

# Raman spectra of bixbyite, $\text{Mn}_2\text{O}_3$ , up to 40 GPa

S.-H. Shim · D. LaBounty · T. S. Duffy

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**Abstract** The Raman spectra of bixbyite,  $\text{Mn}_2\text{O}_3$ , were measured up to 40 GPa at room temperature.  $\text{Mn}_2\text{O}_3$  undergoes a phase transition from the C-type rare earth structure to the  $\text{CaIrO}_3$ -type (post-perovskite) structure at 16–25 GPa. The transition pressure measured in Raman spectroscopy is significantly lower than the pressure reported previously by an X-ray diffraction study. This could be due to the greater polarizability in the  $\text{CaIrO}_3$ -type structure, consistent with high-pressure observation on the  $\text{CaIrO}_3$  type in  $\text{MgGeO}_3$ , although it is still possible that experimental differences may cause the discrepancy. Unlike the change at the perovskite to  $\text{CaIrO}_3$ -type transition, the spectroscopic Grüneisen parameter does not decrease at the C-type to  $\text{CaIrO}_3$ -type transition. The spectroscopic Grüneisen parameter of the low-pressure phase (C type) is significantly lower than thermodynamic Grüneisen parameter, suggesting significant magnetic contributions to the thermodynamic property of this material. Our Raman measurements on  $\text{CaIrO}_3$ -type  $\text{Mn}_2\text{O}_3$  contribute to building systematic knowledge about this structure, which has emerged as one of the common structures found in geophysically important materials.

**Keywords** Raman spectroscopy ·  $\text{Mn}_2\text{O}_3$  · Phase transition · Grüneisen parameter

## Introduction

Understanding the high-pressure behavior of sesquioxides ( $\text{M}_2\text{O}_3$ ,  $\text{M} = \text{Fe}, \text{Mn}, \text{Al}, \text{Cr}$ , etc) is important in geophysics and high-pressure physics. For example, Cr-doped  $\text{Al}_2\text{O}_3$ , i.e., ruby, has been extensively used as a pressure standard at high pressure (Piermarini et al. 1975; Mao et al. 1986). Pressure calibration of the ruby scale can be affected by phase transitions (Funamori and Jeanloz 1997; Duan et al. 1998; Lin et al. 2004; Shim et al. 2004b). Also, many of the 3d transition metals may exist in the mantle as minor elements, and their sesquioxides appear to have pressure–temperature stability fields for phases which also occur in mantle silicates (e.g.,  $\text{MgSiO}_3$ ). For example,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Mn}_2\text{O}_3$  have stability fields for the  $\text{CaIrO}_3$ -type (post-perovskite) structure (Ono et al. 2004; Oganov and Ono 2005; Santillán et al. 2006; Shim et al. 2009), which has been found to be stable in  $(\text{Mg},\text{Fe})(\text{Al},\text{Si})\text{O}_3$  at the pressure–temperature conditions of the lowermost mantle of Earth (Murakami et al. 2004; Oganov and Ono 2004; Shim et al. 2004a; Catalli et al. 2009).

Unlike  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  where the stability field of the  $\text{CaIrO}_3$ -type phase appears after either perovskite or  $\text{Rh}_2\text{O}_3$ -II phase,  $\text{Mn}_2\text{O}_3$  undergoes a phase transition from the C-type rare earth structure (hereafter “C type”) to the  $\text{CaIrO}_3$  type at 27–38 GPa (Yamanaka et al. 2005; Santillán et al. 2006). It is also interesting to point out that the transition to the post-perovskite phase occurs at room temperature in  $\text{Mn}_2\text{O}_3$ . This is likely due to the structural similarities between the two phases as pointed out by Santillán et al. (2006).

Raman spectroscopy provides an alternative tool to study phase transitions. Unlike X-ray diffraction where the number of electrons determines the diffraction intensity, Raman intensities are controlled by polarizability (Fadini

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and Schnepel 1989). A previous study of  $\text{MgGeO}_3$  found that the Raman intensity is much stronger in the  $\text{CaIrO}_3$ -type phase than the perovskite-type phase (Shim et al. 2007). Therefore, it is of interest to determine whether a similar relationship holds with the transition from the C-type phase. In addition, Raman spectroscopy can provide constraints on Grüneisen parameters (Williams et al. 1987; Lu and Hofmeister 1994; Chopelas 1996; Gillet et al. 1998). In case of solids with significant magnetic and electronic contributions, high-pressure Raman measurements can constrain the pure phonon contributions to the thermal properties of a solid, which are not easily accessible with other techniques (Shim and Duffy 2002). Previous studies have shown that the Grüneisen parameter decreases at the perovskite to post-perovskite phase transition in  $\text{MgSiO}_3$ ,  $\text{MgGeO}_3$ , and  $\text{CaIrO}_3$  (Shim et al. 2007, 2008; Hustoft et al. 2008). Therefore, it is also of interest if this is the case for the phase transition from the C-type phase to the  $\text{CaIrO}_3$ -type phase.

