

LETTER

Optical and near infrared spectra of ringwoodite to 21.5 GPa: Implications for radiative heat transport in the mantle

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ABSTRACT

High pressure optical and near infrared spectra of a single crystal of ringwoodite with composition $(\text{Mg}_{0.90}\text{Fe}_{0.10})_2\text{SiO}_4$ were measured to 21.5 GPa. The spectrum at ambient pressure shows a strong band at $12\,265\text{ cm}^{-1}$ with two shoulders at 8678 cm^{-1} and $17\,482\text{ cm}^{-1}$. The bands at $12\,265\text{ cm}^{-1}$ and at 8678 cm^{-1} are due to spin-allowed crystal field transitions of octahedral Fe^{2+} , while the band at $17\,482\text{ cm}^{-1}$ is most likely due to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge transfer. The absorption edge due to ligand-to-metal charge transfer occurs close to $30\,000\text{ cm}^{-1}$. With increasing pressure, both the crystal field and the charge transfer bands shift to higher frequencies. Whereas this is expected for the crystal field bands, this blue shift is surprising for an intervalence charge transfer band. Moreover, neither the crystal field nor the charge transfer bands broaden or intensify significantly with pressure. These results have major implications for radiative heat transfer in the Earth's mantle. It has commonly been assumed that radiative heat transfer is blocked in the mantle, because it was believed that the red shift and the increased intensity of charge transfer bands with pressure would effectively make mantle minerals opaque throughout the near infrared and visible range. Our results demonstrate that this effect does not occur for ringwoodite with a Mg/Fe ratio realistic for the Earth's mantle. Quite to the contrary, the mean free path of photons in ringwoodite actually increases with pressure, because the absorption bands move away from the maximum of the blackbody radiation.

INTRODUCTION

The temperature distribution inside the Earth's mantle depends on the rate of heat transfer by convection and conduction. The bulk thermal conductivity of a material is the sum of lattice conductivity and radiative conductivity (Clark 1957; Schatz and Simmons 1972; Gibert et al. 2003). Radiative conductivity is due to heat transport by emission and absorption of photons. It therefore depends on the absorptivity of the sample in the infrared and optical region, and in the simplest approximation, it is inversely proportional to the average absorption coefficient α . If α were constant, the radiative thermal conductivity should increase with the third power of temperature, and therefore, radiative conduction should dominate heat transfer in the mantle. However, earlier experimental work suggested that most ferromagnesian mantle minerals become opaque in the near infrared and visible range at high pressure, due to an intensification and red shift of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge transfer bands (Mao and Bell 1972; Mao 1976). Accordingly, it is widely believed that radiative heat transfer is relatively unimportant in the mantle. Only recently, there has been a renewed interest in the radiative contribution to the bulk heat flux in the mantle (Dubuffet et al. 2002; Hofmeister 2004).

Direct measurements of radiative conductivity are difficult because, among other things, they require relatively large samples

and nearly isothermal conditions during the measurement (Gibert et al. 2003). Accordingly, no direct measurements of the radiative conductivity are available for most high-pressure phases, while for example the lattice part of the thermal conductivity of wadsleyite and ringwoodite has recently been measured (Xu et al. 2004). Radiative conductivity can, however, be calculated from infrared and optical absorption spectra. In this paper, we report the infrared and optical absorption spectra of ringwoodite to 21.5 GPa and discuss the consequences for radiative conductivity of the transition zone.

EXPERIMENTAL METHODS

Sample

A sample of synthetic ringwoodite of composition $(\text{Mg}_{0.90}\text{Fe}_{0.10})_2\text{SiO}_4$ synthesized at $1400\text{ }^\circ\text{C}$ and 19 GPa was used for all measurements. The sample is part of the charge SZ0107 described by Smyth et al. (2003). The estimated ratio of $\text{Fe}^{2+}/\Sigma\text{Fe}$ is about 10 percent. The sample contains 0.85 wt% H_2O . A doubly polished slab with a thickness of $24\text{ }\mu\text{m}$ was prepared from an optically clear and deeply blue colored grain of ringwoodite.

