1   **Revision 1**

2   **Compression and Structure of Brucite to 31 GPa from Synchrotron X-ray**
3   **Diffraction and Infrared Spectroscopy Studies**

4   Maining Ma[1,2], Wei Liu[1], Zhiqiang Chen[3], Zhenxian Liu[4], Baosheng Li[1,*]

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6   [1]Mineral Physics Institute, Stony Brook University, Stony Brook, NY 11794, USA

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8   [2]Key Laboratory of Computational Geodynamics of Chinese Academy of Sciences,
9   Graduate University of Chinese Academy of Sciences, Beijing 100049, China

10

11   [3]Department of Geosciences, Stony Brook University, Stony Brook, NY 11794, USA

12

13   [4]Geophysical Laboratory, Carnegie Institution of Washington, Washington DC 20015,
14   USA

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16   *Corresponding author
17   Email: Baosheng.Li@sunysb.edu
18   Tel: 1-631-632-9642
19   Fax: 1-631-632-8140

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22   **Running title**: Compression and Infrared Study of Brucite

23   **Abstract**

24   Synchrotron X-ray powder diffraction and infrared (IR) spectroscopy studies on

25   natural brucite were conducted up to 31 GPa using diamond anvil cell (DAC) techniques

26   at beamlines X17C and U2A of National Synchrotron Light Source (NSLS). The lattice

27   parameters and unit-cell volumes were refined in $P\bar{3}m1$ space group throughout the

28   experimental pressure range. The anisotropy of lattice compression decreases with

29   pressure due to a more compressible c axis and the compression becomes nearly isotropic

30   in the pressure range of 10-25 GPa. The unit cell volumes are fitted to the third-order

31   Birch-Murnaghan equation of state, yielding K_0 =39.4(1.3) GPa, K_0' = 8.4(0.4) for the

32   bulk modulus and its pressure-derivative, respectively. No phase transition or

33   amorphization was resolved from the X-ray diffraction data up to 29 GPa, however,

34   starting from ~4 GPa, a new infrared vibration band (~3638 cm^{-1}) 60 cm^{-1} below the OH

35   stretching A_{2u} band of brucite was found to co-exist with the A_{2u} band and its intensity

36   continuously increases with pressure. The new OH stretching band has a more

37   pronounced redshift as a function of pressure (-4.7 cm^{-1}/GPa) than the A_{2u} band (-0.7

38   cm^{-1}/GPa). Comparison with first principles calculations suggests that a structural change

39   involving disordered H sublattice is capable of reconciling the observations from X-ray

40   diffraction and infrared spectroscopy studies.

41

42   **Introduction**

43   Hydrous minerals have long been considered to be the major source for transporting

44   and storing water in the Earth's mantle. Brucite, $Mg(OH)_2$, is of particular interest for the

45   study of hydrous minerals because of its simple structure in comparison with other

46   hydrous minerals in the Earth's crust and mantle. It can be formed through hydration of

47   olivine in regions where fluid rock interactions are present in the upper mantle.

48   Investigations on the behavior and physical properties of brucite are important for

49   thermodynamic modeling of phase transformations and dehydration processes related to

50   the dynamics at crust and mantle depths (Peacock and Hyndman 1999).

51   At ambient conditions, brucite crystalizes in CdI_2–type structure with space group

52    $P\bar{3}m1$ (Fig. 1) ($a = 3.1468$ Å, $c = 4.7568$ Å, $c/a = 1.5116$). The MgO6 layers stack along

53   c axis with an interlayer distance of ~4.71 Å while the H atom resides ~0.95 Å above

54   oxygen along c axis with three H neighbors from the opposing layer. Much of our

55   understanding about its structural behavior and physical properties at high pressure

56   comes from experimental studies using a variety of techniques, including shock

57   compression (Duffy et al. 1991), X-ray and neutron diffraction (Fei and Mao 1993; Duffy

58   et al. 1995a; Xia et al. 1998; Nagai et al. 2000; Fukui et al. 2003; Parise et al. 1994; Catti

59   et al. 1995; Horita et al 2010), Raman and infrared spectroscopy (Duffy et al. 1995b,

60   Kruger et al. 1989), and Brillouin scattering measurements (Xia et al. 1998; Jiang et al.

61   2006). Complementary to those from experimental studies, important and insightful

62   results have also been obtained by many researchers using theoretical approaches at

63   conditions within and/or beyond those attained in experiment studies(e.g., Sherman 1991;

64   Raugei et al. 1999; Mookherjee and Stixrude 2006; Jayachandran and Liu 2006;

65   Hermansson et al. 2008; Mitev et al. 2009). In brucite, the atomic interactions between

66   MgO6 layers along c axis are believed to be weaker than the strong covalent bonds

67   within the layer. This has been demonstrated by data from diffraction studies that the

68   crystallographic c axis is much more compressible than a axis up to ~10 GPa (e.g., Fei

69   and Mao 1993; Xia et al. 1998; Fukui et al. 2003; Duffy et al. 1995a; Nagai et al. 2000).

