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2   # Revision 2

3   # High-Pressure Phase Transition of Fe-bearing

4   # Orthopyroxene Revealed by Raman Spectroscopy

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ABSTRACT

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17   Orthopyroxene is one of the dominant minerals in the Earth's upper mantle. In this study, we

18   used Raman spectroscopy to investigate the lattice vibration and phase transition of

19   orthopyroxene with four different compositions using diamond anvil cells up to 34 GPa at 300 K.

20   Our orthopyroxene samples contain 0 (En_{100}), 9% ($En_{91}Fs_9$), 11% ($En_{86}Fs_{11}$) and 21% ($En_{74}Fs_{21}$)

21   Fe respectively. At ambient conditions, we observed that the Raman modes exhibited a negative

22   dependence on the Fe content, with the exception of the modes at ~850 and 930 cm^{-1}. In contrast,

23   the two Raman modes increase with increasing the Fe content. The phase transition from

24   metastable α- to β-phase was observed at 12.9-15 GPa for our orthopyroxene samples with less

25   than 21 mol.% Fe, and varying Fe content has a minor effect on the phase transition pressure.

26   Besides of Fe, additional 2-24 mol.% Al can cause phase transition pressure increase from 10-13

27   GPa to 14-16 GPa. At 29-30.1 GPa, we observed the second apparent change in the Raman

28   spectra for all of our investigated samples. For Fe-bearing orthopyroxene, this change in the

29   Raman spectra and frequency shift is associated with the phase transition from β- to γ-phase,

30   whereas for En_{100}, it should be caused by the change of coordination number Si from 4 to 6, or

31   the presence of α-popx phase. Using the obtained Raman frequency shifts, we have also

32   calculated the Grüneisen parameters at high pressures. These parameters are useful for

33   understanding the thermoelastic properties of orthopyroxene at high pressures.

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35   **Keywords:** Raman spectroscopy, orthopyroxene, Fe content, phase transition, high pressure

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1. INTRODUCTION

Orthopyroxene, $(Mg_{1-x}Fe_x)SiO_3$, is a crucial constituent of Earth's upper mantle (Bernard et al.,

2021; Herzberg and Gazel, 2009; Li et al., 2018; Shi et al., 2022; Tollan and Hermann, 2019).

According to the pyrolite model, the volume percentage of orthopyroxene is estimated to be 10

vol.% up to 350-km depth (Frost, 2008). Petrological observations suggest that the

orthopyroxene content in the subducted harzburgite and lherzolite layer can be as high as 22

vol.% (Bodinier and Godard, 2003; Ringwood, 1975; Ringwood and Irifune, 1988). Although

mantle orthopyroxene typically contains 6 mol.% Fe, some diamond inclusions originated from

100-500 km depth have shown than the Fe content in peridotitic orthopyroxene could vary from

3 and 19 mol.% (Stachel and Harris, 2008). In some high-pressure metamorphic rocks, the Fe

content in orthopyroxene exhibits a higher compositional range between 50 and 100 mol.%

(Brothers and Yokoyama, 1990; Davidson, 1968; Jaffe et al., 1978; White et al., 2001).

Therefore, investigating the physical properties of orthopyroxene with varying compositions

under relevant pressure and temperature conditions in the Earth's mantle is crucial for

understanding the structure and composition of the Earth's deep interior.