Infrared and optical absorption measurements at 1 bar

All spectroscopic measurements were carried out using a Bruker IFS 125 Fourier transform infrared spectrometer together with an all-reflecting microscope (Bruker IR scope I). The spot size on the sample was limited to a diameter of 50 to $60\text{ }\mu\text{m}$ by an aperture in the rear focal plane of the 15-fold Cassegrainian objective. Measurements were carried out from 1000 to 9000 cm^{-1} using a tungsten source, a Si-coated CaF_2 beam splitter and a narrow-band MCT detector; from 8500 to $25\,000\text{ cm}^{-1}$ using the same tungsten light source, but with a quartz beam splitter with dielectric coating and a Si diode detector; and from $18\,000$ to $30\,000\text{ cm}^{-1}$ using a xenon arc lamp, an Al-coated quartz beam splitter and a GaP diode detector. In

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each spectral range several thousand scans were accumulated. The three resulting spectra were merged to produce the final spectrum.

Infrared and optical absorption measurements at high pressure

High pressure spectra were collected using a modified Merrill-Bassett-type diamond-anvil cell equipped with type I diamonds. Pressure medium was a 4:1 mixture of methanol and ethanol. Pressure was measured by ruby fluorescence. Spectra were acquired with the same spectrometer and microscope as described above, but only in the range from 8500 to 25 000 cm^{-1} , because the pressure medium starts to absorb at lower frequencies, while the absorption of diamond becomes appreciable in the UV. Moreover, this spectral range is sufficient to observe all crystal field and intervalence charge transfer bands of ringwoodite. Usually, 10 000 scans were accumulated at each pressure. The absorption spectrum of the diamonds was separately measured using the empty cell and was subtracted from the raw data to produce the final spectrum.

EXPERIMENTAL RESULTS AND DISCUSSION

Absorption spectrum at 1 bar

The absorption spectrum of ringwoodite at 1 bar, ranging from 1000 cm^{-1} in the infrared to 30 000 cm^{-1} in the UV is shown in Figure 1. The following features can be seen in this spectrum: (1) Several sharp bands below 3000 cm^{-1} are overtones of lattice vibrations. (2) The band around 3140 cm^{-1} is due to the stretching vibrations of OH groups (Smyth et al. 2003). (3) The broad and intense absorption system between 5000 and 25 000 cm^{-1} is due to electronic transitions related to the iron content of the sample (Burns 1993). (4) The rise in absorption from 25 000 cm^{-1} to 30 000 cm^{-1} is due to oxygen-to-metal charge transfer (Burns 1993).

The absorption system due to iron between 5000 and 25 000 cm^{-1} can be deconvoluted into three Gaussian components, see Table 1. Together with a linear baseline defined by the minima in absorption around 4000 and 25 000 cm^{-1} , these Gaussian components reproduce the measured spectrum within experimental error. However, acceptable fits of the spectrum may also be obtained with slightly different combinations of band parameters. The absolute precision of band positions is therefore probably in the order of ± 200 cm^{-1} . The maximum of absorption is due to a band at 12 265 cm^{-1} , with two shoulders at 8678 cm^{-1} and at 17 482 cm^{-1} . The first two bands are due to the ${}^5T_{2g} \rightarrow {}^5E_g$ crystal field transition of Fe^{2+} in an octahedral site. In an undistorted octahedral site, only one band would be expected, however, in virtually all minerals containing ferrous iron, two bands are

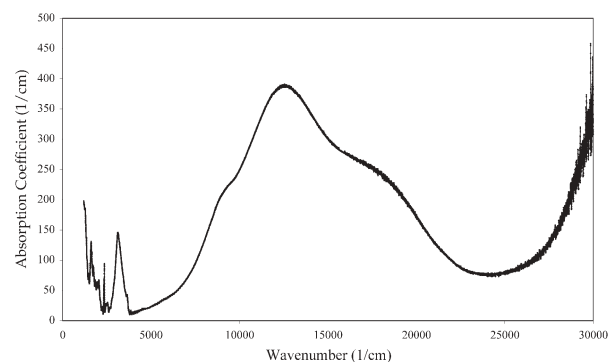


FIGURE 1. Near infrared and optical absorption spectrum of ringwoodite at ambient conditions.