70   Above 10 GPa, however, the H atomic positions and the formation of hydrogen bonding

71   become the main dispute, and the results of lattice parameters from different studies also

72   seem to show noticeable divergence with increasing pressure. Neutron diffraction studies

73   on deuterated brucite $Mg(OD)_2$ (e.g., Parise et al. 1994; Nagai et al. 2000) and molecular

74   dynamic modeling (e.g., Raugei et al. 1999) suggest that there is an increased hydrogen

75   bonding within the hydroxide structure at high pressures when H atoms occupy three

76   off-axial positions (6i site) instead of parallel to c axis (2d site). Hydrogen bonding is also

77   suggested in previous Raman and infrared spectroscopy studies based on the observation

78   of new vibration bands at high pressure and the negative pressure dependence of the new

79   bands (Duffy et al. 1995b; Kruger et al. 1989; Shinoda et al. 2002; Horita et al. 2010).

80   However, first principles calculations by Mookherjee and Stixrude (2006) on a $\sqrt{3}x\sqrt{3}x1$

81   superstructure of brucite (space group $P\bar{3}$, H atom at 6g sites) indicate that the formation

82   of interlayer H bond is not a necessity. A more recent molecular dynamics study by Mitev

83   et al. (2009) also argued that the variation of the electrical field when the $MgO6$ layers

84   are pressed towards each other at high pressure can be responsible for the negative

85   pressure dependence of the OH vibration bands observed in infrared studies without the

86   formation of H bond.

87   In addition to the ambiguities about crystal structure, the equation of state

88   parameters for brucite, namely, the bulk modulus (K) and its pressure derivative (K'),

89   from previous studies are still discrepant, ranging from 33 to 68.3 GPa and 8.9 to 4.0,

90   respectively. In comparison, the results calculated using the elastic constants from

91   Brillouin scattering by Xia et al.(1998) and Jiang et al.(2006) yield a value of 36-37 GPa

92   at ambient conditions. It is commonly believed that discrepancy may be introduced by

93   pressure range of experiments, non-hydrostaticity, as well as system errors in different

94   experimental setups. For brucite, structural complications observed at high pressures,

95   such as possible phase transition suggested by Raman study (Duffy et al., 1995b) or

96   compression mechanism change (Nagai et al. 2000), may cast additional uncertainty on

97   the comparability of the data obtained from different pressure ranges.

98   In this paper, new data from high pressure synchrotron X-ray powder diffraction and

99   synchrotron infrared (IR) spectroscopy studies have been acquired on a natural brucite

100   sample. An updated equation of state is derived from X-ray diffraction data under

101   hydrostatic compressions. Attempts have also been made to provide insights in the

102   behavior of H atom at high pressures based on the results of the infrared spectroscopy in

103   conjunction with first principles calculations.

104   **Experimental procedures**

105   Angle-dispersive X-ray powder diffraction experiments were conducted at ambient

106   temperature up to ~29 GPa using a diamond anvil cell (DAC) at beamline X17C of

107   National Synchrotron Light Source (NSLS). Powder sample of natural brucite

108   (GBW03128) with an average chemical composition of MgO (61.43%), CO_2 (8.08%),

109   CaO (2.51%) was used as starting material. The CO_2 and CaO come from dolomite which

110   occurs as a common impurity in natural brucite (see Fig. 2). Brilliant-cut diamond anvils

111   (Type IA) with 250 µm culets were used in the current experiment. A T301 stainless steel

112   gasket was pre-indented from 250 µm to 62 µm in thickness and a hole of 100 µm in

113   diameter was drilled in the center with EDM (Electric Discharge Machine) to serve as the

114   chamber to contain the pressure medium and the sample. A mixture of 16:3:1

115   methanol-ethanol-water was used as pressure medium. Several small ruby crystals were

116   dispersed in the cell and the pressure was obtained from the ruby pressure scale based on

117   the shift of the fluorescent peak (Mao et al. 1986). A beam of monochromatic X-ray

118   (wavelength 0.4066 Å) was focused to a 23 micron (vertical) × 21 micron (horizontal)

119   area using slits and K-B mirrors. Two dimensional diffraction images were collected by

120   using the Rayonix SX165 CCD detector. The scanning time for collecting X-ray

121   diffraction data ranged from 800 to 1200 second based on the intensities of the incident

122   X-ray source. One dimensional diffraction patterns were obtained by an integration of

123   these images over the entire radial coverage using the FIT2D program (Version: V12.077,

124   ESRF). The integrated X-ray diffraction spectra upon increasing pressures are compared

125   in Figure 2 for some selected pressures. Within the diffracting angle of the current setup,

126   four diffraction lines (100), (011), (012) and (110) were recorded at all pressures. The

127   weak non-brucite diffraction peaks could be indexed by dolomite (Fig. 2). These peaks

128   were discarded in the refinement of lattice parameters and unit-cell volumes using the Le

129   Bail method with the software GSAS and the graphical interface EXPGUI (Larson 2004).

130   Synchrotron infrared (IR) spectroscopy experiments on brucite were performed at

131   ambient temperature up to ~31 GPa using a diamond anvil cell at U2A beamline of NSLS.

132   Powder starting material from the same source as that used in the X-ray diffraction

133   experiment was used in IR experiments. A pair of type IIa diamond anvils with a culet

134   size of 300 μm was employed and a pre-indented T301 stainless steel gasket (~80 μm

135   thick) with a 100 μm diameter hole was used as the chamber for the sample and the

136   pressure medium. KBr powder was used as a pressure medium together with a small ruby

137   ball loaded into the sample chamber as a pressure standard. The IR spectra were collected

138   in transmission mode by a Bruker FTIR spectrometer with a nitrogen-cooled mid-band

139   MCT (MCT-A) detector. The frequencies of the recorded spectra were from 600 to 8000

140   cm^{-1} with a resolution of 4 cm^{-1}.