Along the normal mantle geotherm, the orthorhombic orthopyroxene (*Pbca* space group, α-

phase) transforms to high-pressure clinopyroxene (*C2/c* space group) at ∼8 GPa and then

gradually dissolve into garnet at deeper depth (Akashi et al., 2009; Kung et al., 2005). However,

the path of phase transition in orthopyroxene at high pressures heavily relies on the temperature

and composition (Akashi et al., 2009). The transition of orthopyroxene to high-pressure

clinopyroxene will be inhibited when temperatures are significantly lower than the normal

mantle geotherm (Nishi et al., 2013; Van Mierlo et al., 2013). For example, the α-$MgSiO_3$

61   orthopyroxene (En_{100}) remains metastable and then transforms into its β-phase with a monoclinic

62   structure ($P2_1/c$ space group) at 10.5-13.3 GPa (Kung et al., 2004; Lin, 2004; Xu et al., 2018),

63   which can be preserved to ~40 GPa (Serghiou et al., 2000). Both α- and β-phase can remain

64   metastable up to 800 K at 520-km depth (Xu et al., 2020). Previous studies also investigated the

65   influence of Fe on the phase transition of orthopyroxene (Xu et al., 2020). For orthopyroxene

66   with 9 mol.% Fe ($En_{91}Fs_9$), the transition pressure from α- to β-phase is 12.3 GPa at 300 K,

67   which is similar to the Mg-endmember. However, Fe-bearing β-phase further transforms into the

68   γ-phase (*Pbca* Space group) at 28.4 GPa (Finkelstein et al., 2015). Increasing the Fe content

69   from 30 to 82 mol.% only can weakly decrease the α-β phase transition pressure to 11 GPa and

70   lower the β-γ phase transition pressure to 12 GPa (Dera et al., 2013; Xu et al., 2020). But for

71   pure Fe endmember (Fs_{100}), orthopyroxene transforms into a different monoclinic β-phase with

72   space group *C2/c* at ~6 GPa and then γ-phase at ~13 GPa (HughJones et al., 1996; Xu et al.,

73   2020). Experimental constraints on the transition from β- to γ-phase for orthopyroxene with less

74   than 20 mol.% Fe are still lacking.

75

76   Here, we have performed high-pressure Raman measurements to well constrain the phase

77   transition of orthopyroxene in four different compositions with varying Fe content in symmetric

78   diamond anvil cells (DACs) up to 34 GPa and 300 K. Results from Raman measurements can

79   also be used to identify orthopyroxenes as geological marker (Borromeo et al., 2022). The

80   collected Raman spectra were used to determine the influence of Fe content on the variation of

81   the vibration modes and help to identify the occurrence of the phase transition. Together with

82   previous thermal equation of state, we have calculated thermal Grüneisen parameters of

83   metastable phases at high pressures which are of great importance to calculate the thermal and

84   elastic properties of orthopyroxene.

85

86   **2. EXPERIMENTAL DETAILS**

87   Four orthopyroxene single-crystal samples were used in this study. Composition of these four

88   samples were analyzed using electron microprobe in the Key Laboratory of Crust-Mantle

89   Materials and Environments, University of Science and Technology of China (USTC). The

90   analysis yielded compositions of $MgSiO_3$ (En_{100}), $Mg_{0.91}Fe_{0.09}SiO_3$ ($En_{91}Fs_9$),

91    $Mg_{0.86}Fe_{0.11}Al_{0.02}Ca_{0.01}Si_{0.99}O_3$ ($En_{86}Fs_{11}$) and $Mg_{0.735}Fe_{0.21}Al_{0.07}Si_{0.965}O_3$ ($En_{74}Fs_{21}$). En_{100},

92    $En_{91}Fs_9$ and $En_{86}Fs_{11}$ are single crystals from Yangon, Myanmar. $En_{74}Fs_{21}$ was purchased from

93   Alfa Aesar Corp. Every sample was cut into random orientation with ~25 μm in diameter and

94   double-side polished to ~25 μm in thickness. Rhenium was used as gasket, and the gasket hole

95   was drilled to 235 μm in diameter. Two ruby spheres were loaded into the sample chamber as the

96   pressure calibrant, and argon was used as the pressure medium for high pressure experiments

97   (Dewaele et al., 2004).

98

99   In-situ single-crystal Raman measurements were performed using symmetric DACs equipped

100   with a pair of 400-μm culet diamonds at the High-Pressure Mineral Physics Laboratory, USTC.