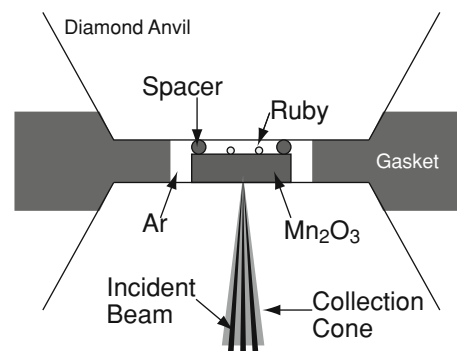
In this paper, we report Raman scattering measurements of  $\text{Mn}_2\text{O}_3$  up to 40 GPa under quasi-hydrostatic stress conditions. Our results provide new constraints on the phase transition and thermal properties of  $\text{Mn}_2\text{O}_3$  at high pressure.

## Experimental method

Synthetic  $\text{Mn}_2\text{O}_3$  (Aldrich, purity 99%) was used in powder form. We confirmed the quality using powder X-ray diffraction and Raman spectroscopy at ambient conditions. The same sample material was also used in Santillán et al. (2006). Thin platelets of  $\text{Mn}_2\text{O}_3$  powder were made by cold compressing the material in a moissanite anvil cell. The sample was loaded in 250- $\mu\text{m}$ -diameter holes in stainless steel gaskets. Low-fluorescence diamond anvils with 500- $\mu\text{m}$  culets compressed the sample using symmetric diamond-anvil cells. Argon was loaded cryogenically as a pressure transmitting medium. The data between 0 and 9 GPa were collected with NaCl as a medium.

The sample foil was loaded in direct contact with one of the diamond anvils, and spectra were measured from this side (Fig. 1). Because diamond is an excellent thermal conductor, this setup reduces the heating of the sample by the laser beam. In order to prevent bridging of the sample between the anvils, we placed spacers on the opposite side of the sample to ensure a gap that allows Ar to flow between the sample and the anvil. The spacer grains were also  $\text{Mn}_2\text{O}_3$ .

Even with this setup, we found that high-intensity laser beam can cause some changes in the Raman spectra. A 100-mW laser beam focused on the sample in the diamond-anvil cell at low pressure produced some new peaks if an