Results and discussion

141

142   *Linear compression anisotropy*

143   In the refinement of the lattice parameters and unit cell volumes, $P\bar{3}m1$ structure

144   is assumed at all pressures, and the results are listed in Table 1. Broadening of the

145   diffraction lines and decreased diffraction intensities are noticeable at pressures above

146   ~14 GPa (Fig. 2), which are believed to be caused by the increased non-hydrostaticity

147   after the solidification of the methanol-ethanol-water pressure medium at ~ 11 GPa (e.g.,

148   Klotz, 2009). As a result, the uncertainties in the refined lattice parameters and unit cell

149   volumes above 14 GPa are about an order of magnitude higher than those below 11 GPa

150   (Table 1). The anisotropic behavior of the lattice compression in brucite is evident when

151   comparing the lattice parameters *a* and *c* as a function of pressure. Fitting the observed

152   lattice parameters in the pressure range of 2.0-11.3 GPa to Eulerian finite strain equations

153   (e.g., Meade and Jeanloz, 1990) yields the linear compressibility for both *a* and *c* axes, β_a

154   = 3.4(2)x10^{-3} GPa^{-1} and β_c = 1.8(1)x10^{-2} GPa^{-1}, indicating that the compressibility along *c*

155   axis β_c is about five times of β_a at ambient pressure. This observation is consistent with

156   the anisotropic compression behavior on natural and synthetic brucite samples reported in

157   previous studies. The change of the compression anisotropy with increasing pressure can

158   be inferred from change of the slope in the plot of *c/a* as a function of pressure based on

159    $\partial(c/a)/\partial P = -(c/a)(\beta_c-\beta_a)$. From ambient pressure to ~10 GPa, $\partial(c/a)/\partial P$ changes from ~

160   -0.017 GPa^{-1} to ~ -0.003 GPa^{-1} together with a decrease of *c/a* from ~1.512 to ~1.440, as

161   a result, the difference between β_c and β_a becomes smaller (~81% reduction in the value

162   of (β_c-β_a)) and thus the linear compression anisotropy decreases. Above 10 GPa, *c/a*

163   becomes less pressure dependent with a slope $\partial(c/a)/\partial P$ close to zero up to ~25 GPa,

164   indicating that $\beta_c \cong \beta_a$ and the lattice compression is nearly isotropic. As compared in

165   Figure 3, the *c/a* values from the current study show a good agreement within 1% with

166   those measured using different techniques except for those from Fei and Mao (1993) with

167   which the agreement is within ~3.5% at ~25 GPa and ~6.5% at 29 GPa. Since no pressure

168   medium was used in Fei and Mao (1993), nonhydrostaticity is therefore believed to be

169   responsible for the discrepancy in Figure 3.

170   The characteristics of the *c/a* ratio and the linear compressibility as a function of

171   pressure are also supported by DFT calculations, although DFT calculations predict a

172   broader pressure range of isotropic compression than those observed in experimental

173   studies (see Fig. 5 in Mookherjee and Stixrude 2006). Both DFT calculations and

174   structural refinement of diffraction data suggest that the initial fast decrease of *c/a* at low

175   pressures can be attributed to the rapid decrease of the distance between MgO6 layer,

176   presumably because of the weak coulomb and electrostatic forces between these layers.

177   Upon further compression, the interlayer forces become comparable to the intralayer

178   covalent bonds and compressions along *a* and *c* axes become comparable, resulting an

179   isotropic compression. It is worth noting that the linear compressibility ratio β_c/β_a

180   calculated using the single crystal elastic constants from Brillouin scattering (Jiang et al.,

181   2006) predicts a value of β_c/β_a =1 around 20 GPa, which corresponds well to the current

182   observation that *c/a* ratio becomes pressure independent (i.e., $\beta_c = \beta_a$) at ~18 GPa. The

183   *c/a* value appears to increase with pressure above 25-28 GPa as indicated in the current

184   study and Fei and Mao (1993) as well as DFT calculations, except that DFT calculations

185   suggest a slower increase rate than that observed in previous quasihydrostatic

186   experiments.

187

188   *Equation of state*

189   The unit cell volumes obtained from the current study are plotted as a function of

190   pressure in Figure 4. Isothermal bulk modulus (K_0) and its pressure derivative ($K_0^{'}$) are

191   constrained by fitting these data to the third-order Birch-Murnaghan equation of state,

192
$$P = \frac{3}{2} K_0 \left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}} \right] \cdot \left\{ 1 + \frac{3}{4}(K_0' - 4) \cdot \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right] \right\}$$

193   where V_0 is the unit cell volume, and the subscript "0" refers to ambient pressure. An

194   unweighted fit to the data in entire pressure range yields $K_0 = 37.0(1.3)$ GPa, $K_0' = 10.6$

195   (0.4) with V_0 fixed at the observed value 40.794 Å^3. Considering that the data at pressures

196   higher than ~11 GPa may be affected by the present of deviatoric stresses as well as a

197   possibility that the compression mechanism changes from interlayer distance shortening

198   to isotropic compression as suggested by Nagai et al. (2000), we therefore performed a fit

199   using the data only up to ~11 GPa where the pressure medium is known to be hydrostatic

200   (e.g., Klotz 2009). The results from the latter fit, $K_0 = 39.4(1.3)$ GPa, $K_0' = 8.4(0.4)$, and

201    $V_0 = 40.909$ Å^3, are believed to be a more reliable constraint for the bulk modulus and its

202   pressure derivative at ambient pressure, and are therefore used as the representative

203   values from the current study (Table 2). Following the analysis of Angel (2000), the

204   negative correlation between K_0 and K_0' in the least square fit is illustrated by the 95%

205   confidence ellipse of the two parameters (Fig. 5).

