Reduced radiative conductivity of low spin FeO₆-octahedra in FeCO₃ at high pressure and temperature

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Abstract

The ability of Earth's mantle to conduct heat by radiation is determined by optical properties of mantle phases. Optical properties of mantle minerals at high pressure are accessible through diamond anvil cell experiments, but because of the intense thermal radiation at $T > 1000$ K such studies are limited to lower temperatures. Accordingly, radiative thermal conductivity at mantle conditions has been evaluated with the assumption of the temperature-independent optical properties. Particularly uncertain is the temperature-dependence of optical properties of lower mantle minerals across the spin transition, as the spin state itself is a strong function of temperature. Here we use laser-heated diamond anvil cells combined with a pulsed ultra-bright supercontinuum laser probe and a synchronized time-gated detector to examine optical properties of high and low spin ferrous iron at 45-73 GPa up to 1600 K in an octahedral crystallographic unit (FeO₆), one of the most abundant building blocks in the mantle. Siderite (FeCO₃) is used as a model for FeO₆-octahedra as it contains no ferric iron and exhibits a sharp optically apparent pressure-induced spin transition at 44 GPa, simplifying data interpretation. We find that the

optical absorbance of low spin FeO_6 increases with temperature due to the partially lifted Laporte selection rule. The temperature-induced low-to-high spin transition, however, results in a dramatic drop in absorbance of the FeO_6 unit in siderite. The absorption edge (Fe-O charge transfer) red-shifts ($\sim 1 \text{ cm}^{-1}/\text{K}$) with increasing temperature and at $T > 1600 \text{ K}$ and $P > 70 \text{ GPa}$ becomes the dominant absorption mechanism in the visible range, suggesting its superior role in reducing the ability of mantle minerals to conduct heat by radiation. This implies that the radiative thermal conductivity of analogous FeO_6 -bearing minerals such as ferropericlase, the second most abundant mineral in the Earth's lower mantle, is substantially reduced approaching the core-mantle boundary conditions.

Keywords: Optical properties; thermal conductivity; spin transition; high pressure; siderite; ferropericlase

1. Introduction

Heat conduction through the Earth largely determines its internal structure¹⁻⁴. Therefore, knowledge of mineral thermal conductivity under relevant mantle pressures and temperatures is vital for our understanding of the Earth's interior. Radiative thermal conductivity (k_{rad}) is believed to play an increasingly important role at $T > 800 \text{ K}$ (Ref.⁵⁻⁷) because of the near-cubic dependence of k_{rad} on temperature¹. Absolute values of k_{rad} are determined by absorbance in the visible and near-infrared (IR) range⁸⁻¹⁰, provided that the mineral grain size in the mantle is sufficiently large⁴. This is why initial proposal of the increasing importance of heat conduction by radiation with depth⁵ had triggered interest in optical properties of Fe-bearing olivine and pyroxene⁸, dominant upper mantle phases. Soon it was realized that optical properties of minerals themselves are highly dependent on temperature and pressure; thus, these must be addressed at relevant mantle conditions. Diamond anvil cells (DACs) have previously been employed to study variations in optical and near-IR absorption at high pressure, but at room

temperature¹¹⁻¹⁹. Likewise, high temperature studies at near-ambient pressures were not conclusive^{9, 10, 20-22}. More recently, examining optical properties of minerals in resistively-heated DACs helped understand the combined effect of pressures and temperature, but the results are scarce and limited to $T < 900$ K (Ref.^{11, 23}).

In the absence of spectroscopic data at simultaneous conditions of high pressure and temperature a common approach has been to use room temperature absorption coefficients to evaluate k_{rad} values as a function of temperature^{13, 15, 16, 18, 24}. Experimental measurements of minerals' optical properties at lower mantle pressure-temperature (P-T) conditions ($P > 24$ GPa, $T > 2000$ K) are needed to test the validity of this traditional approach and to gain accurate values of thermal conductivity.

Absorption spectra of bridgmanite and ferropericlase (FP), the major lower mantle phases, are governed by the crystal field (CF), iron-oxygen, and Fe^{2+} - Fe^{3+} transitions²⁵. Unfortunately, these bands often overlap making it difficult to isolate the contribution of a specific crystallographic environment to the optical properties. In addition, optical properties are sensitive to the spin state of iron-bearing minerals. For example, new bands appear in the absorption spectrum of FP as a result of the high spin (HS) to low spin (LS) transition at $P > 50$ GPa (Ref.¹⁴). Accordingly, a reduced radiative conductivity scenario has been proposed for the LS mantle^{11, 14}.