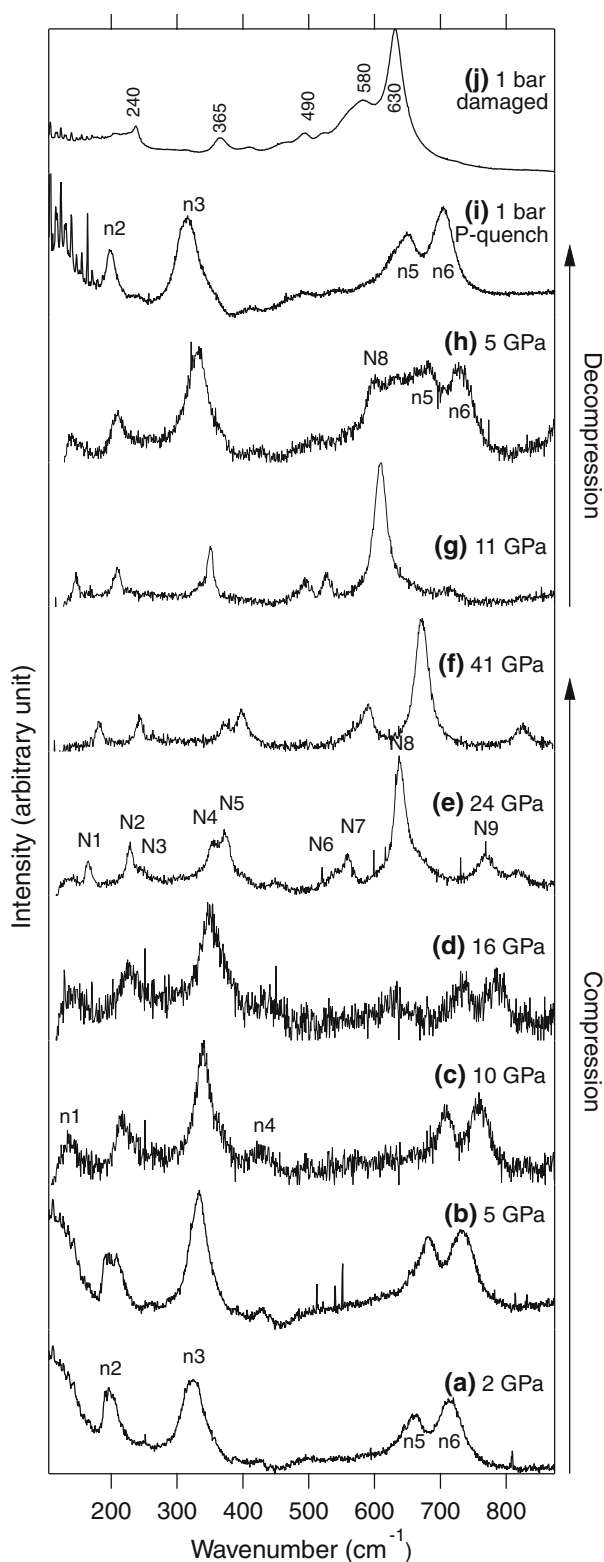


**Fig. 1** Schematic diagram of the sample setup in the diamond-anvil cell

$\text{NaCl}$  medium is used (Fig. 2j). The intensities of these peaks increase with time. The wavenumbers and intensities of the new peaks are consistent with those of  $\text{MnO}_2$  (Buciuman et al. 1999), indicating that high-intensity laser beam can oxidize  $\text{Mn}_2\text{O}_3$  into  $\text{MnO}_2$  (Fig. 2j). This is, perhaps, due to the surface reaction between  $\text{Mn}_2\text{O}_3$  and oxygen, captured during loading under atmosphere, under intense laser beam focused on a small area. It is notable that Raman intensity of  $\text{Mn}_2\text{O}_3$  is much smaller than that of  $\text{MnO}_2$  (Buciuman et al. 1999), and therefore, even small production of  $\text{MnO}_2$  would change the measured spectra significantly (Fig. 2j). In order to avoid the laser-induced reaction, we measured the Raman spectra of the samples in the diamond-anvil cell by varying the power of the laser beam. We found that a laser power of 10–20 mW does not change the spectrum of  $\text{Mn}_2\text{O}_3$  for 3 hours. In this study, we used the spectra that do not have any evidence of the laser-induced reaction.

Three to four ruby chips were loaded at various sample positions for pressure determination using the quasi-hydrostatic ruby scale (Mao et al. 1986). All ruby grains were loaded on the opposite side of the sample surface from which we measured Raman spectra. Because  $\text{Mn}_2\text{O}_3$  remains opaque throughout the examined pressure range, no signal from ruby is observed in our spectra. Pressures measured from different ruby grains did not differ more than  $\pm 1$  GPa, indicating homogeneity in stress condition.

Four different sets of measurements were conducted with two different Raman systems. The micro-Raman system at Princeton University consists of a 200 mW Ar-ion laser, 0.5 m single spectrometer, charge-coupled device (CCD) detector (1,100  $\times$  330 pixels), and holographic optics. The focal spot size was 10–20  $\mu\text{m}$ . The micro-Raman system at MIT consists of a 1.2 W Kr/Ar-mixed ion laser, 0.5 m single spectrometer, CCD detector (1,300  $\times$  100 pixels), and holographic optics. The focal spot is 2  $\mu\text{m}$  in this system. We used a 514.532 nm laser wavelength for Raman scattering. The results from the two instruments are identical to each other.