206   As shown in Table 2, the values of K_0 and K_0' for brucite from previous studies are

207   largely discrepant, ranging from 33 to 68.3 GPa and 8.9 to 4.0, respectively. The values

208   from Brillouin scattering measurements by Xia et al. (1998) and Jiang et al. (2006),

209   however, give a fairly consistent result of 36-37 GPa for the bulk modulus at ambient

210   pressure. Unlike equation of state fit which must incorporate measurements of pressure

211   and volume at high pressures, Brillouin scattering provides direct measurements of

212   acoustic velocities and therefore the elastic constants at each pressure. The good

213   agreement of K_0 and K_0' from the current equation of state fit with the results of $K_0 = 35.8$

214   GPa and $K_0' = 8.9$ derived from Brillouin scattering data of Jiang et al. (2006) further

215   validates the current determinations. When compared to previous compression studies,

216   reasonably good agreement can be found with those from measurements on $Mg(OH)_2$

217   brucite (Horita et al. 2010; Fukui et al. 2003; Catti et al. 1995; Xia et al. 1998) as well as

218   on deuterated brucite $Mg(OD)_2$ (Nagai et al., 2000). A discontinuity has been suggested

219   by Fei and Mao (1993) in the unit cell volume as a function of pressure around 8-11 GPa,

220   but this has not been observed in other studies. Nevertheless, if the data in the pressure

221   range up to 11 GPa from Fei and Mao (1993) are used in equation of state fit, a bulk

222   modulus of 42.8 GPa can be obtained (with $K_0{}'$ and V_0 fixed at the values of the current

223   study), which is in much better agreement with those compared in Table 2. Thus, the

224   primary sources for the observed discrepancy include (1) trade-off between K_0 and $K_0{}'$

225   when fitting datasets obtained from different pressure ranges, and (2) differences in stress

226   states in different experiments (see also Horita et al. 2010, Jiang et al. 2006). While these

227   trade-off between K_0 and $K_0{}'$ can be investigated retroactively using the published

228   volumes, the assessment and correction for the effects of stress on the data listed in Table

229   2, however, are difficult due to the lack of quantitative stress information from these

230   studies.

231

232   OH Vibration and H Position

233   Brucite ($P\bar{3}m1$) has two internal OH vibrational modes at ambient conditions, an

234   infrared active OH stretching mode (A_{2u} mode) at ~3697 cm^{-1} and a Raman active A_{1g}

235   mode at ~ 3650 cm^{-1}. Previously, Kruger et al. (1989) reported that a new infrared band

236   was observed at pressure as low as zero pressure, with its intensity gradually increased to

237   30% of the intensity of A_{2u} mode at 29 GPa. Both the A_{2u} and the new bands were found

238   to exhibit redshift in frequency (i.e., negative pressure dependence). They attributed the

239   new OH stretching band to a transition from the first excited infrared state to its first

240   overtone (A_{2u} X A_{2u}). However, in the reports of Shinoda and Aikawa (1998) and

241   Shinoda et al. (2002), a new peak ~50 cm^{-1} below the fundamental infrared A_{2u} peak was

242   observed only at pressures over ~3 GPa, and it was assigned to a new OH dipole due to

243   the formation of new proton site at high pressure.

244   Our infrared results yielded 3698 cm^{-1} for the frequency of the A_{2u} mode at ambient

245   conditions, which is very consistent with the values reported in previous studies. At ~4

246   GPa, a new vibrational peak started to appear at ~3638 cm^{-1} and its intensity increases

247   with pressure (Fig. 5). The pressures at which the new peak was observed agrees well

248   with the pressure range where new Raman and IR peaks were observed in previous

249   studies (e.g., Duffy et al. 1995b; Shinoda and Aikawa 1998; Shinoda et al. 2002). The

250   current A_{2u} band and the new mode exhibit redshifts as a function of pressure with a slope

251 of -0.7 cm^{-1}/GPa and -4.7 cm^{-1} /GPa, respectively. These results compare well with

252 previously reported values of -0.6 cm^{-1}/GPa and -3.7 cm^{-1}/GPa obtained by Kruger et al.

253 (1989), as well as -0.25 cm^{-1}/GPa and -5.0 cm^{-1}/GPa by Shinoda et al. (2002) (Fig. 6).

254 The redshifts of both the fundamental and the new peak are completely reversible along

255 decompression without noticeable hysteresis. Within the pressure range where the new

256 infrared peak co-exists with the fundamental A_{2u} mode, no phase transition in brucite can

257 be resolved in the X-ray diffraction patterns, except for a change in the linear

258 compression anisotropy as indicated in the *c/a* as a function of pressure in Figure 3.