On top of this, high temperature is expected to affect mineral optical properties²⁵, but the effect of it has been unclear since optical absorption experiments at $T > 1000$ K are very challenging, as the probe signal vanishes in the vast blackbody radiation. The course of this work is focused on overcoming the experimental barriers by combining laser-heated (LH) DACs with an ultra-bright probe synchronized with a time-gated detector.

Here we investigate optical properties of the FeO_6 -octahedron, one of the most common building blocks of mantle minerals, at $P = 45$ -85 GPa and $T = 300$ -1625 K in the LS state and

across the low-to-high spin transition. We chose siderite (FeCO_3) as a model to access optical properties of the FeO_6 -octahedron in FP with only ferrous iron because siderite contains no ferric iron. Conveniently for the direct comparison, both minerals undergo a spin transition at very similar pressures: 44 GPa (siderite)²⁶⁻³⁰ and at $P > 45\text{-}65$ GPa (FP)³¹⁻³⁴. Our results show for the first time that minerals with LS ferrous iron have a substantially increased intrinsic absorption in the visible and near-IR spectral range at high temperatures, suggesting a greatly reduced radiative conductivity. This result underscores the necessity of measurements of optical properties at simultaneous conditions of high pressure and temperature to determine k_{rad} of lower mantle minerals.

2. Experimental Methods

2.1 Samples.

Natural siderite (Panasqueira tungsten mine, Covilhã, Castelo Branco, Portugal) used in this study is identical to that used in our previous report on siderite optical properties at high pressure and room temperature (Ref.²⁶). Chemical composition ($\text{Fe}_{0.95}\text{Mn}_{0.05}\text{CO}_3$), homogeneity, and low impurity content (< 1 at.%) of our samples were confirmed in the Geophysical Laboratory using a JEOL JSM-6500F field emission scanning electron microscope. Flat, rhombohedral single crystals (typically $30 \times 50 \times 10 \mu\text{m}^3$) without observable defects were selected under an optical microscope. Subsequently, the crystals were positioned in the DAC sample cavity (70-120 μm in diameter) between two dried KCl or CaF_2 wafers (10-15 μm thick) serving as a thermal insulation and pressure medium. The ruby R1 fluorescence method³⁵, the position of diamond (anvil) Raman edge³⁶ and siderite CF absorption band²⁶ were used to evaluate pressure. Pressure uncertainty was of the order of 3-4 GPa and reflects typical deviations in apparent pressure using the 3 pressure gauges.

2.2 Optical absorption in laser-heated diamond anvil cell.

A 1070 nm quasi-continuous double-sided laser-heating system was based on the optical setup of McWilliams et al.³⁷. In addition, Leukos Pegasus pulsed supercontinuum [broadband (400-2400 nm)] laser, serving as a light source for absorption measurements, was introduced into the DAC using a broadband beamsplitter. The transmission of the supercontinuum was collected by a grating (300 gr/mm) 300 mm focal length spectrometer with a synchronized iCCD detector (Andor iStar SR-303i-A), wavelength range 350-850 nm. The heating laser was modulated for 1 second, initiating the beginning of one spectral collection. At a specified delay (200 ms, sufficient to reach a steady temperature regime³⁸), a train of supercontinuum pulses (4 ns pulse length, 250 kHz repetition rate) was collected by the gated iCCD detector (gate width 30 ns) operating at ~41 kHz for 500 ms (Fig. 1). The gating of the optical spectra collection combined with a very high brightness of the supercontinuum light source was important to overcome a poor signal-to-noise ratio due to background thermal emission from the heated sample. The repetitive spectra collections were performed at several spectral positions of the spectrograph and these spectra were stitched together for the combined spectrum in the 12500-22500 cm⁻¹ (444-800 nm) spectral range. A spectrum at each grating position was accumulated on the iCCD over 500 ms. The sample absorbance was calculated as

$$A(\nu) = -\log_{10}(I_{sample}^T - Bckg^T / I_{reference}^{300K} - Bckg^{300K}),$$

where I_{sample}^T is the intensity of light transmitted through the sample at temperature T , $I_{reference}^{300K}$ is the intensity of the radiation passed through the pressure medium at room temperature, $Bckg^T$ and $Bckg^{300K}$ are backgrounds at T and room temperature, respectively. High-temperature thermal background of the sample was accumulated at each temperature step using the identical timing and laser-heating power, but with blocked supercontinuum source. Reflection from the sample-medium interface (< 4 % of $I_{reference}^{300K}$) was neglected in absorption measurements as it is comparable to other experimental uncertainties¹².

Fig. 1. Timing of the optical absorption measurements at high temperature. Every sixth pulse of the supercontinuum pulse train is recorded by the detector operated at 41 kHz in a gated mode.