**Fig. 2** Raman spectra of  $\text{Mn}_2\text{O}_3$  measured during compression (a–f) and decompression (g–i). The modes were tentatively assigned in the order of their frequencies for the C-type phase ( $n_1$ – $n_6$ ) and for the  $\text{CaIrO}_3$ -type phase ( $N_1$ – $N_9$ ). A spectrum measured under intense laser illumination at 1 bar is shown in **j** for comparison. In **j**, we present the wavenumbers of the observed peaks

A spectral range of  $100$ – $900\text{ cm}^{-1}$  was measured. The spectrometer was calibrated using the neon emission spectrum. The precision of the measured frequency is better than  $\pm 1\text{ cm}^{-1}$ . An exposure time of  $10$ – $30$  minutes was used.

## Results and Discussion

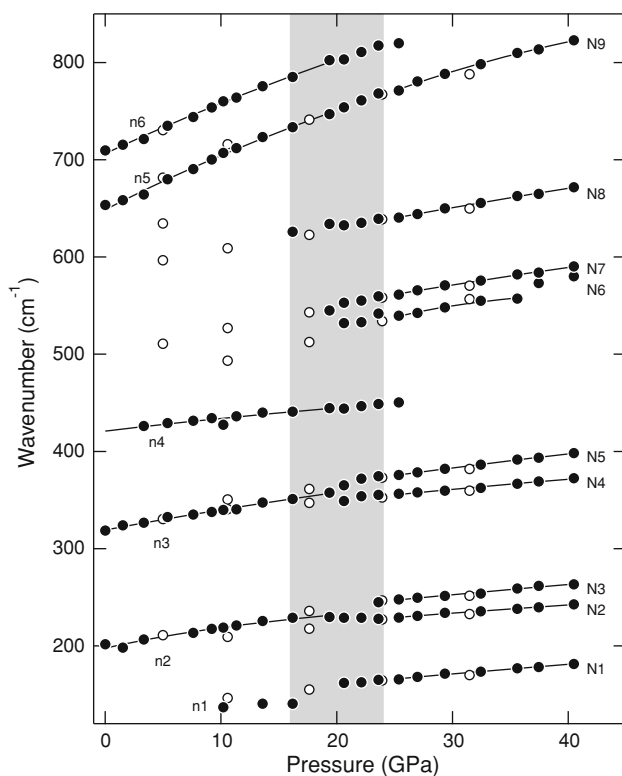
The C-type phase has a cubic structure ( $Ia\bar{3}$ ) and is expected to have 22 Raman-active phonon modes (White and Keramidas 1972).  $\text{Mn}_2\text{O}_3$  transforms from an orthorhombic (distorted C type) structure to a cubic (C type) structure at  $302\text{ K}$  (Grant et al. 1968; Geller 1971). Although the temperature of laboratory was maintained to be  $293\text{ K}$ , it is possible that the temperature of the  $\text{Mn}_2\text{O}_3$  sample might be slightly higher and within the stability field of the cubic phase due to slight heating by laser illumination. In addition, it is thought that pressure may suppress the distortion (Prewitt et al. 1969).

We observed a total of 4 Raman modes ( $n_2$ ,  $n_3$ ,  $n_5$ , and  $n_6$ ) at pressures below  $5\text{ GPa}$  between  $100$  and  $900\text{ cm}^{-1}$  (Fig. 2a). With compression, the peak at  $426\text{ cm}^{-1}$  ( $n_4$ ) gains intensity (Fig. 2b). A large background structure was observed at wavenumbers below  $150\text{ cm}^{-1}$  at pressures lower than  $10\text{ GPa}$ . However, the structure disappears with compression and becomes weak enough to reveal a peak at  $137\text{ cm}^{-1}$  ( $n_1$ ). Therefore, we observed a total of 6 modes within the stability field of the C type. Although this is far less than theoretical predictions (White and Keramidas 1972), our observation is generally in agreement with previous Raman reports on  $\alpha$ - $\text{Mn}_2\text{O}_3$ . White and Keramidas (1972) reported three peaks at  $565$ ,  $620$ , and  $672\text{ cm}^{-1}$ . The latter two appear to be in agreement with our  $n_5$  and  $n_6$ , whereas we do not observe any peaks between  $500$  and  $600\text{ cm}^{-1}$  within the stability field of the C type. Kapteijin et al. (1994) reported three peaks at  $311$ ,  $653$ , and  $697\text{ cm}^{-1}$ , all of which are observed in our study. In addition to these three modes, Buciuman et al. (1999) observed a weak mode at  $360$ – $390\text{ cm}^{-1}$ . Although we do not observe any peak near this wavenumber range at 1 bar,  $n_4$  gains significant intensity with pressure near this wavenumber range (Fig. 2a–c). Lack of previous reports on  $n_1$  and  $n_2$  is, perhaps, due to the fact that the low wavenumber range was not explored in the previous studies. It is also important to mention that high-quality Raman measurements are challenging for opaque materials such as  $\text{Mn}_2\text{O}_3$ .