259 These results appear to agree with previous suggestions that the structural variation of

260 brucite at pressure is primarily associated with the rearrangement of H atoms while the

261 MgO6 sublattice remains unaffected.

262   As inferred in previous studies, H atoms in $Ca(OH)_2$ undergo an order-disorder

263 transition marked by an abrupt increase in the width of the A_{2u} band at ~11-12GPa, and

264 the disordering of H atoms destabilizes the CaO6 sublattice and leads to the

265 amorphization of $Ca(OH)_2$ (e.g., Desgranges et al. 1996; Nagai et al. 2000). In another

266 brucite-type metal hydroxide, $Co(OH)_2$, whose metal cation radius is slightly smaller than

267 Ca, only partially disordered H sublattice was inferred from Raman and infrared data at

268 30 GPa with clear evidence from X-ray diffraction indicating that long range order of

269 CoO6 sublattice was still preserved. By comparison, the width of the A_{2u} band for

270 $Mg(OH)_2$ from the current study shows a linear increase with pressure up to ~30 GPa,

271 consistent with previous observations by Kruger et al. (1989) and Nguyen et al. (1997). It

272 has been suggested that brucite-type hydroxides with large metal cation mirror the atomic

273 interactions and therefore the structural behavior of those with smaller metal cation at

274 higher pressures. Mg has a smaller cationic radius in comparison with Ca and Co, the

275 observation of new band and the lack of abrupt FWHM increase in the fundamental A_{2u}

276 band and the new OH band appear to indicate a partial disorder and the possibility of

277 additional H sites.

278   Quantitative determination of the atomic positions H for brucite under high pressure,

279 however, remains as a challenging task. Neutron diffraction studies on deuterated brucite

280 $Mg(OD)_2$ (Parise et al., 1994) suggest that at non-ambient pressures D atom is displaced

281 from its axial position (2d) to three off-axis positions (6*i*) with equal probability of

282   occupancy, resulting from either random static disorder or anharmonic thermal vibration.

283   The OD distance refined with D atoms at $6i$ sites shows nearly no change from 0 to 2

284   GPa followed by a continuous increase from ~0.95 Å to 1.02 Å to 9.3 GPa. A subsequent

285   neutron diffraction study (Catti et al., 1995) on normal brucite $Mg(OH)_2$, however, finds

286   that H ordered model (H in 2d site) is favored at low pressures (0-7.8 GPa) while both the

287   ordered and disordered (H in $6i$ site) models fit the data at 10.9 GPa equally well. The

288   refinement results revealed a continuous decrease in OH distance from 0.958 Å to 0.915

289   Å with H at 2d site (P < 10 GPa) and $6i$ site (P > 10 GPa). Molecular dynamic simulation

290   (Raugei et al. 1999) indicates that vigorous anharmonic motions of H atoms in $Mg(OH)_2$

291   and $Ca(OH)_2$ can displace H atoms from the threefold axis and result in disordering of H

292   sublattice at high pressures. In addition, the pressure induced redshits of A_{2u} modes

293   observed in previous experiments of Kruger et al. (1989) can be reproduced with such a

294   disordered H model. Mookherjee and Stixrude (2006) conducted first principles

295   calculations on brucite using a √3x√3x1 super cell of brucite, and found that this model

296   structure with H occupying 6g site at ~7° off from threefold axis is energetically favored

297   at high pressure.

298   We conducted *ab initio* calculations for both $P\bar{3}m1$ and $P\bar{3}$ structures using

299   density functional theory (DFT) within the GGA framework as implemented in CASTEP

300   (Clark et al., 2005). An energy cutoff of 800 eV for the plane wave basis set and k point

301   sampling of 9x9x5 ($P\bar{3}m1$) and 7x7x7 ($P\bar{3}$) were used to ensure an energy convergence

302   of 1×10^{-6} eV/atom and 0.02 GPa in pressure. The OH distances in these two structures are

303   found to have very limited sensitivity to pressure. In $P\bar{3}m1$, the OH distance shows a

304   negligible increase from 0.9753 Å at ambient pressure to 0.9757 Å at ~5 GPa (0.04%)

305   followed by a small decrease to 0.9736 Å at 30 GPa. By comparison, the OH distance in

306    $P\bar{3}$ structure (√3x√3x1) slowly increases from 0.9756 at zero pressures to 0.9773 Å at 5

307   GPa and then to 0.9830 Å at 30 GPa. In spite of the minor differences in OH distance and

308   orientation between $P\bar{3}$ and the $P\bar{3}m1$ structures, the $MgO6$ sublattices in both

309   structures remain indistinguishable at high pressures. Attempt to distinguish the structure

310   of brucite based on the OH distances from previous neutron diffraction studies on

311    $Mg(OH)_2$ and $Mg(OD)_2$, however, seems to be difficult due to the discrepancies between

312   the results from these two studies. Comparisons of structural changes and energetics

313   between $P\bar{3}m1$ and $P\bar{3}$ structures in a wide pressure range have been given in detail

314   in the DFT study of Mookherjee and Stixrude (2006), and will not be repeated here.

315   Instead, we will provide supplementary vibration spectroscopy data from DFT

316   calculations to compare with those from high pressure experiments.