101   An Olympus flat field achromatic objective lens was employed for the collection of Raman

102   spectra with a 532-nm wavelength. The Raman spectra were measured in a backscattering

103   geometry in a confocal configuration. The Raman spectra at ambient conditions were determined

104   for all samples outside DACs. At high pressures, we have performed two runs of Raman

105 measurements on the intermediate composition including $En_{91}Fs_9$, $En_{86}Fs_{11}$ and $En_{74}Fs_{21}$. The

106 pure Mg-endmember orthopyroxene was carried out in one run.

107

108 **3. RESULTS**

109 At ambient conditions, 19 to 23 modes were observed for all the investigated orthopyroxene

110 samples. Typical Raman spectra of orthopyroxene with different Fe contents are shown in Figure

111 1. The frequencies of Raman-active modes for our four investigated samples at ambient

112 conditions are shown in Figure 2 and Tables 1-4. The measured frequencies for these

113 orthopyroxene samples are in good relevance with the Fe content. Most frequencies have shown

114 negative linear dependence on the Fe content. The Raman mode at ~400 cm^{-1} for En_{100} shows a

115 similar linear decrease with Fe content up to 50 mol.% but exhibits a much stronger reduction by

116 further increasing the Fe content to 100 mol.%. In addition, we noted that there were two Raman

117 modes around ~900 cm^{-1} increase with Fe content.

118

119 Based on the ambient conditions results, high-pressure Raman spectra for four samples were

120 collected up to 34 GPa at 300 K. For En_{100}, all the frequencies followed a nearly linear increase

121 with pressure up to 13.5 GPa. In exceed of 13.5 GPa, we observed the disappearance of modes at

122 ~425, ~560 and ~590 cm^{-1} accompanied with new modes at ~400, ~500 and ~855 cm^{-1}. Similar

123 change in the Raman spectra and mode frequencies occur at 12.9 GPa for $En_{91}Fs_9$, 15 GPa for

124 $En_{86}Fs_{11}$ and $En_{74}Fs_{21}$ (Figures 4-6). Another obvious change in Raman spectra was noted to

125 occur at approximately 30 GPa for all the investigated orthopyroxene, characterized by the

126 variation in the pressure dependence of Raman frequencies.

127

4. DISCUSSION

4.1. Raman modes at ambient conditions

The obtained results were first used to understand the influence of Fe on the Raman frequency of

orthopyroxene at ambient conditions. Our Raman spectra of orthopyroxene are similar to

previous studies (Chopelas, 1999; Huang et al., 2000). Meaning of each Raman mode for

orthopyroxene has been well interpreted by Stangarone et al. (2016). The variation of the Raman

modes with Fe content are relevant to the vibrational frequency, v, of a simple harmonic

oscillator (Huang et al., 2000; Stangarone et al., 2016), which can be expressed as:

$$v = -\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{1}$$

where μ is the reduced mass, k is the force constant which is assumed to be an inverse function

of interatomic distance. Addition of Fe increases the reduced mass, u, and bond length of

orthopyroxene which explains the negative correlation of most Raman modes with Fe

substitution. When the Fe content in orthopyroxene is less than 50 mol.%, the Raman mode at

~400 cm^{-1} exhibits a similar trend with pressure to most other modes. Yet further elevating the

Fe content above 50 mol.% in orthopyroxene produces an enhanced reduction in the mode

frequencies. This may be due to different substitution mechanism in orthopyroxene by varying

the Fe content. Fe primarily occupies the M2 sites when the Fe content in orthopyroxene is less

than 50 mol.%, whereas it starts to substitute Mg in the M1 sites when the abundance is greater

than 50% (Domeneghetti et al., 1995; Domeneghetti et al., 1985; Proyer et al., 2004; Stangarone

et al., 2016; Stangarone et al., 2023). The correlation of Raman frequency with Fe content is thus

mainly related to the variation of atomic mass, volume and bond length caused by Fe substitutes

for Mg.

