American Mineralogist, Volume 92, pages 433–436, 2007

LETTER

Optical absorption spectra of ferropericlase to 84 GPa

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ABSTRACT

Optical and near infrared absorption spectra of ferropericlase $Mg_{0.88}Fe_{0.12}O$ have been measured to 84 GPa. Under ambient conditions, the spectrum shows two crystal field bands of high-spin Fe^{2+} at 8922 and 12 533 cm^{-1}, which shift to higher frequencies with increasing pressure ($d\nu/dP$ = 50.7 and 85.5 cm^{-1}/GPa). Simultaneously, the intensity of the high-frequency band continuously decreases until it vanishes around 40 GPa, suggesting a quenching of the Jahn-Teller effect. Between 51 and 60 GPa, the absorption spectrum changes drastically. Two new bands appear at 60 GPa at 9728 and 14 592 cm^{-1} with frequency shifts at higher pressures of $d\nu/dP$ = 23.8 and 21.0 cm^{-1}/GPa, respectively. If the change in optical spectra between 51 and 60 GPa were interpreted as being due to spin-pairing, the crystal field parameters of low-spin Fe^{2+} at 60 GPa would be Δ = 10 546 cm^{-1} and B = 377 cm^{-1}. This would imply that the main cause of spin-pairing is not the increase in crystal field splitting Δ, but the stronger covalency of the Fe-O bond as seen in the reduction of the Racah parameter B. Even at 84 GPa, ferropericlase is by no means opaque. In particular, the inferred spin-pairing transition between 51 and 60 GPa reduces radiative thermal conductivity only by about 15%. Spin-pairing in ferropericlase is therefore unlikely to have major consequences for the temperature distribution or the mode of convection in the lower mantle. The absorption edge of the high-pressure phase appears to be deeper in the UV than for the low-pressure phase, which could imply a reduced electrical (polaron) conductivity.

Keywords: Ferropericlase, spin-pairing, low-spin, iron, optical spectra, radiative conductivity, crystal field splitting, Racah parameter, Jahn-Teller effect

INTRODUCTION

The possibility of spin-pairing of Fe^{2+} in the lower mantle has been discussed for decades (e.g., Ohnishi 1978; Burns 1991). Spin-pairing, i.e., the transition from a high-spin state to a low-spin state could be important essentially for three reasons: (1) it considerably reduces the ionic radius of Fe^{2+}, which could lead to a major density change; (2) the change in ionic radius and electron configuration could affect the partitioning of Fe; and (3) changes in the optical absorption spectra could affect the radiative thermal conductivity in the Earth's mantle. Badro et al. (2003) have recently reported evidence for spin-pairing in ferropericlase between 60 and 70 GPa based on X-ray emission spectra. Kantor et al. (2006) found evidence for spin-pairing in Mössbauer experiments under similar conditions, but with a wider range of pressures required for the completion of the transition. Spin-pairing occurs in the outer d-subshell of an atom and accordingly, both X-ray emission spectroscopy and Mössbauer spectroscopy probe this effect only indirectly, as they are based on processes occurring in the inner electronic shell or the nucleus of an atom. Optical spectroscopy, on the other hand, offers a much more direct access to spin transitions, as it directly probes the energy separation of the d-orbitals involved in the transition. Moreover, optical spectroscopy provides a direct measure of radiative thermal conductivity. Since the work of Mao and Bell (1972), it has almost universally been assumed that all Fe-bearing minerals become opaque at high pressures due to an intensification and red-shift of charge-transfer bands. This would imply that radiative thermal conductivity in the deeper mantle is negligible. However, Keppler and Smyth (2005) demonstrated that ringwoodite remains quite transparent to more than 20 GPa.

Shankland (1968) and Shankland et al. (1974) studied the optical absorption spectra of ferropericlase to about 4 GPa. Recently, Goncharov et al. (2006) reported some optical absorption spectra of ferropericlase to 74 GPa and they assigned some features in the high-pressure spectra to low-spin Fe^{2+}. Moreover, they concluded that spin-pairing could have a major effect on the radiative thermal conductivity of the lower mantle. However, the samples studied by Goncharov et al. were prepared at atmospheric pressure. Pressure has a major effect on the defect equilibria in ferropericlase (Bolfan-Casanova et al. 2002). Samples annealed under the same oxygen fugacity become poorer in Fe^{3+} at higher pressures. Even traces of Fe^{3+} have a drastic effect on optical absorption, as they cause intense Fe^{2+}-Fe^{3+} intervalence charge transfer bands (Burns 1993). Therefore, the effect of annealing ferropericlase at high pressure can often be observed with the naked eye as a color change from dark brown to light green. In this paper, we report the optical absorption spectra of ferropericlase samples annealed at high pressure under reducing conditions. The defect equilibria and therefore the optical absorption spectra of these samples are probably more realistic