317   Infrared spectra for both $P\bar{3}m1$ and P-3 structures at high pressures are calculated

318   using a linear response approach with norm-conserving potentials as implemented in

319   software CASTEP. It has been demonstrated that the harmonic OH stretching frequencies

320   derived within GGA show good agreement with the experimental frequencies resulting

321   from a cancellation of the overestimation of bond length and the underestimation of

322   harmonic frequencies associated with GGA approximation in DFT calculations (Balan et

323   al., 2007). The fundamental frequency of the A_{2u} mode for $P\bar{3}m1$ from the current

324   calculation is 3651 cm^{-1}, which is within 1.5% agreement with the experimental results

325   from the current as well as previous studies (3698-3700 cm^{-1}). The calculated Raman

326   active OH modes A_{1g} (3612 cm^{-1}) is within ~1% of the single crystal data reported by

327   Duffy et al. (1995a) (3652 cm^{-1}). With increasing pressure from 0 to 10 GPa, the A_{2u}

328   mode displays a slight decrease in frequency with a pressure dependence of $d\upsilon/dP \sim$ -0.7

329   cm^{-1}/GPa, which is consistent with the experimentally observed value (Fig. 6). Above 10

330   GPa, the OH vibration frequencies increase slightly with pressure with a rate of ~1.0

331   cm^{-1}/GPa. No pressure induced new vibration band was observed when the H positions

332   maintain parallel to the c-axis at the 2d positions in $P\bar{3}m1$ structure. In $P\bar{3}$ structure

333   with H atom inclined at ~7.4° from the threefold axis at zero pressure, an OH stretching

334   vibration frequency of 3643 cm^{-1} is observed which is slightly lower than the A_{2u} mode in

335   the $P\bar{3}m1$ structure. With increasing pressure, the OH stretching vibration frequency in

336    $P\bar{3}$ decreases at a rate of -5.0 cm^{-1}/GPa, which is in excellent agreement with the

337   pressure dependence of the new band (-4.7 cm^{-1}/GPa) observed in our experiment (Fig. 6).

338   Interestingly, the new Raman modes observed in previous study by Duffy et al. (1995b)

339   can be found in the Raman active modes for $P\bar{3}$ structure. In comparison, previous

340   calculation on $Mg(OH)_2$ (Mitev et al. 2009) predicts that the redshift of A_{2u} mode under

341   an isotope isolated configuration has a slope of $d\upsilon/dP$ = -4 cm^{-1}/GPa with H parallel to

342   c-axis (H at 2d site) and a much larger pressure dependence (-11 cm^{-1}/GPa) for OH

343   stretching band when H atoms are displaced from the c axis (H at 6g site, $P\bar{3}$).

344   Qualitatively, the current findings agree with previous suggestions that H atoms

345   occupying off-axis positions are capable of producing the new OH stretching band

346   observed in high pressure infrared data (e.g., Raugei et al. 1999; Mookherjee and

347   Stixrude 2006; Mitev et al. 2009; Jochym et al. 2010). Quantitative comparison of $d\upsilon/dP$

348   between current calculations and experimental infrared data seems to suggest that the

349   co-existence of the original A_{2u} band and the new OH stretching band observed in

350   infrared experiments requires H atoms to take occupancies at both axial and off-axis

351   positions. Possible scenarios include the development of off axis H atoms in a locally

352   ordered form (e.g., a $P\bar{3}$-like structure) as a separate phase/cluster/domains as driven by

353   the lower enthalpy, or a structure involving intermixed axial and off-axial H atoms which

354   maintains a long range order within the crystal but with locally disordered H sites. If it is

355   the former, the interaction of the H sublattices from each phase is insignificant and the

356   characteristics of each structure are preserved in experimental measurements. Evidences

357   supporting this model include weak neutron diffraction lines besides those from $P\bar{3}m1$

358   structure (e.g., Horita et al. 2010), volume discontinuities at 8-11 GPa (see Fei and Mao

359   1993), new Raman (Duffy et. al. 1995b) and infrared data as shown above, as well as

360   lower enthalpy of $P\bar{3}$ structure in DFT results. Along this line, the increase of the

361   FWHM for both OH stretching bands (Fig. 5) may suggest that the disordering of H in

362   the two phases continues to increase with pressure, when the two OH vibrations bands

363   merge into a broad band at higher pressures, and it may result in full disorder. It is

364   interesting to note that a recent X-ray diffraction study suggests that the behavior of

365   $Ca(OH)_2$ at high pressure appears to follow this pathway, in which a crystal-crystal phase

366   transition was indeed observed prior to its amorphization (Iizuka et al. 2011).

367   Alternatively, a structure model with intermixed (locally disordered) H atoms and

368   long-range order is equally valid. Previously, infrared studies with polarized and

369   unpolarized sources by Shinoda et al. (2002) suggested that brucite at high pressures

370   undergoes a proton state transition from one proton site to two proton state in which the

371   H bonds of trifurcated and bent types are responsible for the original and pressure

372   induced new OH bands. A recent molecular dynamics study also indicated that H atoms

373   could be decoupled from brucite lattice into "lock-in" off-axis positions. We constructed

374   a 3 x 3 x 1 supercell of brucite in $P\bar{3}$ structure (see Fig. 5 of Mitev et al. 2009) and

375   performed structure optimization using DFT within GGA. We found that if the initial H

376   atoms are at the off-axis potions, structure optimization results in a lower enthalpy