149

150 **4.2. Phase transition of orthopyroxene**

151 We have also plotted the wavenumber of β- and γ-phase as function of Fe content at 16 and 30

152 GPa, respectively (Figures S1-S2 in the supplemental material). The Raman shifts of the β- and

153 γ-phase generally exhibit a negative correlation with Fe substitution, similar to the α-phase.

154 Specifically, around ~1000 cm^{-1}, the Raman mode for the β-phase increases with Fe content. The

155 phase transition in orthopyroxene at 300 K was determined by the frequency discontinuities and

156 change in the pressure dependence of some modes at high pressures (Figures 3-6). We identify

157 the α- to β-phase transition to occur at 13.5 GPa for En_{100}, 12.9 GPa for $En_{91}Fs_9$, 15 GPa for

158 $En_{86}Fs_{11}$, and 15 GPa for $En_{74}Fs_{21}$ (Figure 7). Together with previous experimental results, our

159 experimental results have shown that the α-β phase transition pressure for Al-free orthopyroxene

160 with varying Fe content is lower than the corresponding Al-bearing phase. Transition from the α-

161 to β-phase for Al-free orthopyroxene with less than 60 mol.% Fe occurs between 10 and 13 GPa

162 (Dera et al., 2013; Finkelstein et al., 2015; Lin, 2004; Xu et al., 2020; Xu et al., 2018; Zhang et

163 al., 2013a; Zhang et al., 2013b). Further elevating the Fe content above 60% leads to a dramatic

164 decrease in the phase transition pressure (Dera et al., 2013; Xu et al., 2020). Addition of Al leads

165 to an increase in the α- to β-phase transition pressure. Orthopyroxene with 2-24 mol.% Al has a

166 phase transition to occur at 14-16 GPa (Xu et al., 2022; Zhang et al., 2013b). In contrast, $En_{91}Fs_9$

167 contained virtually no other trace elements, consistent with previous research results. The phase

168 boundary of the En_{100} sample was found to be higher than those reported in previous studies,

169 primarily due to the large pressure intervals used in earlier experiments (Lin, 2004; Xu et al.,

170 2020; Xu et al., 2018; Zhang et al., 2013b).

171

172   The change in the pressure dependence of Raman modes at ~29 GPa for all of our orthopyroxene

173   samples expect En_{100} is related to the β- to γ-phase transition (Figure 7). We observed that in

174   En_{100}, the Raman frequencies at around ~650 and ~1100 cm^{-1} have merged into a single mode,

175   each comprising three peaks. All the Raman modes above 31 GPa exhibit different pressure

176   dependence compared to modes between 14 and 30 GPa. This change in the Raman modes could

177   be related to the coordination number change of Si from 4 to 6 or the transition to α-popx phase

178   which have been reported by two previous experimental studies (Finkelstein et al., 2015;

179   Serghiou et al., 2000). Our experimental results indicate that the transition pressure from β- to γ-

180   phase are nearly independent of Fe when the Fe content in orthopyroxene is less than 60 mol.%.

181   Further increasing Fe content up to 82 mol.% leads to a substantial decrease in the phase

182   transition pressure (Dera et al., 2013; Xu et al., 2020). Once the Fe content in orthopyroxene is

183   above 80 mol.%, addition of Fe has minimum effect on the phase transition pressure to the γ-

184   phase. As a result, β-phase exists in a much narrow pressure range for orthopyroxene with 82-

185   100 mol.% than the corresponding phase with less than 82 mol.% Fe.