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0003-004X/07/0203–433$05.00/DOI: 10.2138/am.2007.2454

for the lower mantle than those reported by Goncharov et al. (2006). While their spectra were dominated by charge transfer bands that much obscured the crystal field bands, we can clearly observe the evolution of the crystal field bands throughout the entire range of pressures studied.

Experimental methods

Sample synthesis

Ferropericlase containing 12 mol% of FeO was synthesized in a CO/CO_2 gas-flowing furnace at 1200 °C and $\log f_{O_2} = -17.4$. Starting material for the synthesis were pure MgO and Fe_2O_3 powders, which were carefully ground, mixed together and compressed to pellets. The sample was annealed for ~100 hours and during this period twice crushed and re-ground to achieve good chemical heterogeneity. The sample then was rapidly quenched into a cold reservoir containing the same gas mixture to prevent possible surface oxidation. The ferropericlase powder was then annealed at 25 GPa and 1800 °C for 24 hours in a 6–8 type multianvil apparatus at Fe-FeO buffer conditions inside an Fe capsule. The quenched material contained several large crystals (60–100 µm) that were selected and doubly polished for the measurements. Crystals were transparent of greenish color without any visible impurities. The purity of the samples was also checked by X-ray diffraction. The $Fe^{3+}/\Sigma Fe$ ratio was below 2%, as measured by Mössbauer spectroscopy. Electron microprobe analysis yielded the composition $Mg_{0.88(1)}Fe_{0.12(1)}O$.

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 (culet size 300 µm, diameter of the gasket hole 100 µm). Pressure medium was argon. Pressure was measured by ruby fluorescence. All spectroscopic measurements were carried out using a Bruker IFS 120 or 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 40 µm by an aperture in the rear focal plane of the 15-fold Cassegranian objective. Background measurements were carried out without the diamond cell in the beam path. Measurements were carried out from 1000 to 10000 cm^{-1} using a tungsten source, a Si-coated CaF_2 beam splitter and a narrow-band MCT detector; from 8500 to 22000 cm^{-1} using the same tungsten light source, but with a quartz beam splitter with dielectric coating and a Si diode detector; and from about 18000 to 26000 cm^{-1} using a xenon arc lamp, an Al-coated quartz beam splitter, and the Si-diode diode detector. In each spectral range several thousand scans were accumulated. Absorbance spectra were calculated according to $A(\nu) = \log I_0(\nu)/I(\nu)$, where $I(\nu)$ is the intensity with the sample, $I_0(\nu)$ the intensity without sample. The three resulting absorbance spectra were merged. The same measurements were carried out at each pressure with the beam only passing though the argon medium in the diamond cell, again measuring the background without the diamond cell in the beam. The resulting merged absorbance spectrum was then subtracted from the merged absorbance spectrum of the sample to produce the final spectrum.

Experimental results

Near infrared and optical absorption spectra obtained on two samples (A and B) are shown in Figures 1 and 2. Sample A was compressed to 43.7 GPa until the gasket became unstable. Sample B was measured up to 84 GPa. In the spectra of this sample (Fig. 2), some slight oscillations are seen below 10000 cm^{-1}, which are artifacts due to interference fringes. These fringes are absent from sample A (Fig. 1). Therefore, spectra up to 43 GPa are only shown for sample A, but the spectra obtained from sample B below 43 GPa are comparable to those measured on the other sample, aside from the presence of some interference fringes.

The following observations are obvious from the spectra: (1) At low pressures (e.g., 18.0 and 25.7 GPa, Fig. 1), the main absorption band consists of two components. They can be assigned to the $^5T_{2g} \rightarrow {}^5Eg$ crystal field transition of high-spin Fe^{2+} in an octahedral site (site symmetry O_h), split into two components by the Jahn-Teller effect. (2) Around 40 GPa, only one band is visible, suggesting that the Jahn-Teller distortion has disappeared. (3) There is a major change in the absorption spectrum between 51 and 60 GPa. New bands appear, while at the same time, the high-frequency absorption edge shifts into the UV.

