectroscopy (Hålenius et al. 2002).

Polished single crystals selected for spectroscopic studies were mounted on glass slides and carbon coated for chemical analyses using a Cameca electron microprobe operating at an acceleration voltage of 15 kV and a sample current of 15 nA. Synthetic MgO, Fe_2O_3, and Al_2O_3 standards were used, and a synthetic $MgAl_2O_4$ sample was used as reference material for quality monitoring. Raw data were reduced with the aid of the PAP computer program (Pouchou and Pichoir 1984). Contents of FeO and Fe_2O_3 were calculated on the basis of stoichiometry requirements (3 cations per 4 O atoms) and turned out to

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be in reasonable agreement with Mössbauer data collected from the same material (Hålenius et al. 2002).

Site distributions of Mg and Al as well as Fe^{2+} and Fe^{3+} (Andreozzi and Lucchesi 2002) were determined from site-scattering and bond-distance information obtained by combining structural and microchemical data with a minimization procedure that has provided excellent results in the past (Lucchesi et al. 1998, 1999). The cation distributions (Table 1) were also confirmed by Mössbauer data (Hålenius et al. 2002).

Experimental method

Unpolarized room-temperature micro-FTIR spectra were obtained from the same double-sided polished synthetic single crystals used by Hålenius et al. (2002) for optical absorption spectroscopy in the UV-VIS spectral range. The crystals were mounted in epoxy resin on glass slides and they range from 11 to 245 μm in thickness (Table 1) as determined by means of a digital micrometer. The accuracy of the thickness measurements are estimated to be within ±1 μm, which results in estimated relative errors of 0.5–9% for data retrieved from our spectra, with the largest errors for the most Fe-rich samples.

The FTIR spectra were recorded in the range 2000–8000 cm^{-1} with 64 to 128 scan cycles and a spectral resolution of 4 cm^{-1}, using a Perkin Elmer Spectrum 2000 instrument equipped with an IR microscope. Clear areas free of cracks were selected for analysis; these were masked with square-shaped 50 to 100 μm apertures. Background spectra were from the glass slides.

All spectra were fitted using the peak resolution program Jandel PeakFit 4.0. In the fitting process all bands were assumed to be of Gaussian shape. A number of different fitting models were explored as detailed in the following section.

Results and conclusions

The FTIR spectra (Fig. 1) reveal a prominent absorption band centered at ~5000 cm^{-1} with a distinct shoulder at ~3500 cm^{-1}. On visual inspection of the absorption envelope, which ranges from ~2500 to ~7000 cm^{-1}, a number of additional inflexion points are evident. Furthermore, an absorption edge, which increases in intensity with the $[Fe^{3+}]\cdot[Fe^{2+}]$ product, is observed in the high-energy parts of the spectra. This absorption represents the low-energy tails of strong bands caused by $^{VI}Fe^{2+}$-$^{VI}Fe^{3+}$ IVCT and ECP-transitions at ~14500 and ~10000 cm^{-1} (Hålenius et al. 2002). Some additional sharp and weak absorption bands due to vibronic transitions in traces of embedding material and spinel/hercynite lattice modes occur below ~3000 cm^{-1}.

Different fitting models, using up to five Gaussian band components, were applied to quantify the total net integral absorption coefficient of the broad $^{IV}Fe^{2+}$-absorption envelope in the interval 2500–7000 cm^{-1}. Excellent fits of the envelope were