For double-sided temperature measurements (grating centered at 700 nm), the sample was imaged simultaneously from both sides (using a D-mirror) on the 2D iCCD detector array and these images were shifted from each other in the non-spectral direction (vertically). Temperature was measured spectroradiometrically with collection times ranging from 0.1 to 10 seconds depending on the emission intensity. The optical response of the system was calibrated using a standard white lamp (Optronics Laboratories OL 220C) and the emission spectrum was fitted to the Planck black body radiation function using the T-Rax software (C. Prescher) to extract the temperature value.

Typical collection runs involved: (i) optical absorption measurement before LH, (ii) temperature measurement, (iii) optical absorption measurement at high temperature, (iv) high-temperature background measurement, (v) optical absorption measurement in quenched sample, and (vi) temperature measurement. The second temperature measurement was to verify temperature stability over the cycle. Typical differences between 2 such measurements were < 50 K. Temperatures reported here are averaged over the 2 temperature collections and from both DAC sides. The heating effect of the probe laser was estimated as smaller than 50 K based on the

power difference of the probe and laser-heating beams, which is within the overall uncertainties of ± 100 -150 K, typical of spectroradiometry temperature measurements in LH DAC³⁹.

3. Results and Discussion

At $P < 44$ GPa absorbance of HS siderite was identical to that reported for siderite in Ne pressure medium²⁶. Briefly, HS siderite remains visually colorless and overall optical absorbance is small with only a weak CF band centered at $\sim 14100 \text{ cm}^{-1}$ (43 GPa). This is why we could not couple the 1070 nm heating laser to siderite at $P < 44$ GPa and did not examine the HS phase at high temperature. Upon the spin transition in the relatively rigid KCl or CaF₂ pressure medium siderite turned visually black (probably due to sample cleavage), showing 0.3-0.5 higher absorbance as compared to the samples of similar thickness, but in the Ne pressure medium (Fig 2)²⁶, although the spectra are qualitatively similar.

3.1 45 GPa

The strong absorption band centered at $\sim 15500 \text{ cm}^{-1}$ observed in the optical absorption spectra before and after laser-heating (Fig. 2) is characteristic of LS siderite and is attributed to the $^1A_{1g} \rightarrow ^1T_{1g}$ transition in Fe^{2+} electronic structure split by an octahedral CF²⁶. At 1200 and 1300 K this absorption peak is no longer present in the spectrum, but substituted by a weak absorption band centered at $\sim 14500 \text{ cm}^{-1}$, attributed to the $^5T_{2g} \rightarrow ^5E_g$ transition in HS siderite. The band assignment was based on the energy and number of spin-allowed excitations for a HS and LS $d6$ ion in an octahedral CF²⁶. The abrupt change in the siderite optical absorption and correspondence with room temperature spectra of HS and LS siderite (gray curves in Fig. 2) indicate that LS to HS transformation at 1200-1300 K has completed. The absorption edge (AE) of LS siderite red-shifts with increasing temperature which was previously observed in Fe-bearing silicates and attributed to the band gap closure due to the electronic band broadening^{20, 22, 25, 40}. Please note that the absorption spectra before and after LH are almost identical, indicating a reversible character of the observed transformations in the heating cycle. Heating to $T > 1400$ -

1500 K produced an opaque region in the heated spot, which remains in the quenched sample. A phase transition⁴¹ and decomposition⁴² scenarios have been previously proposed for this P-T region of FeCO₃ phase diagram, both consistent with our observations.

Fig. 2. Measurements of high-temperature siderite absorption spectra at 45 GPa. The spectra measured before heating and quenched after 1300 K heating are shown in light and dark blue, respectively. Green and red curves are absorption spectra at 1200 K and 1300 K, respectively. Spectra shown in gray represent room temperature absorption data on HS (43 GPa) and LS (45.5 GPa) siderite after Lobanov et al.²⁶, shown for comparison. Note the temperature-induced (300 to 1300 K) red-shift of the AE (absorption edge) of LS siderite. The difference in the absorbance magnitude of these measurements and the results of Lobanov et al.²⁶ is due to the sample cleavage introduced by the rigid pressure medium used in this study (CaF₂ vs Ne in Ref.²⁶)