377   structure with two distinct groups of OH distances and off-axis angles. This implies that

378   when the distance between MgO6 layers decreases with increasing pressure, if some H

379   atoms are displaced into off axis positions due to either anharmonic motions or

380   electrostatic forces, the resulting structure with locally disordered H atoms can be

381   energetically favored. This is also observed in a 2 x 2 x 1 supercell in $P\bar{3}$ (20 atoms/cell,

382   H at 2d and 6g sites, Mg: 1a and 3e sites), in which the co-existing two H sites resemble

383   those in $P\bar{3}$ (H off axis) and $P\bar{3}m1$(H parallel to axis) structures. At 20 GPa, the

384   optimized 2 x 2 x 1 supercell has an enthalpy ~0.005 eV/atom lower than $P\bar{3}m1$ (H at

385   2d site) but 0.003 eV/atom higher than the $P\bar{3}$ (H atoms all at 6g sites). We calculated

386   the infrared spectra for the 2 x 2 x 1 supercell, and two separate OH stretching bands

387   were indeed observed. However, the redshifts of the OH stretching bands from our DFT

388   calculations yielded results similar to those reported for isotope-isolated OH frequencies

389   (Mitev et al. 2009), which are much larger than those observed in the infrared

390   experiments.

391

Concluding Remarks

393   We have conducted synchrotron X-ray powder diffraction, infrared spectroscopy,

394   and DFT studies to investigate the structural behavior under compression, equation of

395   state and vibrational properties of brucite. Refinements of the lattice parameters and

396   unit-cell volumes were performed in $P\bar{3}m1$ space group throughout the experimental

397   pressure range. The current results suggest that under pressures equivalent to the Earth's

398   upper mantle and transition zone, the compressibility of brucite along *c* and *a* axes

399   gradually changes from anisotropic to isotropic. The unit cell volumes under hydrostatic

400   pressures are fitted to the third-order Birch-Murnaghan equation of state, yielding $K_0 =$

401   39.4(1.3) GPa, $K_0{}' =8.4(0.4)$ for the bulk modulus and its pressure-derivative,

402   respectively. These results are in good agreement with previous compression studies at

403   similar pressure conditions. Discrepancies in literature values may arise from differences

404   in pressure range, non-hydrostaticity on the sample, and the possibility that brucite

405   experiences a compression mechanism change or phase transition at high pressures.

406   While the new OH vibration band observed in infrared data is in general agreement

407   with trifurcated H atoms suggested by Neutron diffraction and molecular dynamics, a

408   comparison of the infrared spectra from DFT calculations with those from experiments

409   indicates that the dυ/dP of the original OH band is similar to the A_{2u} band in $P\bar{3}m1$ with

410   H atoms at 2d site, while the dυ/dP of the new OH band is nearly identical to the OH

411   stretching band in $P\bar{3}$ with H at off-axis positions (6g site). We investigated two

412   scenarios at high pressure which only involve the change of H atoms in the lattice, the

413   first is that brucite slowly transforms into a new phase with lower enthalpy and off-axis H

414   positions (e.g., a $P\bar{3}$ like structure) so that within crystal scale H atoms appear to be

415   disordered but ordered in each phase; the second is that both axial and off-axial OH

416   bonds closely intermixed to form locally disordered H atoms in the new structure with

417   long range order within the crystal. While direct experimental evidences to discern these

418   two candidates are still lacking, a comparison with existing experimental data, especially

419   the pressure dependence of the redshifts of OH stretching bands, seems to favor the

420   development of off axial H positions in a separate phase, although the test for the

421   intermixed OH bonds might suffer from uncertainties caused by the small size of

422   supercell investigated in this study. In either cases, the increased FWHM of the OH

423   stretching bands may be interpreted as the increased disordering of H atoms at high

424   pressure, which may ultimately lead to a fully disorder H sublattice and possibly

425   amorphization following the pathways suggested in $Ca(OH)_2$ (Iizuka et al. 2011).

437

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530

531   **Figure Captions:**

532   Fig. 1. Crystal structure of brucite ($P\bar{3}m1$) viewed along c axis (a) and a axis (b). H

533   atoms are shown as light colored balls, and the red balls are oxygen and orange balls are

534   Mg atoms.

535

536   Fig. 2. X-ray diffraction patterns of brucite at six selected pressures during compression

537   at room temperature ("D" denotes peaks from dolomite).

538

539   Fig. 3. Comparison of c/a from this study with those from previous experimental studies.

540

541   Fig. 4. (a) Comparison of V/V_0 from the current study with previous experimental results.

542   (b) Confidence ellipse of $K_0 - K_0'$ from the current least square fit to the data within

543   hydrostatic pressure limit (0-11.3 GPa). The symbols are the $K_0 - K_0'$ values from

544   previous experimental studies listed in Table 2 (except Fei and Mao 1993). H: Horita et al.

545   (2010); J: Jiang et al. (2006); F: Fukui et al. (2003); N: Nagai et al. (2000); X: Xia et al.

546   (1998); C: Catti et al. (1995); D: Duffy et al. (1995).

547

548   Fig. 5. Infrared spectroscopy data of brucite at high pressure and ambient temperature

549   along compression (a), (b), and decompression (c).

550

551   Fig. 6. Comparison of pressure-induced redshifts of the OH vibration frequencies from

552   experimental and theoretical studies.

