Raman spectroscopy of CaIrO$_3$ postperovskite up to 30 GPa

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ABSTRACT

We have measured Raman spectra of the postperovskite (PPv) phase in CaIrO$_3$ up to 30 GPa to constrain the Grüneisen parameter ($\gamma$). We identified a total of 4 strong modes between 200 and 650 cm$^{-1}$, which is in contrast with the Raman spectra of Mn$_2$O$_3$ and MgGeO$_3$-PPv where at least nine different modes have been detected. We found no sign of a phase transition in the Raman spectra of PPv CaIrO$_3$, which supports the stability of the PPv phase up to 30 GPa and room temperature in CaIrO$_3$. The spectroscopic Grüneisen parameter, $\gamma_{th,0} = 1.66$–1.72, constrained from our Raman data, is in excellent agreement with the thermodynamic Grüneisen parameter, $\gamma_{th,0} = 1.75 \pm 0.05$, calculated from recent XRD measurements (Martin et al. 2007) on CaIrO$_3$-PPv synthesized at high pressure and temperature similar to our starting material. Our result suggests that $\gamma_{th}$ constrained by Raman measurements provides a reasonable estimate on the $\gamma_{th}$ of the PPv phase in CaIrO$_3$.

Keywords: Postperovskite, CaIrO$_3$, Gruneisen parameter, Raman spectecroscopy, thermal equation of state

INTRODUCTION

Recent studies have shown that the dominant lower-mantle phase, (Mg,Fe)SiO$_4$-postperovskite (Pv), undergoes a phase transition at the pressure ($P$)-temperature ($T$) conditions relevant to the D"{o}r discontinuity, the postperovskite (PPv) transition (Murakami et al. 2004; Oganov and Ono 2004; Shim et al. 2004). It has been suggested that some enigmatic seismic observations at the core–mantle boundary (CMB) region can be explained by the properties of the PPv phase (e.g., Helmberger et al. 2005; Wookey et al. 2005; Wentzcovitch et al. 2006; Monnereau and Yuen 2007; Shim et al. 2006; Merkel et al. 2007—see Hirose 2006; Shim 2008, for review). Theoretical studies have suggested that the new phase is isotypic to CaIrO$_3$ (Murakami et al. 2004; Oganov and Ono 2004; Tsuchiya et al. 2004) and this has been further supported by a recent Rietveld study of (Mg,Fe)SiO$_4$-PPv at P-T conditions relevant to the CMB (Shim et al. 2008). Because CaIrO$_3$-PPv is stable at ambient conditions, it has been recently studied extensively: phase equilibria (Hirose and Fujita 2005; Kojitani et al. 2007), thermoelastic properties (Ballaran et al. 2007; Lindsay-Scott et al. 2007; Martin et al. 2007; Tsuchiya and Yamazaki 2007), lattice preferred orientation (Walte et al. 2007; Miyajima et al. 2006; Niwa et al. 2007), and kinetics (Yoshino and Yamazaki 2007).

The thermal equation of state (EOS) of mantle silicate PPv is particularly important for understanding both the dynamic stability of the PPv lenses documented in recent seismic studies (Lay et al. 2006; van der Hilst et al. 2007) and mantle flow at the CMB region (Buffett 2007). Although the EOS of mantle silicate PPv has been studied at high $P$ and room $T$ (Shieh et al. 2006; Mao et al. 2006; Guignot et al. 2007; Shim et al. 2008), the EOS fit for the volumes ($V$) of PPv measured at high $P$-$T$ suffers larger uncertainties due to unconstrained parameters (e.g., volume at ambient conditions, $V_0$), pressure scale issues, and other technical difficulties (e.g., Guignot et al. 2007; Komabayashi et al. 2008). Vibrational spectroscopy, i.e., Raman and infrared spectroscopy, provides an alternative means of constraining thermoelastic parameters (Gillet et al. 1998).

Recent Raman spectroscopy measurements by Shim et al. (2007) have suggested that the Grüneisen parameter ($\gamma$) decreases by 25 $\pm$ 10% across the PPv transition in MgGeO$_3$. In an X-ray diffraction (XRD) study of (Mg,Fe)SiO$_4$, a similar magnitude of decrease in $\gamma$ has been documented (Shim et al. 2008).