All of these observations can be further quantified by a Gaussian deconvolution of the main absorption bands. Illustrative examples are given in Figure 3. They show clearly that from 1.9 to 36.7 GPa, the intensity of one of the Jahn-Teller split band components continuously decreases until it disappears around 40 GPa. The evolution of band frequencies as a function of pressure is shown in Figure 4. At low pressures, there are two bands, which shift to higher frequencies with increasing pressure (dv/dP = 50.7 cm^{-1}/GPa for the low-frequency band and 85.5 cm^{-1}/GPa for the high-frequency band). The extrapolated frequencies at 1 bar are 8922 and 12533 cm^{-1}. Band positions and frequency shifts are quite comparable to Shankland (1968) and Shankland et al. (1974). There is a clear discontinuity between 51 and 60 GPa. Two new bands appear at 60 GPa at 9728 and 14 592 cm^{-1}

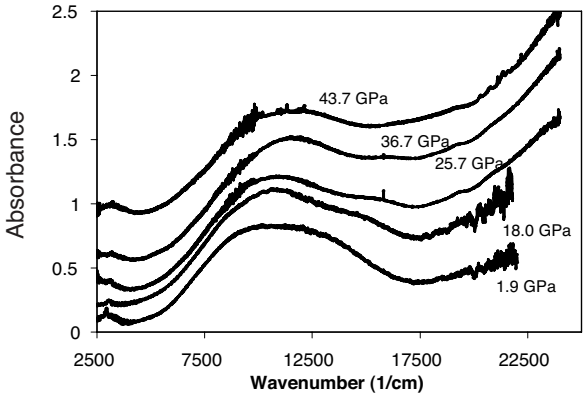

Figure 1. Optical absorption spectra of ferropericlase $Fe_{0.12}Mg_{0.88}O$ to 43.7 GPa. Sample A, thickness about 40 µm. The absorption coefficient can be obtained by dividing the measured absorbance by the sample thickness. Spectra are offset vertically for clarity.

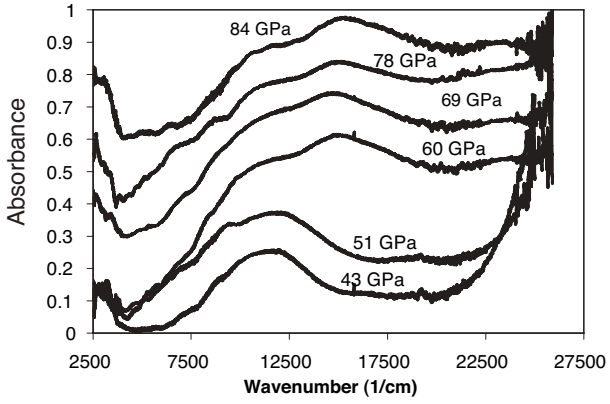

Figure 2. Optical absorption spectra of ferropericlase $Fe_{0.12}Mg_{0.88}O$ to 84 GPa. Sample B, thickness 21 µm. The absorption coefficient can be obtained by dividing the measured absorbance by the sample thickness. Spectra are offset vertically for clarity. Note the drastic change in the absorption spectrum between 51 and 60 GPa. The slight oscillations below 10000 cm^{-1} are artifacts (interference fringes).

with frequency shifts at higher pressures of $d\nu/dP$ = 23.8 and 21.0 cm^{-1}/GPa, respectively.

Discussion

The main problem in the data presented here is the interpretation of the change in the spectra occurring between 51 and 60 GPa. The band positions above this transition are not very different from those observed at lower pressures and they are quite within the range of frequencies reported for the crystal field bands of high-spin Fe^{2+} in octahedral sites (Burns 1993). However, it would be difficult to explain why the bands of high-spin Fe^{2+} should abruptly decrease in frequency with increasing pressure, unless a structural phase transition occurs that expands the Fe-O bond length. In the light of changes in the X-ray emission and Mössbauer spectra observed at similar pressure (Badro et al. 2003; Speziale et al. 2005; Kantor et al. 2006), one could assign the observed changes in the optical spectra to a transition from high-spin Fe^{2+} to low-spin Fe^{2+} (Badro et al. 2005; Goncharov et al. 2006). The two new bands observed above 60 GPa would then correspond to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ absorption bands of low-spin Fe^{2+}. From the observed frequencies and the Tanabe-Sugano diagram for a d^6 system (Figgis 1966), the crystal field parameters of low-spin Fe^{2+} at 60 GPa can be calculated. This yields a crystal field splitting Δ of 10 546 cm^{-1} and a Racah parameter B of 377 cm^{-1}. The value of Δ is not very different from that observed for many Fe^{2+}-bearing minerals at ambient conditions (Burns 1993). This is a surprising result, as it would imply that spin-pairing, if it indeed occurs around 60 GPa, would not be triggered by an increase in the crystal field splitting Δ, but by a strong reduction of the Racah parameter B far below its free-ion value (1060 cm^{-1}, Figgis 1966), indicating a change toward a more covalent nature of the Fe-O bond. This increase in covalency could also be the reason for the quenching of the Jahn-Teller effect observed immediately before the onset of the inferred spin-pairing transition, since the delocalization of electrons into ligand orbitals may reduce the asymmetry of the