Beginning from  $16\text{ GPa}$ , we found severe changes in the Raman spectra of  $\text{Mn}_2\text{O}_3$  (Fig. 2d). A peak appears at  $626\text{ cm}^{-1}$  ( $N_8$ ) and gains intensity with compression. This peak ultimately becomes the most intense peak for the

high-pressure phase of  $\text{Mn}_2\text{O}_3$ . Two new peaks appear at  $530\text{--}550\text{ cm}^{-1}$  ( $N_6$  and  $N_7$ ), and two low-pressure phase peaks ( $n_2$  and  $n_3$ ) split into  $N_2 + N_3$  and  $N_4 + N_5$ , respectively (Figs 2d, e and 3). The wavenumber of  $n_1$  appears to show a discontinuous increase at the phase transition (Fig. 3). Two low-pressure features disappear at the phase transition ( $n_4$  and  $n_6$ ).  $n_5$  appears to survive through the phase transition and continues up to the maximum pressure of this study ( $N_9$ ).

Caracas and Cohen (2006) showed that 12 modes among a total of 30 modes are Raman active for the  $\text{CaIrO}_3$ -type ( $Cmcm$ ) structure. In this study, we identify a total of 9 modes in  $\text{Mn}_2\text{O}_3$  between  $100$  and  $900\text{ cm}^{-1}$  (Fig. 2e). In  $\text{MgGeO}_3$ , a total of 10 modes were found in the Raman spectra of the  $\text{CaIrO}_3$  type between  $100$  and  $900\text{ cm}^{-1}$  (Shim et al. 2007). In Fig. 2 of Hustoft et al. (2008), we compared the Raman spectra of the  $\text{CaIrO}_3$ -type phase between  $\text{MgGeO}_3$  and  $\text{Mn}_2\text{O}_3$ . Striking similarity can be found between these two materials. In contrast, only 5 modes were found for  $\text{CaIrO}_3$  itself (Hustoft et al. 2008).



**Fig. 3** Pressure-induced shifts of the Raman modes of  $\text{Mn}_2\text{O}_3$ . *Solid and open symbols* represent data points measured during compression and decompression, respectively. Fitting of the data is shown by *curves*. The size of *error bar* for mode frequency is smaller than that of the symbols. Uncertainty in pressure is 3%. The *gray area* indicates where the phase transition was observed. The compression data below and above 9 GPa were measured using a NaCl medium and an Ar medium, respectively

This is perhaps related to the very different bonding characters in  $\text{CaIrO}_3$ , compared with  $\text{MgGeO}_3$  and  $\text{Mn}_2\text{O}_3$ .

It is important to make sure that the new peaks observed at high pressure are not from the reaction by the illumination of intense laser beam. As discussed earlier, we investigate threshold laser intensity to prevent laser-induced reaction of the sample.  $\text{MnO}_2$ , a possible oxidation product by laser-induced reaction as found in our test measurements (Fig. 2j), has a phase transition from the rutile-type structure to the  $\text{CaCl}_2$ -type structure at 1 GPa and does not show any phase transition up to 49 GPa at room temperature (Haines et al. 1995). Furthermore, only subtle changes in Raman spectra are expected at the rutile type to the  $\text{CaCl}_2$  type phase transition, while the changes observed in our study are much more significant (Fig. 2). In addition, if  $\text{MnO}_2$  forms at high pressure during measurements, it should remain in the spectra measured for pressure quenched samples. However, we found that the new high-pressure peaks disappear after pressure quench (Fig. 2h, i).

Liu et al. (2002) found a new intense mode in  $\text{Mn}_3\text{O}_4$  at  $600\text{ cm}^{-1}$  at 10 GPa. The wavenumber is close to the most intense mode of the high-pressure phase,  $N_8$ , found in our study. However, Liu et al. (2002) found that the new high-pressure mode of  $\text{Mn}_3\text{O}_4$  remains in the spectra even after pressure quench, while we found that  $N_8$  disappears with decompression (Fig. 2h, i). More importantly, according to our measurements, intense laser illumination on  $\text{Mn}_2\text{O}_3$  produces  $\text{MnO}_2$  not  $\text{Mn}_3\text{O}_4$  in the diamond-anvil cell.