Yet it should be mentioned that estimates of $\gamma$ using vibrational spectroscopy (hereafter $\gamma_v$ or spectroscopic $\gamma$) do not include the effect from dispersion and often use a smaller number of normal modes than expected from the group theory. Nevertheless, previous studies have shown that $\gamma_v$ still provides a reasonable estimate for the thermodynamic Grüneisen parameter ($\gamma_{th}$) for many mantle minerals: for forsterite $\gamma_{sp}=1.09$ and $\gamma_{th}=1.17$ where only 19 Raman modes out of 84 total modes were used (Chopelas 1990), and for MgSiO$_3$-spinel $\gamma_{sp}=1.10$ and $\gamma_{th}=1.25$ where only five Raman modes out of 42 total modes were used (Chopelas et al. 1994).

However, agreement between $\gamma_v$ and $\gamma_{th}$ has not been confirmed for PPv structured materials. CaIrO$_3$ provides an opportunity to examine the agreement between $\gamma_v$ and $\gamma_{th}$, as some of the key parameters for calculating its $\gamma_v$ are available in the literature (e.g., Ballaran et al. 2007; Lindsay-Scott et al. 2007; Martin et al. 2007). In this study, we measure the Raman spectra of CaIrO$_3$-PPv up to 30 GPa. This data set enables us to constrain the $\gamma_v$ of PPv...
from the $P$-induced shift of mode frequencies. Using this result, we compare the $\gamma_a$ and $\gamma_b$ of CaIrO$_{3}$-PPv.

**EXPERIMENTAL METHODS**

To synthesize CaIrO$_3$, we mixed CaCO$_3$ and IrO$_2$ with a molar ratio of 1:1:0.2. This mixture was then heated in air at 1173 K for 2 h and at 1253 K for 3 h. Diffraction measurements using a laboratory X-ray diffractometer showed that the product is a CaIrO$_3$-Pv + CaIrO$_3$ + IrO$_2$ mixture. This mixture was then vacuum-sealed in a silica tube and heated to 1253 K at ambient pressure for 68 h. The product was a CaIrO$_3$-Pv + CaIrO$_3$-PPv mixture with small amounts of Ca$_2$IrO$_4$ and IrO$_2$. This mixture was then compressed to 7.7 GPa and heated at 1370 K for 4 h in a large-volume press at beamline 13IDD of the GSECARS sector at the Advanced Photon Source (APS). The product was a pre-sintered polycrystalline aggregate of CaIrO$_3$-PPv (space group Cmcm) as confirmed by synchrotron powder XRD.

The aggregate was crushed to produce powder. Platelets of CaIrO$_3$ with 10 $\mu$m thickness were prepared by pressing the powder between mica nitrite anvil. A platelet was loaded into a stainless steel gasket. A hole 150 $\mu$m in diameter was drilled in the indentation of the gasket. Three different pressure media were used in four separate high-$P$ runs: Ar, a methanol-ethanol (4:1) mixture, and NaCl. Small grains of ruby were loaded together with the sample to measure pressure (Mao et al. 1986). A platelet was loaded such that the sample is in contact with one of the diamond anvils. Because diamond is an excellent heat conductor, this sample setup reduces the heating of the sample by a laser beam. No sign of chemical reaction or laser radiation damage was recognized throughout our runs except for one run with a methanol-ethanol medium. In this run, we used a relatively high-intensity laser beam and this perhaps generated sufficient heat to induce chemical reaction on the surface of the dark-colored CaIrO$_3$. Therefore, we have not used this data set. In a separate run with a methanol-ethanol mixture, we reduced laser power sufficiently low and did not find any evidence of chemical reaction. This latter data set is used for data analysis.

The sample in the diamond-anvil cell was illuminated with an Ar/Kr mixed ion laser at 514.5 nm, with a spot size of 2 $\mu$m at the sample surface. Raman scattering was measured for 10–30 min using a CCD detector at the end of a 0.5 m single spectrometer. A Ne lamp was used to calibrate the positions of the Raman modes. The precision of our measurements is ~1 cm$^{-1}$.

To examine the possible existence of modes at a spectral range between 10 and 200 cm$^{-1}$, we used a triple spectrometer setup in a subtractive mode for the sample in the diamond-anvil cell at 1 GPa (shown in the inset of Fig. 1). In this measurement, we used a 488 nm line of an Ar/Kr mixed ion laser.

**RESULT AND DISCUSSION**

A total of four intense peaks are observed between 200 and 650 cm$^{-1}$ up to 30 GPa (Fig. 1). A weak mode ($v_4$, in Fig. 1) is found in some of our measurements. This mode is more readily observed during decompression than compression. Hirose and Fujita (2005) reported a Raman spectrum of CaIrO$_3$-PPv at ambient conditions. Mode frequencies in our measurements are in good agreement with the result by Hirose and Fujita (2005). Yet, $v_1$ and $v_4$ are more intense and less intense, respectively, in our study.