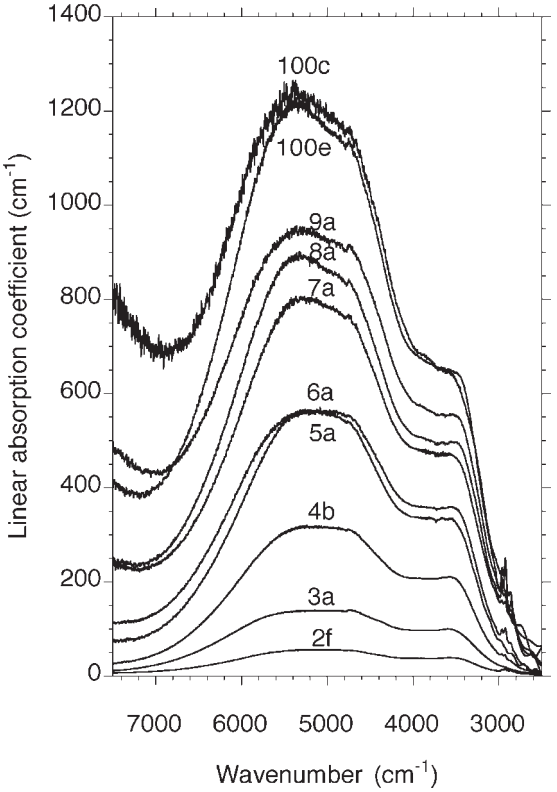

Figure 1. Room-temperature single crystal spectra of spinel-hercynite mix crystals. Spectra plot in decreasing order of absorption from the most Fe-rich sample (100c) at the top of the graph to the Fe-poorest sample (2f) at the bottom.

Table 1. Chemical and spectroscopic data

Sample	100c	100e	9a	8a	7a	6a	5a	4b	3a	2f	
Al_2O_3 (wt%)*	55.1	57.0	57.3	60.0	61.5	63.3	65.8	67.3	69.9	71.1	
Fe_2O_3 (wt%)*	4.4	1.9	3.7	2.3	2.6	2.1	1.0	0.8	0.8	0.2	
MgO (wt%)*	0.0	0.0	4.2	7.0	10.5	13.7	16.6	19.4	25.5	26.9	
FeO (wt%)*	40.8	41.0	34.5	30.9	25.8	21.2	17.2	12.9	4.7	2.1	
Oxide sum (wt%)	100.3	99.9	99.7	100.2	100.4	100.3	100.6	100.4	100.9	100.3	
$^{IV}Fe^{2+}$ (apfu)†	0.849	0.853	0.713	0.630	0.531	0.424	0.347	0.272	0.111	0.046	
$^{IV}Fe^{2+}$ (mol/L)	21.2	21.3	17.6	16.1	13.2	10.7	9.0	6.7	2.4	1.1	
Absorber t (μm)	11	11	14	14	16	25	19	52	116	245	Mean (sd)
ν_1 (cm^{-1})	5285	5290	5255	5283	5223	5322	5234	5264	5292	5218	5267 (34)
$FWHM_1$ (cm^{-1})	2081	2087	2229	1940	2051	1952	1907	1892	2045	2014	2020 (102)
A_1 (10^6 cm^{-2})‡	2.561	2.678	2.208	1.846	1.732	1.127	1.136	0.634	0.302	0.119	
ν_4 (cm^{-1})	3409	3413	3414	3416	3435	3432	3452	3454	3445	3446	3432 (17)
$FWHM_4$ (cm^{-1})	672	606	599	560	593	571	578	552	565	566	586 (35)
A_4 (10^6 cm^{-2}) ‡	0.291	0.274	0.217	0.206	0.189	0.150	0.113	0.082	0.037	0.015	
A_{SUM} (10^6 cm^{-2}) ‡	3.155	3.218	2.623	2.302	2.092	1.510	1.404	0.834	0.393	0.151	

* From Hålenius et al. (2002).
† From Andreozzi and Lucchesi (2002).
‡ Net integral absorption coefficient.

obtained by applying a four-band model (Fig. 2) and no significant improvements were noted when additional band components were introduced. This four-band model can neither be regarded as a unique fitting solution nor will it necessarily identify the true positions and widths of the band components that contribute to the absorption envelope. As the primary aim of our spectral fittings was to quantify the net total absorption of this split absorption feature such requirements were however not necessary.