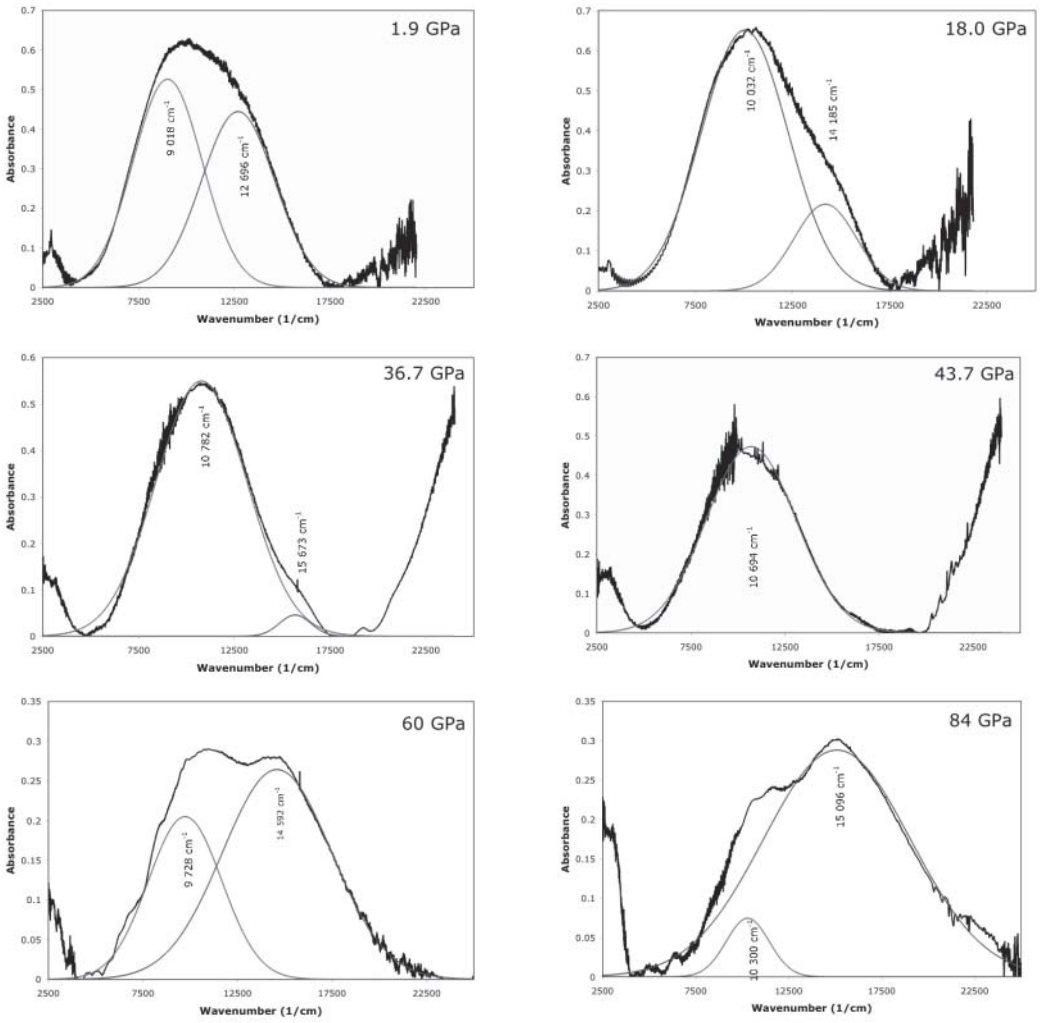

Figure 3. Deconvolution of the optical absorption spectra of ferropericlase $Fe_{0.12}Mg_{0.88}O$ into Gaussian components after subtraction of a linear baseline. The spectra from 1.9 to 43.7 GPa are from sample A (about 40 μm thick), the spectra at 60 and 84 GPa are from sample B (21 μm thick). At low pressure, two bands are seen which are due to the Jahn-Teller distortion of high-spin Fe^{2+}. One of the two bands gradually decreases in intensity until it vanishes at about 40 GPa. Between about 40 and 50 GPa, only one band is seen, while two bands appear again at higher pressures.