No Raman modes are detected between 10 and 200 cm$^{-1}$ (in the inset of Fig. 1, a sharp spike at 30 cm$^{-1}$ is not from sample). Although the throughput of a triple spectrometer setup used for the low-frequency measurement is lower than that of a single spectrometer setup by 1 order of magnitude, the detection of the $v_1$ mode in the triple setup documents that no Raman mode with significant intensity exists at the low-frequency region.

More than 9 modes have been detected in the PPv phases of Mn$_3$O$_4$ and MgGeO$_4$ (Shim et al. 2007). Furthermore, strong resemblance in the Raman spectra between these two compounds has been recognized, as also shown in Figures 2b and 2c. From group theory for space group Cmcm, 12 modes among a total of 30 modes are Raman active (Caracas and Cohen 2006). Therefore, only about 1/3 of the Raman-active modes are detected for CaIrO$_3$ in this study, whereas almost all the Raman-active modes have been observed in Mn$_3$O$_4$ and MgGeO$_4$. Raman intensities are determined by polarizability, which is related to the deformability of the electronic clouds of the atoms in the crystal lattice (Fadini and Schnepel 1989). Therefore, the smaller number of observed modes in CaIrO$_3$-PPv compared with other PPv phases is perhaps related to different bonding characteristics in CaIrO$_3$.

The $v_2$ and $v_3$ peaks have asymmetric shapes at lower $P$. Becchstedt and Peucker (1975) and Balkanski et al. (1975) found that electron-phonon coupling can result in asymmetric peak shapes of Raman modes observed in semiconductors and transition metal oxides (e.g., Manlief and Fan 1972; Sakita et al. 2001). Therefore, the observed asymmetric shapes of phonon modes in CaIrO$_3$ may be due to electron-phonon coupling. Asymmetric peak shapes in Raman scattering can also result from anharmonicity (Foster et al. 1993).

Up to 30 GPa we do not identify any significant changes in the Raman spectra of CaIrO$_3$-PPv (Fig. 1). Furthermore, no significant discontinuous changes are detected in the $P$-induced mode shifts (Fig. 3). These observations indicate that CaIrO$_3$-PPv does not undergo any phase transition up to 30 GPa at room temperature.

Mode Grüneisen parameters ($\gamma_i$) can be obtained from the
The widths of peaks are systematically larger in a run with a NaCl medium than in runs with either a methanol-ethanol mixture or Ar medium (Fig. 1). Also the mode frequencies of CaIrO$_3$ measured in a NaCl medium are systematically lower. This is perhaps due to higher deviatoric stresses in a NaCl medium. Therefore, we do not use the data points measured in a NaCl medium for the calculation of $\gamma_i$.

We do not use $\nu_4$ because of its weak intensity and limited observation. Furthermore, its mode shift behavior is very different from the other modes. The P-induced shifts of $\nu_1-\nu_3$ are strongly non-linear, whereas the behavior of $\nu_5$ is almost linear (Fig. 3). The strong non-linearities result in high $q_i$ values (Table 1) and also rapid decreases in $\gamma_i$ at high $P$ for the corresponding modes.

<table>
<thead>
<tr>
<th>$\omega_{i,0}$ (cm$^{-1}$)</th>
<th>$\gamma_{i,0}$</th>
<th>$q_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>226</td>
<td>2.17(4)</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>312</td>
<td>1.86(3)</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>450</td>
<td>1.50(2)</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>563</td>
<td>1.115(3)</td>
</tr>
</tbody>
</table>

Average Grüneisen parameter $\overline{\gamma}$ = 1.72(8) $\overline{q_i}$ = 1.66(8)

Notes: We also present average Grüneisen parameters calculated from two different methods (see text for detail). The numbers in the parentheses are 1$\sigma$ uncertainties. Because of small non-linearity of $\nu_5$, $q_5$ is fixed to 0.
ferent from other CaIrO$_3$ modes. Therefore, we cannot rule out the possibility of this peak being associated with either a minor impurity in the sample or a reaction product from long exposure to the laser beam. We note that the $\nu_4$ mode becomes more visible during decompression, after at least 6 h of laser illumination on the surface of the sample.

A weighted average Grüneisen parameter, $\overline{\gamma}_i$, can be obtained from:

$$\overline{\gamma}_i = \frac{\sum C_i \gamma_{i,0}}{\sum C_i}$$

where $C_i$ is the Einstein heat capacity. We obtain $\overline{\gamma}_0 = 1.72 \pm 0.08$. A simple average, $<\gamma_{i,0}>$, yields 1.66 $\pm$ 0.08.