Four absorption bands centered at 5270 (±30), 4590 (±20), 3925 (±20), and 3430 (±20) cm^{-1} with band widths (FWHM) of 2020 (±100), 540 (±50), 710 (±40), and 590 (±35), respectively, were identified in our preferred fitting model. The relative integral absorption of the respective bands were similar for spectra within the entire composition range, although some data scatter was observed for the two weakest components ($\nu 2$ = 4590 and $\nu 3$ = 3925 cm^{-1}), which are also poorly resolved in the spectra. The integral absorption of the two strongest components ($\nu 1$ = 5270 and $\nu 4$ = 3430 cm^{-1}), which are reasonably well resolved, shows very good linear correlation (R_2 = 0.988 and 0.990, respectively) with the $^{IV}Fe^{2+}$ content of the samples (Table 1). This indicates that the absorption distribution within the envelope between 2500 and 7000 cm^{-1} remains virtually constant along the entire spinel-hercynite join.

The total net integral absorption coefficient for the entire absorption envelope (A_{sum}) shows an excellent positive linear correlation (R_2 = 0.995) with the $^{IV}Fe^{2+}$ concentrations (Fig. 3). From this analysis, the integral molar absorption coefficient for the split band was determined to be $1.49 \cdot 10^8$ cm/mol.

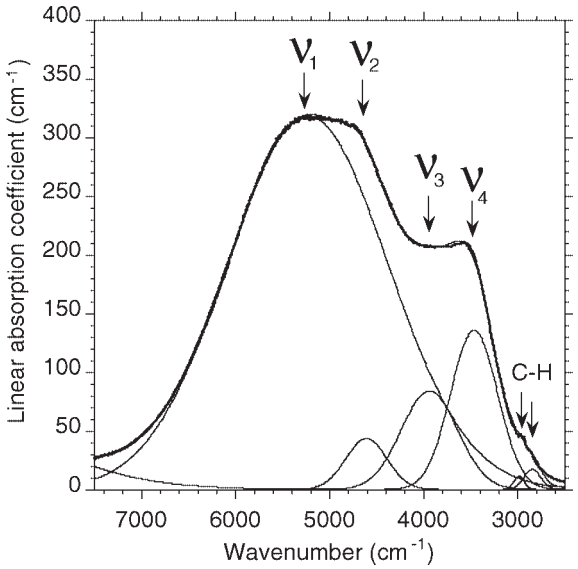

FIGURE 2. Example of a fitted spectrum (sample 4b) showing the four band components (ν_1, ν_2, ν_3, and ν_4) used to evaluate the total net integral absorption of the split spin-allowed electronic *d-d* transition $^5E \rightarrow {}^5T_2$ in tetrahedrally coordinated ferrous iron. The two fitted weak and narrow bands labeled C-H at ~2900 cm^{-1} are due to vibronic transitions in very thin layers (≤1 μm) of the epoxy embedding material. The thick solid line represents experimental data. Fitted Gaussian shaped bands as well as the sum of these functions are shown as thin solid lines.

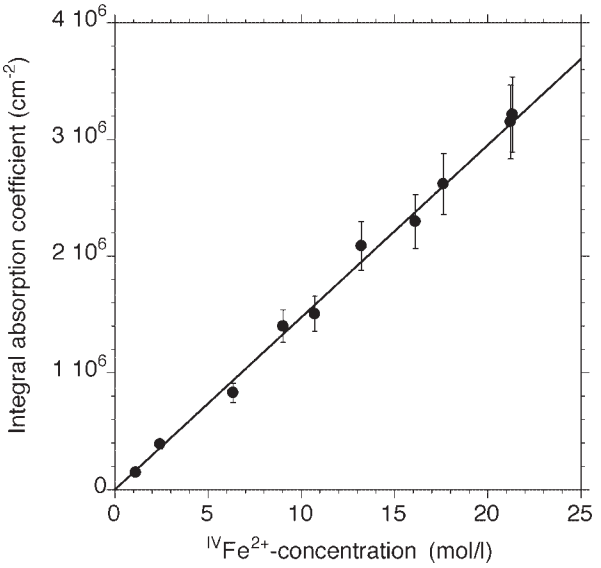

FIGURE 3. Plot of total net integral absorption coefficient (A_{SUM}) of the split $^5E \rightarrow {}^5T_2$ band in spinel-hercynite spectra vs. $^{IV}Fe^{2+}$ concentration. The solid diagonal line represents a linear least-squares fit of the data set. Errors (bars) in absorption coefficient values are mainly related to uncertainties in absorber thickness determinations.