3.2 55 GPa

Heating of LS siderite to $T \sim 1000$ K at 55 GPa broadens, red-shifts, and intensifies the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ band (Fig. 3A). Thermal broadening of CF bands results from the participation of excited vibrational states in the electron transfer²⁵. The red-shift is likely due to the thermal expansion as the energy separation between the t_{2g} and e_g orbitals is inversely proportional to the fifth power of the metal-ligand distance²⁵. Intensity variations of CF bands with temperature reported in the literature show a less regular behavior^{9-11, 22, 23, 43, 44}, but often may be understood

in terms of temperature-induced changes in the CF symmetry⁴⁰ lifting the Laporte selection rule, which impedes electron transfer among the same parity states (*e.g.* *d-d* transitions). Several mechanisms may partially lift the Laporte selection rule. For example, an interaction of *d*-orbitals with thermally activated odd-parity vibrational states (termed vibronic coupling) has been proposed to explain the temperature-enhanced absorption of Fe²⁺ CF bands in olivine^{9, 21, 25}. Alternatively, distorting the centrosymmetric octahedral CF may lead to an increased mixing of iron 3*d* and 4*p* orbitals partially lifting the Laporte selection rule²⁵.

Fig. 3. Measurements of high-temperature siderite absorption spectra at 55 GPa. Light and dark blue curves are spectra measured before heating and after heating to corresponding temperatures. Green (~ 1000 K), orange (1200 K), and red (1625 K) curves in **A** and **B** are high-temperature spectra. Temperature-induced red-shift of the AE (absorption edge) is evident in **B**. Gray dashed lines are guides to the eye. Pressure medium is KCl.

At 1200 K the intensity of the CF band has dropped, signaling an increased contribution of the HS states ($^5T_{2g} \rightarrow ^5E_g$ transitions) which are less absorbing (Fig. 3A), broadly consistent with the $(Mg_{0.35}Fe_{0.65})CO_3$ spin state diagram⁴⁵. At 1625 K it was no longer possible to reliably trace the CF band due to its progressive broadening and overlap with the red-shifted AE (Fig. 3B). All high-temperature spectra show an increased absorption at the lower wavenumbers (12500-15000 cm⁻¹) compared to corresponding room temperature spectra, which might be due to the temperature-induced asymmetrical broadening and red-shift of the $^1A_{1g} \rightarrow ^1T_{1g}$ band. Likewise, the red-shifted AE that becomes broader with P and T may contribute to the sample

absorption at 12500-15000 cm^{-1} at $T > 1200$ K. Absorption spectra of quenched samples after LH to ~ 1000 K and 1200 K are identical to the corresponding before-heating spectra, indicating a reversibility of the temperature-induced transformations. The spectrum collected after heating to 1625 K is slightly less absorbing probably due to stresses annealing at high temperature.

3.3 73 GPa

Figure 4 shows absorption spectra of LS siderite at 73 GPa. At this pressure the $^1A_{1g} \rightarrow ^1T_{1g}$ CF band is centered at > 17000 cm^{-1} and was barely resolved because of the overlap with the AE and the overall large absorbance reaching ~ 4 , which is close to the detection limit of the spectrometer. The spectra at high T are dominated by the AE, which shows an apparent red-shift with increasing temperature (~ 1 cm^{-1}/K), making the CF band extremely difficult to follow. One peculiar feature is an increased absorbance at 12500-16000 cm^{-1} at $T = 1000$ K (**Fig. 4A**). We attribute this to the intensification, broadening, and red-shift of the $^1A_{1g} \rightarrow ^1T_{1g}$ band, as in the absorption spectrum of LS siderite at ~ 1000 K at 55 GPa where the temperature-enhanced CF band is more apparent (**Fig. 3A**). Accordingly, we assign the 1000 K spectrum to LS siderite. Further temperature increase to 1225 K results in the decrease of absorbance at 12500-16000 cm^{-1} (**Fig. 4A**) indicating, perhaps, a higher population of the HS states which are less absorbing. At 1425 K, however, the red-shifted AE causes a gradual increase in absorbance at 13000-16000 cm^{-1} (**Fig. 4B**).

Fig. 4. Measurements of high-temperature siderite absorption spectra at 73 GPa. Light and dark blue curves are spectra measured before heating and after heating to corresponding temperatures. Green (1000 K), orange (1225 K), and red (1425 K) curves are high-temperature spectra. The absorption spectrum red-shifts upon heating to 1000 K (green arrow), but it blue-shifts upon heating to 1225 K (orange arrow). Further heating to 1425 K causes a gradual red-shift of $\sim 1 \text{ cm}^{-1}/\text{K}$ (red arrow). Gray dashed lines are guides to the eye. Pressure medium is KCl.