We did not include $\nu_4$ for the calculation of $\overline{\gamma}_0$ and $<\gamma_{i,0}>$ due to the reasons mentioned above. In addition, unambiguous determination of $\gamma_{i,0}$ is difficult because $\nu_4$ is not well resolved below 1 GPa and therefore $\omega_{i,0}$ is unconstrained. Furthermore, its limited $P$ range makes it difficult to constrain $\omega_i$. Therefore, we fix $\omega_i = 0$ and vary $\omega_{i,0}$ and $\gamma_{i,0}$ in the fitting. This yields $\omega_{i,0} = 2.27$. If we include $\nu_4$, then $\overline{\gamma}_0$ and $<\gamma_{i,0}>$ increase to 1.80 and 1.77, respectively.

The asymmetry observed for the $\nu_3$ and $\nu_4$ peaks at lower $P$ is not sufficiently high to make doublet peak fitting better than singlet fitting. Therefore, we treat them as singlets. As mentioned earlier, the asymmetry likely results from electron-phonon coupling or anharmonicity in CaIrO$_3$. Even if they are due to peak overlaps of two different adjacent phonon modes, the assumption of singlets would not introduce much artifact in the $\gamma$ calculations, because the $P$-induced frequency shifts (therefore $\gamma$) of individual modes in the doublets should be very similar with each other as peak shapes do not change much with $P$ in our study.

Thermodynamic $\gamma$ can be obtained from:

$$\gamma_{i,0} = \frac{\alpha K_i V}{C_V}$$

where $\alpha$ is the thermal expansion parameter, $K_i$ is the isothermal bulk modulus, $V$ is the volume, and $C_V$ is the heat capacity. Two existing reports on $K_i$ show an excellent agreement: $K_{i,0} = 181 \pm 3$ GPa (Ballaran et al. 2007) and $K_{i,0} = 180 \pm 3$ GPa (Martin et al. 2007). The $V$ is well constrained by several measurements. The $C_V$ of CaIrO$_3$-PPv is unknown. Kojitani et al. (2007) estimated the $C_V$ of CaIrO$_3$-PPv by adding the $C_V$ of CaO (Berman 1988) and the $C_V$ of IrO$_2$ (Knacke et al. 1991). For enstatite (MgSiO$_3$) and forsterite (Mg$_2$SiO$_4$), the error involved in this type of estimation does not exceed 0.5%. In addition, the difference between $C_P$ and $C_V$ is typically <1% (Navrotsky 1994).

However, there exists a large discrepancy between two existing measurements of $\alpha$: 2.84(3) $\times$ 10$^{-4}$ K$^{-1}$ (Martin et al. 2007) and 2.42(3) $\times$ 10$^{-4}$ K$^{-1}$ (Lindsay-Scott et al. 2007) at 1 bar and 300 K. These two results yield: $\gamma_{0,0} = 1.75 \pm 0.08$ when the result by Martin et al. (2007) is used and $\gamma_{0,0} = 1.49 \pm 0.08$ when the result by Lindsay-Scott et al. (2007) is used. The $\gamma_{0,0}$ calculated from the result by Martin et al. (2007) is in much better agreement with our $\gamma_{i,0}$.

It is difficult to determine the cause of the discrepancy in $\alpha$. However, it is notable that Martin et al. (2007) used CaIrO$_3$-PPv synthesized at 6 GPa and 1223 K, which is similar to our synthesis conditions. However, Lindsay-Scott et al. (2007) used CaIrO$_3$-PPv synthesized at ambient pressure. Together with our own experience, recent studies (e.g., Martin et al. 2007; Hirose and Fujita 2005) have shown that synthesis of CaIrO$_3$-PPv at ambient pressure could result in many different by-products, such as Ca$_3$IrO$_{14}$, IrO$_2$, and CaIrO$_3$-Pv, as well as CaIrO$_3$-PPv. In fact, Lindsay-Scott et al. (2007) observed Ir and IrO$_2$ in their sample. Therefore, we conclude that it is more appropriate to make comparison between the results on the samples synthesized at similar $P$-$T$ conditions.

We have shown that the spectroscopically constrained Grüneisen parameter ($\gamma_{0,0} = 1.66$–1.80) from Raman spectroscopy is in agreement with the thermodynamic Grüneisen parameter ($\gamma_{0,0} = 1.75 \pm 0.08$) for CaIrO$_3$-PPv synthesized at similar $P$-$T$ conditions (Martin et al. 2007). Our study demonstrates that Raman spectroscopy is as a valuable tool to understand the physical properties of the PPv structured phases.

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