186

187   **4.3. Grüneisen parameters**

188   The obtained Raman frequency shifts allow us to derive the isothermal Grüneisen parameters at

189   high pressures. The isothermal Grüneisen parameter can be calculated as follows:

$$\gamma_i = -\frac{\partial \ln v_i}{\partial \ln V} = -\frac{V}{v_i}\frac{dv_i}{dV} = \frac{K_T}{v_i}\frac{dv_i}{dP} \qquad (2)$$

190   where v_i is the ith mode of the lattice vibration, V is the unit-cell volume, and K_T is the isothermal

191   bulk modulus at a given pressure. The values of v and dv/dP were derived by fitting the

192   experimental data using a polynomial function in this study. The influence of Fe on the bulk

193   modulus of α-orthopyroxene at ambient conditions, K_{T0}, was summarized in Figure 8 using

194 previous experimental results (Dera et al., 2013; Hovis et al., 2021; Hugh-Jones and Angel, 1997;

195 Jackson et al., 2003; Nestola et al., 2008; Xu et al., 2020; Xu et al., 2022; Xu et al., 2018; Zhang

196 et al., 2013a; Zhao et al., 1995). There is a strong trade-off between the bulk modulus K_{T0} and its

197 pressure derivative, K' determined from the X ray diffraction study. For α-orthopyroxene, the

198 value of K' is greater than general mantle minerals with values ranging between 7.5 and 8.5.

199 Here, we used an average K' of 8 and re-analyzed previous experimental results to constrain K_{T0}

200 and obtained (Figure 8):

201 $$K_{T0} (\text{α-phase}) = -0.05X_{Fe} + 109.80$$

202 Experimental constraints on the equation of state and elastic properties of both β- and γ-phase are

203 limited (Xu et al., 2020; Xu et al., 2022; Xu et al., 2018). We used fixed $K'=4$ to derive K_{T0}, and

204 the effect of Fe on K_{T0} is (Figure 8):

205 $$K_{T0} (\text{β-phase}) = 0.81X_{Fe} + 139.71$$

206 $$K_{T0} (\text{γ-phase}) = -0.01X_{Fe} + 131.71$$

207 Grüneisen parameters, γ, at high pressures for each Raman mode was calculated and shown in

208 Table S5 in the supplemental material. In general, there is not a very clear correlation between

209 changes in Fe content and the γ value (Figure 9). In the α-phase, an increase in Fe content to 11%

210 leads to a decrease in γ for mode v_{10}. Among the compositions, $En_{91}Fs_9$ exhibits a lower γ value

211 than the other three in the β-phase. In the γ-phase, there is no discernible trend in the γ value with

212 varying Fe content. For mode v_{24} and v_{32} in the α-phase, variations in Fe content have a

213 negligible influence on γ, considering calculation uncertainties. However, in both the β and γ-

214 phases, the relationship between changes in Fe content and the Grüneisen parameter remains

215 unclear.

216

IMPLICATIONS

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218   Orthopyroxene is an important mineral component of the mantle, but the β- and γ-phases of

219   metastable orthopyroxene that exist above 10 GPa can only be present in the cold subduction

220   zone harzburgite and lherzolite layers with temperatures 700-1000 K lower than the normal

221   mantle (Finkelstein et al., 2015; Ganguly et al., 2009). The significance of our study lies in the

222   detailed characterization of the effect of Fe content changes on the structural phase transition of

223   metastable orthopyroxene and the influence of the transitions on the Grüneisen parameter, which

224   can be directly applied to understand the effects of compositional changes on the sound velocity

225   and density structure of cold harzburgite and lherzolite layers in the subduction slab. Combined

226   with previous high-pressure research results, we observed that the effect of Fe content changes

227   from 0-80% on the α- to β-phase transition pressure of orthopyroxene is small, and the transition

228   mainly occurs from the bottom of the upper mantle to the top of the transition zone. For instance,

229   the α- to β-phase transition for orthopyroxene with 11% Fe has a small effect on the longitudinal

230   and transverse wave velocities, less than 2%, and a density change of about 2% (Li et al., 2022).