553

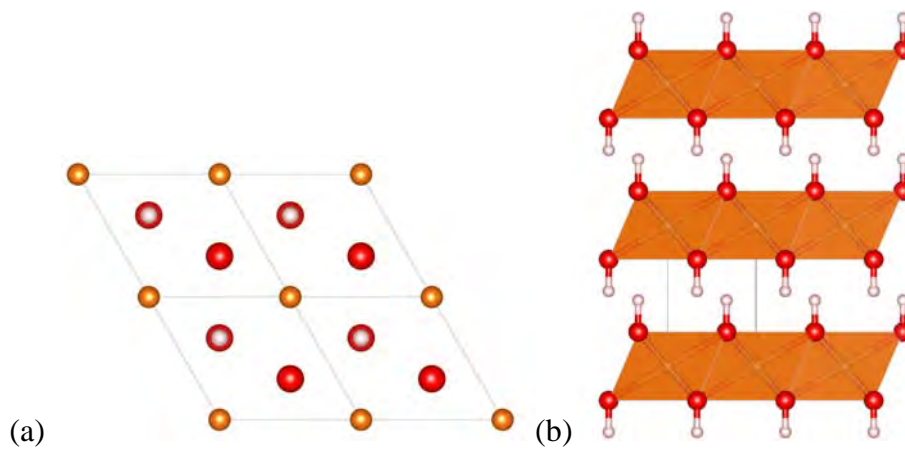**Table 1.** Refined lattice parameters and unit-cell volumes at ambient temperature.

P (GPa)	a (Å)	c (Å)	Volume (Å³)
0	3.1468(9)	4.7568(12)	40.794(19)
1.58	3.121(4)	4.6897(12)	39.56(7)
2.30	3.1241(4)	4.6188(16)	39.039(16)
3.03	3.1159(4)	4.5867(17)	38.566(16)
3.92	3.1056(5)	4.5504(18)	38.008(17)
4.91	3.0960(6)	4.5187(23)	37.510(22)
5.91	3.0863(6)	4.4896(23)	37.035(22)
7.01	3.0748(6)	4.4591(23)	36.509(22)
8.28	3.0631(7)	4.4279(25)	35.978(23)
9.55	3.0528(8)	4.4041(31)	35.545(28)
11.30	3.0435(8)	4.3781(28)	35.121(26)
12.47	3.0367(10)	4.354(4)	34.769(32)
14.18	3.0282(13)	4.334(5)	34.42(4)
16.81	3.0144(19)	4.300(7)	33.84(6)
18.26	3.0037(15)	4.293(5)	33.54(5)
19.78	3.0019(19)	4.250(7)	33.17(6)
20.70	2.9865(27)	4.280(10)	33.06(9)
22.28	2.9725(26)	4.274(10)	32.71(9)
24.90	2.9642(28)	4.244(11)	32.29(9)
26.60	2.9436(30)	4.266(12)	32.01(10)
28.92	2.9224(14)	4.317(4)	31.93(4)

Table 2. Experimental and calculated bulk modulus (K_0) and its pressure derivative (K_0') from this study and the literature

V_0 (Å^3)	K_0(GPa)	K_0'	Method	Pressure Medium	Source
Experimental					
40.909	39.4(1.3)	8.4 (0.4)	Powder X-ray	Methanol-ethanol-	This study[1]
40.794	37.0 (1.3)	10.6 (0.4)	Powder X-ray	water (16:3:1)	This study[2]
41.1752	39.0 (2.8)	11.1 (2.0)	Powder neutron	Fluorinert	Horita et al. 2010
	35.8 (0.9)	8.9 (0.4)	Brillouin scattering	Methanol-ethanol (4:1)	Jiang et al. 2006
40.930	41.8 (1.3)	6.6 (0.3)	Powder X-ray	Magnesium oxide	Fukui et al. 2003
40.746	44 (1)	6.7 (fixed)	Powder X-ray	Methanol-ethanol (4:1)	Nagai et al. 2000
40.8	39.6 (1.4)	6.7 (0.7)	Powder X-ray	Boron nitride	Xia et al. 1998
40.986	39 (1)	7.6 (0.7)	Powder neutron	NaCl	Catti et al. 1995
40.851	42 (2)	5.7 (0.5)	Single-crystal X-ray	None or Ne	Duffy et al. 1995
40.878	54.3 (2)	4.7 (0.2)	Powder X-ray	None	Fei and Mao 1993
Theory					
41.699	39.7	6.75	DFT (GGA)		Mitev et al. 2009
42.991	33		B3LYP		Hermansson et al. 2008
36.7	65	6.0	DFT (LDA)		Mookherjee and Stixrude 2006
41.7	43	5.7	DFT (GGA)		
40.86	68.3	4.0	Hartree-Fock		Sherman 1991

[1]: Fit without weight, hydrostatic pressures, 0-11.3 GPa,

[2]: Fit without weight, all data, 0-28.9 GPa.

(a) (b)

Figure 1.

Figure 2.

Figure 3.

(a)

(b)

Figure 4.

(a)

(b)

(c)

Figure 5.

Figure 6.

(a)   (b)

Figure 1.

Figure 2.

Figure 3.

(a)

(b)

Figure 4.

(a)

(b)

(c)

Figure 5.

Figure 6.