The assignment of 1225 and 1425 K spectra (Fig. 4B) to the mixed spin state disagrees with the spin diagram of magnesiosiderite $[(\text{Mg}_{0.35}\text{Fe}_{0.65})\text{CO}_3]$ (Ref.⁴⁵) in the onset temperature of the LS to HS transition. We believe that this discrepancy is due to a combination of (i) contrasting sample compositions, (ii) different spin state diagnostic techniques – optical spectroscopy is very sensitive to a minute presence of the HS state, (iii) different heating techniques (resistive-heating below 800 K and laser-heating to 1200 K in Ref.⁴⁵ vs laser-heating only in this study).

4. Radiative thermal conductivity of the spin transition zone

Traditionally, the key assumption for quantifying radiative thermal conductivity of Fe-bearing minerals is that the absorption coefficient is temperature-independent in a wide spectral range (*e.g.* 2000-25000 cm^{-1})^{5, 6, 8-18, 23, 24, 46} to allow using the room temperature absorption coefficient in the absence of high-temperature absorption data. Our results are at odds with this assumption because optical properties of Fe-bearing minerals appear sensitive to high temperature. Specifically, distortions of FeO_6 -units, their spin state, and position of the AE at high temperature govern sample absorbance in the 12500-22500 cm^{-1} spectral range.

In order to estimate the difference between the traditionally determined k_{rad} (from 300 K absorption data) and k_{rad} , quantified using high-temperature absorption data, we extend the 73 GPa spectra (Fig. 4) to $< 12500 \text{ cm}^{-1}$ using the previously reported near- and mid-IR siderite absorption data²⁶ and assuming the absorption spectrum at $< 12500 \text{ cm}^{-1}$ is temperature-independent, as it is featureless. In quantifying the absorption coefficients at 300, 1000, 1225, and 1425 K we suppose a sample thickness of 10 μm , as we are interested only in relative

differences in k_{rad} . We may now use the 300, 1000, 1225, and 1425 K absorption coefficients within the traditional approach (as if the high-temperature absorption coefficients were collected at 300 K)^{9, 10, 23, 24} to understand the magnitude of differences in k_{rad} introduced by assuming temperature-independent absorbance (Fig. 5). The absolute values, however, are arbitrary because of the uncertainty introduced by the increased overall absorption due to the use of rigid pressure medium.

Fig. 5. Apparent radiative thermal conductivity (k_{rad}) of siderite at 73 GPa calculated using absorption spectra shown in Figure 4 appended to near- and mid-IR data reported by Lobanov et al.²⁶ in the 2500-12500 cm^{-1} spectra range (71.5 GPa, 300 K) and assuming absorbance at $< 12500 \text{ cm}^{-1}$ is temperature-independent. The color refers the curves to the absorption spectra shown in Figure 4. Maximum differences in k_{rad} are on the order of 21 % at 4500 K.

Importantly, the curves shown in Figure 5 reflect differences in k_{rad} due to (i) intrinsic temperature-dependent absorption of LS siderite (green curve), (ii) changes in absorption due to the LS to HS transition (orange and red), and (iii) red-shifting AE (orange and red). These three mechanisms of temperature-induced variations in optical absorbance of Fe-bearing minerals were previously unknown at high pressure and temperature conditions. We propose that the revealed mechanisms may be significant for LS FP, affecting its radiative conductivity in the lower mantle albeit substantially higher temperatures than in this study.

Moderate differences in k_{rad} calculated using 300 K vs high-temperature absorption data peak at the highest temperatures (up to 21 % for the LS state) because of the increased overlap of the siderite absorption features with the blackbody radiation spectrum. Radiative thermal conductivity of siderite with a mixed iron spin state (1225 and 1425 K reference absorption spectra) appears < 6% lower than the curve produced by the 300 K absorption coefficient. This is a direct consequence of siderite low optical absorbance at < 13500-14000 cm^{-1} (Fig. 4B). In FP the correction may be larger as its CF bands are located at 5000-15000 cm^{-1} and, therefore, closer to the peak position of the thermal radiation spectrum (Refs.^{14, 15, 17}). The previously inferred k_{rad} of FP is < 0.1 W/mK (based on 300 K absorption coefficient) at the core-mantle boundary (CMB) conditions^{11, 12}. Theoretical computations indicate that the fraction of HS states is small (< 0.5) at the base of the lower mantle⁴⁷⁻⁵⁰. If such, the temperature-induced broadening and intensification of the $^1A_{1g} \rightarrow ^1T_{1g}$ band as well as the red-shift of the AE ($\sim 1\text{cm}^{-1}/\text{K}$) observed in this study will diminish the ability of LS FP to conduct heat by radiation at CMB conditions. The latter is consistent with the finite-temperature first-principles molecular dynamic simulations indicating a semimetallic behavior of FP at the base of the mantle⁴⁸. In this scenario, radiative thermal conductivity of FP is negligible at CMB conditions.

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