A synchrotron X-ray diffraction study of  $\text{Mn}_2\text{O}_3$  by Santillán et al. (2006) showed that the phase transition to the  $\text{CaIrO}_3$ -type structure occurs at  $27\text{--}38$  GPa at room temperature. The pressure interval for the mixed phase region is measured to be 11 GPa indicating a sluggish phase transition at room temperature. New peaks and peak splittings, which are clear evidence for the phase transition, occur at much lower pressures in our Raman measurements,  $16\text{--}24$  GPa.

One possibility is the large difference in the polarizability of bonds between the lower-pressure (C type) and high-pressure ( $\text{CaIrO}_3$  type) phases. Although the polarizability in the C-type phase is not well known, it has been found that the Raman intensity of the  $\text{CaIrO}_3$  type is much greater than that of the perovskite type in  $\text{MgGeO}_3$  (Shim et al. 2007). If the polarizability in the  $\text{CaIrO}_3$  type is much greater than the C-type structure, it is likely that even small amounts of the high-pressure structure can show up strongly in the Raman spectra of  $\text{Mn}_2\text{O}_3$ , while the low-pressure phase would seem disappear at a lower pressure. In contrast, the X-ray intensity is mainly determined by number of electrons and symmetry. The number of electrons does not change in case of an isochemical phase transition in  $\text{Mn}_2\text{O}_3$ . Therefore, Raman data may provide a

more reliable pressure for the first appearance of the CaIrO<sub>3</sub> type in Mn<sub>2</sub>O<sub>3</sub>.

However, it is also possible that the difference may be caused by experimental conditions. While we use the same pressure medium in the X-ray study (Santillán et al. 2006) and Raman study, as phase transition pressure could be sensitive to stress conditions, a slight difference in stress conditions between the two measurements can contribute to the difference. While we attempted to reduce the heating of the opaque Mn<sub>2</sub>O<sub>3</sub> during our Raman measurements (Fig. 1), slight heating of Mn<sub>2</sub>O<sub>3</sub> by laser beam can reduce the kinetic effects and therefore stimulate the phase transition at a lower pressure. The diffraction study (Santillán et al. 2006) documented metastable persistence of the CaIrO<sub>3</sub>-type phase down to 4.5 GPa during decompression. In our Raman study, the most intense peak of the high-pressure phase (N<sub>8</sub>) can be observed at 5 GPa (Fig. 2i), consistent with the X-ray observation.

Grüneisen parameters for individual modes ( $\gamma_i$ ) can be obtained from the pressure-induced shifts of phonon mode frequencies (Born and Huang 1954; Wallace 1972). We follow the approach presented by Shim et al. (2007) by combining the following two relations:

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V}, \quad (1)$$

and

$$\gamma = \gamma_r \left( \frac{V}{V_r} \right)^q, \quad (2)$$

where  $\omega_i$  is the frequency of mode  $i$ ,  $V$  is volume,  $q$  is the logarithmic volume derivative of Grüneisen parameter ( $\gamma$ ), which is assumed to be a constant, and subscript  $r$  denotes the reference conditions.

Using volume compression data (Santillán et al. 2006) and the second-order Birch–Murnaghan equation, we obtained  $K_0 = 144 \pm 5$  GPa for  $V_0 = 31.407 \text{ \AA}^3$  for the C-type structure. In case of the CaIrO<sub>3</sub>-type phase, because it becomes metastable at lower pressures, we set the reference state at 25 GPa where the lowest pressure/volume data point exists for the CaIrO<sub>3</sub>-type phase in Santillán et al. (2006). This method follows the approach presented by Sata et al. (2002) and Shim et al. (2008) and can reduce uncertainties in the fitting results. We obtained  $K_{25\text{GPa}} = 231 \pm 20$  GPa for a second-order Birch–Murnaghan equation fit, and the value projected at 1 bar is  $K_0 = 127 \pm 20$  GPa. Although the difference in  $K_0$  between the C type and the CaIrO<sub>3</sub> type is not statistically significant, it is interesting to note that the CaIrO<sub>3</sub>-type phase may have the lower bulk modulus. A lower bulk modulus of the post-perovskite (CaIrO<sub>3</sub>) type compared with a lower-pressure phase (in this case perovskite) was also reported in