231   Additionally, the transition from metastable β-orthopyroxene to γ-phase occurs at pressures

232   exceeding 29 GPa. Therefore, the possibility of metastable γ-phase for orthopyroxene with less

233   than 20% Fe existing in the mantle is small from the 300-K experimental results. However, the

234   Clapeyron slope of the β-γ phase boundary remains unknown. Further high pressures and

235   temperatures experimental research is thus needed which is crucial for our understanding of the

236   density and sound velocity structure of subduction slabs in response to compositional changes.

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411   **FIGURE 1.** Typical Raman spectra of orthopyroxene at high pressures and 300 K. (a) En_{100}; (b)

412    $En_{91}Fs_9$; (c) $En_{86}Fs_{11}$; (d) $En_{74}Fs_{21}$. Blue ticks: Raman modes of α-orthopyroxene; red ticks:

413   Raman modes of β-orthopyroxene; orange ticks: Raman modes of γ-orthopyroxene.

414

415   **FIGURE 2.** Raman shifts of orthopyroxene with different Fe content at ambient conditions.

416   Solid circles: this study; open circles: previous experimental results (Chopelas, 1999; Huang et

417   al., 2000). Red lines: fitting results.

418

419   **FIGURE 3.** Raman shifts of En_{100} at high pressures and 300 K. Blue: α-orthopyroxene; red: β-

420   orthopyroxene; orange: γ-orthopyroxene.

421

422   **FIGURE 4.** Raman shifts of $En_{91}Fs_9$ at high pressures and 300 K. Blue: α-orthopyroxene; red: β-

423   orthopyroxene; orange: γ-orthopyroxene; circles and diamonds represent different experimental

424   runs.

425

426   **FIGURE 5.** Raman shifts of $En_{86}Fs_{11}$ at high pressures and 300 K. Blue: α-orthopyroxene; red:

427   β-orthopyroxene; orange: γ-orthopyroxene; circles and diamonds represent different

428   experimental runs.

429

430   **FIGURE 6.** Raman shifts of $En_{74}Fs_{21}$ at high pressures and 300 K. Blue: α-orthopyroxene; red:

431   β-orthopyroxene; orange: γ-orthopyroxene; circles and diamonds represent different

432   experimental runs.

433

434   **FIGURE 7.** Phase diagram of orthopyroxene at high pressures. Red: this study; green: (Lin,

435   2004); pink: (Zhang et al., 2013b); gray: (Zhang et al., 2013a); yellow: (Dera et al., 2013);

436   purple: (Finkelstein et al., 2015); blue: (Xu et al., 2018); orange: (Xu et al., 2020); black: (Xu et

437   al., 2022); circle: Fe-bearing orthopyroxene; diamond: Fe- and Al-bearing orthopyroxene; solid

438   lines: phase boundary for the Al-free orthopyroxene; dash line: phase boundary for the Al-

439   bearing orthopyroxene. The subscript in Al on the figure shows the Al content in orthopyroxene:

440   Al/(Mg+Fe+Al).

441

442   **FIGURE 8.** Unit cell volume (V_0) and isothermal bulk modulus (K_{T0}) of orthopyroxene at

443   ambient conditions. (a) V_0 for α-orthopyroxene; (b) V_0 for β-orthopyroxene; (c) V_0 for γ-

444   orthopyroxene; (d) K_{T0} for α-orthopyroxene; (e) K_{T0} for β-orthopyroxene; (f) K_{T0} for γ-

445   orthopyroxene; We reanalyzed the pressure-volume data in literature with fixed $K_{T0}' = 8$ for α-

446   orthopyroxene (Dera et al., 2013; Hovis et al., 2021; Hugh‐Jones and Angel, 1997; Nestola et

447   al., 2008; Xu et al., 2020; Xu et al., 2022; Xu et al., 2018; Zhang et al., 2013a). For both β- and

448   γ-phase, with fixed $K_{T0}' = 4$, V_0 and K_{T0} are from previous experimental studies (Xu et al., 2020;