observed due to a static or dynamic Jahn-Teller distortion of the site. Compared to olivine, the crystal field bands are shifted to higher frequencies, as expected from the smaller cation-oxygen distance r in the octahedral site of ringwoodite as compared to the octahedral sites in olivine. The average of the two crystal field bands of Fe^{2+} equals the crystal field splitting, which varies with r^{-5} according to electrostatic theory (Burns 1993). The Mg-O distance is 2.066 Å in ringwoodite (Smyth et al. 2003) as compared to 2.129 Å for the M2-site in forsterite (Burns 1993). Compared to Mg-rich olivines, the crystal field bands of Fe^{2+} in ringwoodite should therefore be shifted to higher frequencies by 16%. From the average band position of 9387 cm^{-1} for Fe^{2+} in the M2-site of olivine with $\text{Mg}/(\text{Mg} + \text{Fe}) = 0.9$ (Ullrich et al. 2002), one would therefore expect an average band position for ringwoodite of the same composition of 10 908 cm^{-1} , which is reasonably close to 10 471 cm^{-1} , the average band position of the two crystal field bands observed in the ringwoodite spectrum.

The position and width of the band at 17 482 cm^{-1} suggests that it is due to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ intervalence charge transfer, consistent with the presence of about 10% of the total iron as Fe^{3+} as inferred from Mössbauer spectra (Smyth et al. 2003). Crystal field bands of Fe^{3+} are not observed. This is not surprising, since the sample only contains less than 1 wt% of ferric iron and because all possible transitions in Fe^{3+} are spin-forbidden and therefore hardly visible in optical spectra. Bands due to tetrahedrally coordinated Fe^{2+} around 5000 cm^{-1} are also absent.

The intensity of the crystal field bands of Fe^{2+} in ringwoodite is striking. Compared to olivine, the extinction coefficient increased by more than a factor of ten, despite that the coordination polyhedron around Fe^{2+} in ringwoodite is less distorted than in olivine. A similar intensification of the crystal field bands of Fe^{2+} has been observed in several silicate minerals containing both Fe^{2+} and Fe^{3+} in adjacent polyhedra (Smith 1978; Mattson and Rossman 1987). However, the physical mechanism behind this intensification is not yet fully understood. The explanation may be related to the Laporte selection rule that states that transitions between states of equal parity, e.g. between two d -orbitals are forbidden. This selection rule can be lifted, if the geometry of the orbitals involved becomes distorted due to interaction with neighboring ions in such a way that the center of symmetry in the d -orbitals disappears. For this reason, Fe^{2+} in acentric sites absorbs more strongly than Fe^{2+} in a centrosymmetric site. It may be that an Fe^{3+} ion substituting for a divalent ion close to the Fe^{2+} site generates such a strong local charge imbalance and electric field gradient that it results in a highly non-centrosymmetric electron density distribution inside the Fe^{2+} ion that could explain the high extinction coefficients observed.

TABLE 1. Deconvolution of the optical absorption spectrum of ringwoodite into Gaussian components

Band assignment	Position (cm^{-1})	Peak height (cm^{-1})	Width
$\text{Fe}^{2+}; {}^5T_{2g} \rightarrow {}^5E_g$	8678	70.86	2291
$\text{Fe}^{2+}; {}^5T_{2g} \rightarrow {}^5E_g$	12 265	319.53	5 012
Fe^{2+} - Fe^{3+} intervalence charge transfer	17 482	182.55	5 798

Note: Peak height is the linear absorption coefficient. Linear molar extinction coefficients for the two crystal field bands of Fe^{2+} are 15.7 $\text{L}/(\text{mol}\cdot\text{cm}^{-1})$ for the 8678 cm^{-1} band and 70.7 $\text{L}/(\text{mol}\cdot\text{cm}^{-1})$ for the 12 265 cm^{-1} band.

Absorption spectra at high pressure

Absorption spectra of ringwoodite to 21.5 GPa are shown in Figure 2 and band positions obtained from Gaussian deconvolution are given in Table 2 and Figure 3. The frequencies of both the main crystal field band at 12 265 cm^{-1} and of the intervalence charge transfer band at 17 482 cm^{-1} increase linearly with pressure, with slopes of 77.5 $\text{cm}^{-1}/\text{GPa}$ and 146 $\text{cm}^{-1}/\text{GPa}$, respectively. The behavior of the band at 8678 cm^{-1} is not so clear; it first appears to increase in frequency with pressure with a slope similar to the main crystal field band, whereas it appears to decrease in frequency at the highest pressures. The latter effect, however, may be an artifact, because this band is only a weak shoulder in the spectrum located close to the cutoff frequency of the Si diode detector. Neither the main crystal field band nor the charge transfer band show any significant broadening or change in intensity with pressure.