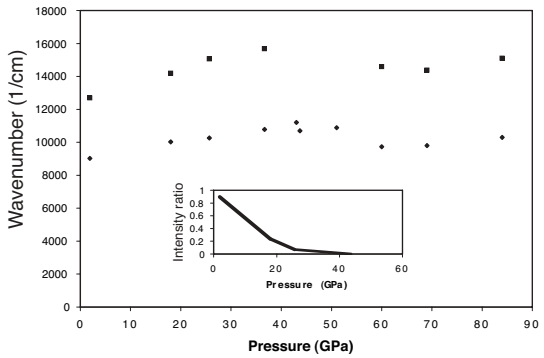

FIGURE 4. Frequencies of the optical absorption bands of ferropericlase $Fe_{0.12}Mg_{0.88}O$ to 84 GPa. The inset shows the intensity ratio of the high-frequency band over the low-frequency band to about 40 GPa. Between about 40 GPa and 50 GPa, only one band is seen, while two bands appear again at higher pressures. While these bands occur at similar frequencies as the two bands observed below 40 GPa, their frequencies are somewhat offset and their intensities are also different.

electron distribution in the d-orbitals. Such a coupling between the Jahn-Teller effect and spin-pairing is not uncommon (Kambara 1979).

GEOLOGICAL IMPLICATIONS

The transition observed between 51 and 60 GPa clearly changes the optical transparency of ferropericlase and as such, it affects the radiative thermal conductivity of the lower mantle. In the simplest approximation, radiative conductivity is proportional to the emissivity of a black body E divided by the linear absorption coefficient A of the material (Clark 1957). Therefore, radiative thermal conductivity k_{rad} will be proportional to the integral over E/A:

$$k_{rad} \sim \int_{\nu} \frac{E(\nu)}{A(\nu)} d\nu$$

Evaluating this integral for a temperature of 2500 K and using the measured absorption spectra at 51 and 60 GPa yields a decrease of radiative conductivity by a mere 15% across the inferred spin-pairing transition (Fig. 5[1]). This is due to the fact that radiative conductivity will be dominated by those parts of the spectrum where the emissivity of the black body is highest and absorbance is lowest, i.e. the region around 2500–7500 cm^{-1} (Fig. 2). In this region, the spectra at 51 and 60 GPa are hardly different. There are major differences in the visible region, but here the black body emission is weaker and the absorptivity of ferropericlase higher anyway and accordingly, these differences contribute little to the magnitude of radiative conductivity. We, therefore, conclude that the spectral changes observed around 60 GPa have no important implications for the temperature distribution or the mode of convection in the lower mantle. If at higher Fe contents, the change in spin-state occurs more gradually over a larger range of pressures (Sturhahn et al. 2005), the effects will be subtle. However, ferropericlase is by no means opaque even at the highest pressures studied and therefore, the radiative contribution to thermal conductivity may not be negligible. The much stronger absorbances observed in previous studies (e.g., Goncharov et al. 2006) are probably due to intervalence charge transfer related to elevated contents of ferric iron which are not realistic for the lower mantle. For fully quantitative models of radiative conductivity in the lower mantle, combined high-*P* and high-*T* absorption spectra for both ferropericlase and magnesium silicate perovskite are required.

The observation that above 60 GPa, the absorption edge appears to be shifted deeper into the UV as compared to lower pressures could imply a higher activation energy for oxygen to metal charge transfer which could result in a reduced electrical (polaron) conductivity of ferropericlase

[1] Deposit item AM-07-006, Figure 5 (estimate of radiative thermal conductivity). Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

ACKNOWLEDGMENTS

We gratefully acknowledge constructive reviews by Michail Taran and an anonymous referee. This work was supported by German Science Foundation (DFG, Leibniz award to H.K.).

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MANUSCRIPT RECEIVED SEPTEMBER 19, 2006
MANUSCRIPT ACCEPTED OCTOBER 17, 2006
MANUSCRIPT HANDLED BY BRYAN CHAKOUMAKOS