Our data provide no evidence for Fe^{2+} clustering as the cause for the observed split character of the band. Neither a non-linear correlation of the total integral absorption coefficient of the band with the $^{IV}Fe^{2+}$ content nor a compositionally dependent absorption distribution, features expected for a clustering-driven band splitting, could be positively observed in the spectra of our samples. In fact, the data obtained from our FTIR study of spinel-hercynite solid-solution single crystals are fully consistent with the previously proposed explanation for the split character of the transition in terms of interactions through the dynamic Jahn-Teller effect (Slack et al. 1966).

Finally, it is worth noting that we can find no evidence for Fe^{3+} affecting the split $^5E \rightarrow {}^5T_2$ transition in $^{IV}Fe^{2+}$ in spinel-hercynite minerals. This is nicely illustrated by the identical (within error) absorption data obtained from the FTIR spectra of samples 100c and 100e, which contain very similar amounts of $^{IV}Fe^{2+}$ (0.849 and 0.853 apfu, respectively) but differ strongly in concentrations of Fe^{3+} (0.075 and 0.041 apfu, respectively).

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REFERENCES CITED

Andreozzi, G.B. and Lucchesi, S. (2002) Intersite distribution of Fe^{2+} and Mg in the spinel (sensu stricto)-hercynite series by single-crystal X-ray diffraction. American Mineralogist, 87, 1113–1120.

Andreozzi, G.B., Hålenius, U., and Skogby H. (2001) Spectroscopic active $^{IV}Fe^{3+}$-$^{VI}Fe^{3+}$ clusters in spinel-magnesioferrite solid solution crystals: a potential monitor for ordering in oxide spinels. Physics and Chemistry of Minerals, 28, 435–444.

Dickson, B.L. and Smith, G. (1976) Low temperature optical absorption and Mössbauer spectra of staurolite and spinel. Canadian Mineralogist, 14, 206–215.

Gaffney, E.S. (1973) Spectra of tetrahedral Fe^{2+} in $MgAl_2O_4$. Physical Review B, 8, 3484–3486.

Hålenius, U., Skogby, H., and Andreozzi, G.B. (2002) Influence of cation distribution on the optical absorption spectra of Fe^{3+}-bearing spinel *s.s.*-hercynite crystals: evidence for electron transitions in $^{VI}Fe^{2+}$-$^{VI}Fe^{3+}$ clusters. Physics and Chemistry of Minerals, 29, 319–330.

Lucchesi, S., Della Giusta, A., and Russo, U. (1998) Cation distribution in natural Zn-aluminate spinels. Mineralogical Magazine, 62, 41–54.

Lucchesi, S., Russo, U., and Della Giusta, A. (1999) Cation distribution in natural Zn-spinels: franklinite. European Journal of Mineralogy, 11, 501–511.

Mao, H.K. and Bell, P.M. (1975) Crystal-field effects in spinel: oxidation states of iron and chromium. Geochimica Cosmochimica Acta, 39, 865–874.

Pouchou, J.L. and Pichoir, F. (1984) A new model for quantitative X-ray microanalysis. I. Application to the analysis of homogeneous samples. La Recherche Aérospatiale, 3, 13–36.

Rossman, G.R. and Taran, M.N. (2001) Spectroscopic standards for four- and fivefold-coordinated Fe^{2+} in oxygen-based minerals. American Mineralogist, 86, 896–903.

Slack, G.A. (1964) $FeAl_2O_4$-$MgAl_2O_4$: Growth and some thermal, optical, and magnetic properties of mixed single crystals. Physical Review A, 134, 1268–A1280.

Slack, G.A., Ham, F.S., and Chrenko, R.M. (1966) Optical absorption spectra of tetrahedral Fe^{2+} ($3d^6$) in cubic ZnS, CdTe and $MgAl_2O_4$. Physical Review, 152, 376–402.

Taran, M.N. and Langer, K. (2001) Electronic absorption spectra of Fe^{2+} in oxygen-based rock-forming minerals at temperatures between 297 and 600 K. Physics and Chemistry of Minerals, 28, 199–210.

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