While the shift of the crystal field bands to higher frequencies with increasing pressure is expected, the behavior of the intervalence charge transfer band is surprising. Since the work of Mao and Bell (1972) and of Mao (1976) it is generally believed that intervalence charge transfer bands intensify and shift to lower frequencies with pressure (Burns 1993). Indeed, since pressure reduces the distance between the Fe^{2+} and Fe^{3+} ions involved in intervalence charge transfer, one would intuitively expect that the energy required for transferring an electron from Fe^{2+} to Fe^{3+} should decrease with pressure. In particular, this is a plausible explanation if the coordination polyhedra around Fe^{2+} and Fe^{3+} share a common face. In the structure of ringwoodite, however, Fe^{2+} and Fe^{3+} are located on octahedral sites, which form chains of edge-sharing octahedra. In this situation, the vector pointing from the Fe^{2+} ion to the Fe^{3+} ion passes through the middle of an octahedral edge defined by two oxygen atoms. During compression of the ringwoodite structure, these two oxygen atoms also move more closely together and therefore, the electrostatic potential wall, which the electron needs to overcome during transfer from Fe^{2+} to Fe^{3+} , may increase. Interestingly, Taran and Langer (1998) also observed some shifts of intervalence charge transfer bands toward higher frequency with increasing pressure, although the effects observed in that study are smaller than those reported here for ringwoodite.

In the spinel structure ($Fd\bar{3}m$), there is a single octahedral site and a single tetrahedral site. The octahedra do not share edges with the tetrahedra as they do in olivine. The octahedra share edges with other octahedra to form chains in the [110] direction. The point symmetry of the octahedron is $\bar{3}m$ (centric). An octahedron has twelve edges. In spinel, six of these edges are shared with other octahedra, and six are unshared. In the silicate spinels, the shared edge is slightly longer than the unshared edge, whereas the converse is true of most oxide spinel structures. With pressure, the distortion of the octahedron decreases and the longer shared edge compresses more than the shorter unshared edge (Smyth et al. 2004). So the oxygen-oxygen separation along the shared edge decreases more quickly than the cation-cation separation. If the oxygen-oxygen separation forms a barrier to Fe^{2+} - Fe^{3+} charge transfer, this barrier may increase with pressure accounting for the apparent blue-shift with pressure.

While there might be a reasonable physical explanation for

the observed blue shift of the intervalence charge transfer band, it is more difficult to understand the discrepancy between the results of this study and the work by Mao and Bell (1972) and Mao (1976). These authors studied the optical and near infrared spectra of pure Fe_2SiO_4 spinel at pressures up to 27 GPa and observed a strong increase in absorption in the visible and infrared region that they attributed to a red shift of the absorption edge caused by charge transfer. This effect causes Fe_2SiO_4 spinel to become completely opaque in the visible range above 20 GPa. Possibly, the difference between our study and the work of Mao and Bell (1972) and Mao (1976) is related to the different bulk iron content of the sample. In pure Fe_2SiO_4 spinel, continuous chains made of octahedrally coordinated Fe^{2+} and Fe^{3+} exist that may lead to complete electron delocalization, whereas this is not possible in magnesian ringwoodite, where the iron atoms

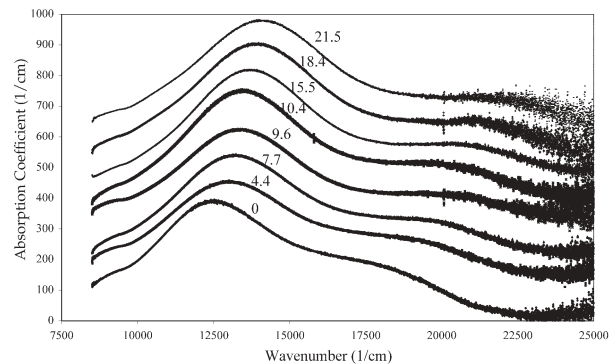


FIGURE 2. High-pressure optical absorption spectra of ringwoodite. Numbers are pressure in GPa.

