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Radiative conductivity and abundance of post-perovskite in the lowermost mantle

Sergey S. Lobanov [a,b,*,1], Nicholas Holtgrewe [a,c,1], Jung-Fu Lin [d,e], Alexander F. Goncharov [a,f]

[a] Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA
[b] Sobolev Institute of Geology and Mineralogy, Siberian Branch Russian Academy of Sciences, Novosibirsk 630090, Russia
[c] Howard University, 2400 Sixth Street NW, Washington, DC 20059, USA
[d] Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, Austin, TX 78712, USA
[e] Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 130012, China
[f] Key Laboratory of Materials Physics, Institute of Solid State Physics CAS, Hefei 230031, China

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A B S T R A C T

Thermal conductivity of the lowermost mantle governs the heat flow out of the core energizing planetary-scale geological processes. Yet, there are no direct experimental measurements of thermal conductivity at relevant pressure–temperature conditions of Earth's core–mantle boundary. Here we determine the radiative conductivity of post-perovskite at near core–mantle boundary conditions by optical absorption measurements in a laser-heated diamond anvil cell. Our results show that the radiative conductivity of $Mg_{0.9}Fe_{0.1}SiO_3$ post-perovskite (∼1.1 W/m/K) is almost two times smaller than that of bridgmanite (∼2.0 W/m/K) at the base of the mantle. By combining this result with the present-day core–mantle heat flow and available estimations on the lattice thermal conductivity we conclude that post-perovskite is at least as abundant as bridgmanite in the lowermost mantle which has profound implications for the dynamics of the deep Earth.

1. Introduction

The lowermost 200–400 km of the mantle is a critical region responsible for the core–mantle interaction powering all major geological processes on Earth (Lay et al., 2008). Specifically, thermal conductivity of the thermal boundary layer (TBL) above the core–mantle boundary (CMB) determines the heat flow out of the core that provides energy to sustain the mantle global circulation and to drive the geodynamo (Lay et al., 2008). Seismic structures of the lowermost mantle, however, are complex (Lay et al., 2006; van der Hilst et al., 2007) implying that the thermal conductivity of the region is non-uniform due to variations in chemical (e.g. iron) and/or mineralogical contents as well as texturing of the constituting minerals. The nature of the seismic heterogeneity near the CMB, including a sharp increase in shear wave velocity and anti-correlations of seismic parameters, has been linked to the bridgmanite (Bdgm) to post-perovskite (Ppv) transition (Murakami et al., 2004; Oganov and Ono, 2004), as these phases have contrasting elastic, rheological, and transport properties (Oganov and Ono, 2004). Indeed, measurements and computations of lattice thermal conductivity (k_{lat}) in Bdgm and Ppv have revealed that Ppv conducts heat 50–60% more efficiently than Bdgm (Ammann et al., 2014; Haigis et al., 2012; Ohta et al., 2012), suggesting that the distribution of the Ppv phase can significantly enhance the heat flux out of the core. However, no mineral physics constraints are available on the radiative thermal conductivity (k_{rad}) of Ppv, which should play an increasingly important role at high temperature (Hofmeister, 2014), as well as on the Ppv abundance in the lowermost mantle. This has hampered our understanding of how the heat flux across the CMB may vary laterally and what magnitude of the energy source in the mantle and the outer core is needed to power their convections.

Previous estimates of radiative thermal conductivity at lower mantle conditions were based on high-pressure room-temperature measurements of the absorption coefficients of representative minerals in the mid/near-infrared and visible spectral range (Goncharov et al., 2006, 2008, 2009, 2015; Keppler et al., 2008). The presence of an intense thermal radiation emitted from the hot sample

* Corresponding author at: Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA.
E-mail addresses: slobanov@carnegiescience.edu, slobanov@igm.nsc.ru (S.S. Lobanov).

[1] These authors contributed equally to this work.

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makes measurements of the optical properties at high temperatures relevant to the lowermost mantle (approximately 3000 K) very challenging as common light sources have similar radiative temperatures. In the absence of the experimental data, the effect of temperature was neglected. It has been argued that temperature-induced variations in the absorption spectrum of Bdgm are small as intensity of the crystal-field band is determined by a symmetry distortion of the $Fe^{2+}O_{12}$-polyhedra in Bdgm (Keppler et al., 2008). However, the intensity of the crystal field spectrum in iron-bearing minerals can be sensitive to pressure, temperature, iron concentration, and iron spin states (Burns, 1993; Goncharov et al., 2006, 2010; Keppler et al., 2007; Lobanov et al., 2015, 2016, 2017). Moreover, due to a substantial amount of Fe^{3+} in Bdgm and Ppv at lower mantle conditions (Sinmyo et al., 2006), the absorption coefficients and thus the radiative conductivity of these minerals are also governed by the Fe^{2+}–Fe^{3+} charge transfer (CT) (Burns, 1993), which is expected to diminish with temperature (Mattson and Rossman, 1987). Therefore, to ascertain the presently unknown radiative conductivity of iron-bearing minerals at expected CMB conditions, it is of fundamental importance to underpin physical mechanisms that govern optical absorption of lower mantle minerals at simultaneous high pressure–temperature conditions. It is also desirable to assess the intensity of the absorption bands as a function of the total iron content because the solubility of iron in lower mantle minerals can vary with pressure, temperature, and phase/spin transitions (Ismailova et al., 2016).