**Table 1** Fitting results for the phonon modes of the C type in Mn<sub>2</sub>O<sub>3</sub> at 1 bar ( $\omega_0$ ,  $\gamma_0$ , and  $q$ ) and 25 GPa ( $\gamma_{25\text{GPa}}$ )

	$\omega_{i,0}$	$\gamma_{i,0}$	$q$	$\gamma_{i,25\text{GPa}}$
n <sub>2</sub>	198	1.96 (20)	5.8 (2.0)	0.91
n <sub>3</sub>	319	1.03 (3)		1.03
n <sub>4</sub>	421	0.50 (3)		0.50
n <sub>5</sub>	649	1.38 (5)	0.8 (6)	1.24
n <sub>6</sub>	706	1.15 (1)		1.15
$\langle \gamma_i \rangle$		1.20 (53)		0.97 (29)
$\bar{\gamma}$				0.93 (10)

$\omega_0$  for n<sub>4</sub> was obtained from projection of the fitting result to 1 bar, while the other  $\omega_0$  values were obtained directly measurements at 1 bar. Except for n<sub>2</sub> and n<sub>5</sub>, no significant pressure dependence ( $q$ ) was resolved for  $\gamma_i$ . Average ( $\langle \gamma_i \rangle$ ) and standard deviation of  $\gamma_i$  are given, together with weighted average following the method by Kieffer (1982),  $\bar{\gamma}$

**Table 2** Fitting results for the phonon modes of the CaIrO<sub>3</sub> type in Mn<sub>2</sub>O<sub>3</sub> at 25 GPa ( $\omega_{25\text{GPa}}$ ,  $\gamma_{25\text{GPa}}$ , and  $q$ )

	$\omega_{i,25\text{GPa}}$	$\gamma_{i,25\text{GPa}}$	$q$
N <sub>1</sub>	166	1.42 (10)	
N <sub>2</sub>	230	0.90 (8)	
N <sub>3</sub>	247	1.04 (7)	
N <sub>4</sub>	356	0.72 (5)	
N <sub>5</sub>	376	0.94 (5)	
N <sub>6</sub>	539	1.19 (26)	
N <sub>7</sub>	562	0.79 (3)	
N <sub>8</sub>	641	0.76 (3)	
N <sub>9</sub>	772	1.23 (10)	6.3 (2.7)
$\langle \gamma_i \rangle$		1.00 (24)	
$\bar{\gamma}$		1.01 (10)	

Except for N<sub>9</sub>, no significant pressure dependence ( $q$ ) was resolved for  $\gamma_i$ . Average ( $\langle \gamma_i \rangle$ ) and standard deviation of  $\gamma_i$  are given, together with weighted average following the method by Kieffer (1982),  $\bar{\gamma}$

(Mg,Fe)SiO<sub>3</sub> (Wentzovitch et al. 2006; Shieh et al. 2006; Shim et al. 2008).

For the C-type phase, we performed the fitting of the data between 0 and 16 GPa by fixing the wavenumbers of the phonon modes at 1 bar ( $\omega_0$ ) (Table 1). Because n<sub>4</sub> only becomes observable at pressures above 4 GPa, we fit  $\omega_0$  together with  $\gamma_i$  in case of n<sub>4</sub>. Because n<sub>1</sub> was only observed in a few spectra, we do not perform the fitting for n<sub>1</sub>. Except for n<sub>2</sub> and n<sub>5</sub>, no significant pressure dependence of mode Grüneisen parameter ( $q$ ) was found (Table 1).

For the CaIrO<sub>3</sub>-type phase, we conducted fitting for the data between 25 and 40 GPa (Table 2). Data between 20 and 25 GPa were excluded because of the transient mode shift behaviors observed in this range (Fig. 3). For N<sub>6</sub>, because of abrupt changes in the mode shift at 36 GPa, we

did not include the data points near this pressure. The abrupt change might be an artifact due to the difficulty in fitting the weak  $N_6$  at the shoulder of  $N_7$  (Fig. 2). Except for  $N_9$ , we did not resolve any pressure dependence of mode Grüneisen parameter. In order to avoid long extrapolation back to 1 bar, we set the reference pressure at 25 GPa for this phase.