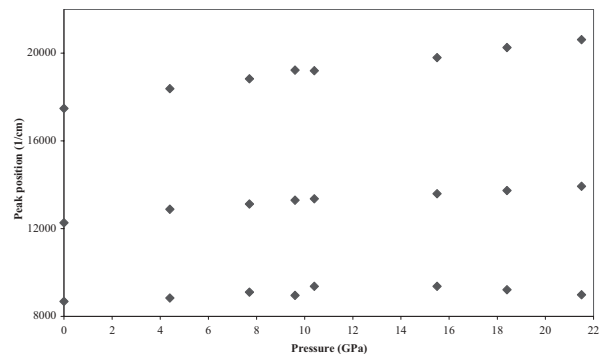


FIGURE 3. Evolution of major band positions of ringwoodite with pressure.

TABLE 2. Band positions in the optical absorption spectrum of ringwoodite at high pressure

Pressure (GPa)	Band position (cm^{-1})		
4.4	8838	12 880	18 387
7.7	9108	13 128	18 835
9.5	8961	13 302	19 235
10.4	9369	13 361	19 204
15.5	9371	13 594	19 805
18.4	9213	13 742	20 265
21.5	8987	13 932	20 621

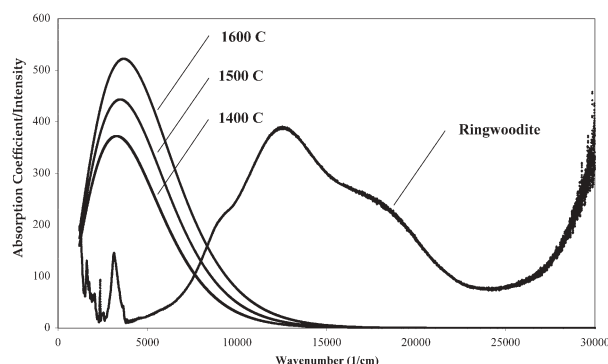


FIGURE 4. Comparison of the absorption spectrum of ringwoodite at ambient conditions with calculated blackbody radiation curves for 1400, 1500, and 1600 °C. The absorption coefficient is in cm^{-1} , the blackbody curves give the energy density of a blackbody in Joule per cm^3 and wavenumber interval.

are separated by Mg^{2+} . Another possible explanation could be that the early work by Mao and Bell (1972) and Mao (1976) was carried out in an un-gasketed diamond-anvil cell, where large pressure gradients may have led to a partial amorphization of the sample at high pressure. Part of the apparent increase of absorbance with frequency may also be due to light scattering on the polycrystalline aggregates used in that study.

Implications for radiative heat transfer in the mantle

The most important implication of this work is that radiative heat transfer in the mantle does not necessarily become blocked at high pressure due to the intensification and red shift of charge transfer bands. For ringwoodite of realistic composition, radiative conductivity actually increases with pressure, because with pressure all major absorption bands shift to higher frequencies, i.e., they move away from the maximum of the blackbody radiation (Fig. 4).

To fully quantify radiative conductivity in ringwoodite, additional data on the temperature dependence of absorption are required. Although the extinction coefficients of iron in ringwoodite are more than ten times higher than in olivine, this does not imply that the radiative conductivity of ringwoodite is necessarily lower, because at the same time, the absorption bands occur at higher frequencies than for olivine, so that ringwoodite is actually quite transparent in the frequency region where the maximum of blackbody radiation occurs at transition zone temperatures (Fig. 4). The radiative conductivity of ringwoodite would only be drastically reduced, if the crystal field bands broaden sufficiently at high temperature to close the window of transparency in the ringwoodite spectrum. This requires experimental testing, however, high-temperature spectra of olivine show only moderate broadening of the crystal field bands with temperature (Ullrich et al. 2002). Moreover, if the high intensity of the Fe^{2+} crystal field absorption bands in ringwoodite is indeed due to enhancement by interaction with Fe^{3+} , the integral

absorption coefficient may actually decrease with temperature (Taran et al. 1996).

More generally, our results cast serious doubts on the idea that ferromagnesian minerals necessarily become opaque in the visible and infrared range at high pressure. Also, the striking differences between the absorption spectrum of ringwoodite and olivine imply that one cannot simply assume that all ferromagnesian minerals including high-pressure phases have comparable radiative conductivity.

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