2. Experimental methods

2.1. Absorption measurements in the visible (13000–22000 cm^{-1}) and near-infrared ranges (6200–11000 cm^{-1}) were divided into heating runs at two laser-heating systems equipped with different spectrometers and detectors (denoted hereafter as VIS and IR runs). A Leukos Pegasus pulsed supercontinuum light source (400–2400 nm) was inserted into the optical path of both systems, serving as a probe. For the VIS, the transmitted probe light was collected using a spectrometer with a 300 gr/mm grating and 300 mm focal length and a gated iCCD detector (Andor iStar SR-303i-A) synchronized with the supercontinuum pulses, identically to that described in Lobanov et al. (2016). For the IR, we used Action Spectra Pro 2300i spectrometer equipped with a 150 gr/mm grating and an ungated InGaAs detector (Princeton Instruments Model 7498-0001). The collection of 2500 supercontinuum pulses over 10 ms was initiated 200 ms after the start of the 1 s laser heating. The large number of bright probe pulses in a short accumulation window was important to increase signal-to-noise ratio and suppress thermal background. Absorption coefficient at high temperature (T) was evaluated as $\alpha(\upsilon) = \ln(10) * \frac{1}{d} * (-\log_{10}(\frac{I^T_{sample} - Bckg^T}{I^{300\ K}_{reference} - Bckg^{300\ K}}))$, where d is the sample thickness, I^T_{sample} is the intensity of light transmitted through the sample at T, $I^{300\ K}_{reference}$ is the intensity of light through the pressure medium at 300 K, $Bckg^T$ is background at T, and $Bckg^{300\ K}$ is background at 300 K. Reflections from the sample-medium interface were neglected as these are typically small (<2%) in the frequency range of interest (Goncharov et al., 2009). Background at high T was collected right after the high T absorption measurement at identical laser-heating power and timing setup. The gap in absorption coefficients at ∼9000–10500 cm^{-1} is due to the filters used to block the 1070 nm heating pulse, while the gap at 11000–13000 cm^{-1} is due to the limited sensitivity of the iCCD and InGaAs detectors. The sample absorbance in these ranges was extrapolated based on the room temperature data collected with a conventional light source. The 2500–6200 cm^{-1} region was extrapolated in a similar way and assumed temperature-independent as it is essentially featureless. Below 2500 cm^{-1}, a strong absorption due to phonons (fundamentals and overtones) is not expected to change substantially with temperature (Thomas et al., 2012); thus, this region does not contribute significantly to the radiative conductivity and was excluded from the integration. Likewise, we excluded the range above 25000 cm^{-1} where the Planck function is essentially zero at all temperatures of interest.

2.2. Double-sided laser-heating and temperature measurements in the VIS runs were identical to that of Lobanov et al. (2016). For the IR runs, at double-sided laser-heating we could only perform single-sided temperature measurements for which the grating was centered at 1320 nm and the supercontinuum was blocked. In both VIS and IR, temperatures measurements were taken before and after the corresponding collection of the absorbance data at an identical laser power. The laser power was optimized to achieve comparable temperatures in the VIS and IR runs (within 50–100 K). Optical responses of the VIS and IR systems were calibrated using a standard white lamp (Optronics Laboratories OL 220C). To extract the temperature, the emission spectra were fitted to the Planck black body function using the T-Rax software (C. Prescher). The reported temperature is an average of the VIS and IR measurements.

2.3. Sample thickness required to deduce the absorption coefficient of $Mg_{0.6}Fe_{0.4}SiO_3$–Ppv was determined via white light interferometry at 130 GPa through the NaCl pressure medium (3.6 μm). Additionally, the sample thickness was confirmed by direct SEM imaging of the recovered sample at 1 atm (∼5 μm). The difference in sample thickness between the two estimates is the main source of uncertainty in k_{rad} (∼25%). Other contributions to the uncertainty include ambiguities in the refractive index of Ppv at high pressure, and to a lesser extent, high temperature (∼1%/1000 K Ruf et al., 2000).

3. Results and discussion

In this work we have studied optical properties of iron-rich, Fe^{3+}-bearing Ppv ($Mg_{0.6}Fe_{0.4}SiO_3$) at 300–2050 K and 130 GPa using laser-heated diamond anvil cells combined with a pulsed ultra-bright supercontinuum probe (400–2400 nm) synchronized with the collection windows of gated visible and infrared detectors. The latter allowed diminishing the contribution of thermal radiation to the optical signal at high temperature by several orders of magnitude. We determined quantitatively the reduction in intensity of all Ppv absorption bands in the visible-infrared range at high pressure and temperature. These, in turn, have allowed us to constrain the spin and valence states of iron in Ppv and its radiative conductivity at expected CMB conditions. Combined with literature data on the absorption coefficients of Bdgm and ferropericlase (Fp), these results enable us to construct a radiative thermal conductivity model for the lowermost mantle in order to address the CMB heat flux and Ppv content in the region.

Iron-rich ($Mg_{0.6}Fe_{0.4}SiO_3$) Ppv was synthesized in a diamond anvil cell using enstatite powder of the corresponding composition sandwiched between NaCl layers, similar to procedures used in previous reports on the spin and valence states in Ppv (Lin et al., 2008). The sample was compressed to 130 GPa at room temperature and then laser-heated at 2500–2800 K for 6–8 hr at 13IDD beamline of GSECARS, Advanced Photon Source. To avoid chemical segregation upon laser-heating, the hot spot was moved during the process. Synthesis was confirmed by synchrotron x-ray diffraction that showed a complete transformation to the Ppv phase (Supplementary Fig. S1). However, several weak unindexed peaks suggest that the sample is not homogeneous and contains minor impurities. After successful synthesis of Ppv, analysis of the measured room-temperature absorption spectrum in the 6000–22500 cm^{-1}