We used two different averaging schemes to obtain the spectroscopic Grüneisen parameter ( $\gamma_{sp}$ ): simple average ( $\langle \gamma_i \rangle$ ) and a weighted average ( $\bar{\gamma}$ ) following the weighting scheme presented by Kieffer (1982):

$$\bar{\gamma} = \frac{\sum_i C_i \gamma_i}{\sum_i C_i} \quad (3)$$

where  $C_i$  is the Einstein heat capacity of the  $i$ th mode.

In order to make a more effective comparison of the averaged spectroscopic Grüneisen parameter between the two phases, we calculate the averages at 25 GPa based on the fitting results (Tables 1 and 2). We find that the value of the spectroscopic Grüneisen parameter does not change much with different averaging schemes for the same phase. Although the difference in spectroscopic Grüneisen parameter between the low- and high-pressure phases is not statistically significant, the spectroscopic Grüneisen parameter of the C-type phase ( $0.93 \pm 0.10$ ) is lower than that of the  $\text{CaIrO}_3$  type ( $1.01 \pm 0.10$ ). This is in contrast to the findings in  $\text{MgGeO}_3$ ,  $(\text{Mg,Fe})\text{SiO}_3$ , and  $\text{CaIrO}_3$  (Shim et al. 2007, 2008; Hustoft et al. 2008) where a decrease in Grüneisen parameter (20–30%) was observed at the perovskite-type to  $\text{CaIrO}_3$ -type transition.

The average Grüneisen parameter for the C-type  $\text{Mn}_2\text{O}_3$  can also be calculated using the following thermodynamic relationship:

$$\gamma_{th} = \frac{\alpha K_S}{\rho C_P}, \quad (4)$$

where  $\rho$  is the density (Geller 1971),  $C_P$  is the isobaric heat capacity (Robie and Hemingway 1985), and  $\alpha$  is the thermal expansivity obtained from volume data by Grant et al. (1968).  $K_S$  is the adiabatic bulk modulus. We obtained the isothermal bulk modulus from Santillán et al. (2006) by fitting the pressure–volume data to the second-order Birch–Murnaghan equation. The difference between adiabatic and isothermal bulk modulus does not normally exceed 5%. From these, we obtained  $\gamma_{th} = 3.0 \pm 0.3$ , which is significantly larger than the spectroscopic estimation of the Grüneisen parameter for the C type. It is important to note that spectroscopic Grüneisen parameter includes phonon effects only, while the thermodynamic Grüneisen parameter includes all the effects including magnetic behavior.  $\text{Mn}_2\text{O}_3$  is antiferromagnetic at ambient conditions (Grant et al. 1968). Therefore, it is possible that the large difference is due to unaccounted magnetic effects in the

spectroscopic estimation of Grüneisen parameter ( $\gamma_{sp}$ ). It is also possible that the discrepancy is due to the detection of only a fraction of Raman-active phonon modes in  $\alpha\text{-Mn}_2\text{O}_3$ . Yet, it is worth noting that good agreement between spectroscopic and thermodynamic Grüneisen parameters has been documented in insulating silicates (Chopelas 1990, 1994) despite the fact that these studies also detect only 10–20% of all the available Raman-active phonon modes. Hofmeister and Mao (2002) proposed that the good agreement is because Raman-active modes are involved in vibrations at the whole unit cell level.

## Summary

We report the Raman spectra of the C-type and  $\text{CaIrO}_3$ -type phases in  $\text{Mn}_2\text{O}_3$  up to 40 GPa under quasi-hydrostatic stress conditions. We detect the phase transition at lower pressures in Raman spectroscopy than in X-ray diffraction, which is, perhaps, due to the larger polarizability of the bonds in the  $\text{CaIrO}_3$ -type structure or experimental factors. The Raman spectra of the  $\text{CaIrO}_3$  type in  $\text{Mn}_2\text{O}_3$  are very similar to those of the  $\text{CaIrO}_3$  type in  $\text{MgGeO}_3$ , while they are different from those of  $\text{CaIrO}_3$  itself. We estimate the phonon contribution to the Grüneisen parameters of the C type and  $\text{CaIrO}_3$  type, finding that Grüneisen parameter does not change significantly at the C-type to  $\text{CaIrO}_3$ -type phase transition. The large difference between spectroscopic and thermodynamic Grüneisen parameters in  $\alpha\text{-Mn}_2\text{O}_3$  (C type) may indicate a large magnetic contribution to the parameter at 1 bar and room temperature.

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