449   Xu et al., 2022; Xu et al., 2018).

450

451 **FIGURE 9.** Grüneisen parameter of orthopyroxene at high pressures. (a) v_1; (b) v_{10}; (c) v_{24}; (d)

452 v_{32}. Blue: En_{100}; red: $En_{91}Fs_9$; orange: $En_{86}Fs_{11}$; black: $En_{74}Fs_{21}$. The data are calculated using the

453 single experimental Raman-active mode in this study together with data summarized in Figure 8,

454 Table S5. Calculated uncertainties are shown as vertical ticks on the bottom left.

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460   **TABLE 1.** Regression constants of En_{100} for Raman modes determined in $\Delta v = v_0 + aP$ at high

461   pressures and 300 K.

		α-orthopyroxene			β-orthopyroxene			γ-orthopyroxene		
	v_i	v_0	a	R^2	v_0	a	R^2	v_0	a	R^2
v1	237.9	239.2	1.34	0.985	241.5	0.95	0.987	253.4	0.35	1.000
v2								301.3	0.54	1.000
v3	279.0	282.1	2.04	0.963	304.1	1.40	0.994	279.9	1.83	1.000
v4	302.4	302.0	2.45	0.984	315.6	1.82	0.997	342.2	0.83	1.000
v5								348.8	1.33	1.000
v6										
v7								398.9	0.62	1.000
v8					364.4	2.42	0.983			
v9										
v10	345.4	348.5	4.99	0.994	376.9	2.60	0.992	397.7	1.79	1.000
v11	385.6	385.1	3.16	0.992						
v12	403.0	405.3	3.43	0.986	433.9	1.20	0.970			
v13	421.1	423.2	2.15	0.977	410.8	2.86	0.932			
v14					439.4	2.07	0.979			
v15	446.2	446.4	2.27	0.999	447.1	2.22	0.997	490.2	0.92	1.000
v16								492.3	1.25	1.000
v17								515.1	1.13	1.000
v18					442.0	3.84	0.987	517.3	1.54	1.000
v19	524.4	523.6	2.69	0.995						
v20	540.3	539.8	1.77	0.954						
v21	551.0	551.3	2.66	0.994						
v22	579.9	579.9								
v23	663.8	664.2	3.34	1.000	663.0	3.10	0.998			
v24	686.5	687.3	3.08	0.999	678.4	2.94	0.997	718.0	1.83	1.000
v25					691.9	3.33	0.998			
v26	753.3	753.3								
v27					825.2	2.43	0.994	856.4	1.46	1.000
v28	853.7	847.6	2.11	0.914	844.5	3.44	0.994	881.3	1.46	1.000
v29	933.8	933.0	2.40	0.831						
v30										
v31					1016.5	3.32	0.995			
v32	1011.8	1013.5	5.22	0.998	1029.3	3.83	0.990	1102.2	0.75	1.000
v33	1033.3	1035.0	4.77	0.998	1041.2	4.14	0.993			

462   v_i, v_0, and Δv are in cm^{-1}, P in GPa, and the constant, a has the corresponding units. v_i is the frequency measured at

463   ambient conditions. R^2 is the correlation coefficient.

464

465 **TABLE 2.** Regression constants of $En_{91}Fs_9$ for Raman modes determined in $\Delta v = v_0 + aP$ at high
466 pressures and 300 K.

	v_i	α-orthopyroxene			β-orthopyroxene			γ-orthopyroxene		
		v_0	a	R^2	v_0	a	R^2	v_0	a	R^2
v1	236.9	239.5	1.14	0.961	234.6	1.38	0.980	245.6	0.87	0.702
v2								256.7	1.15	0.884
v3		288.8	1.20	0.894	289.9	0.83	0.302	291.7	0.72	0.600
v4	301.3	302.0	1.67	0.858	303.8	1.38	0.964			
v5					316.6	1.98	0.992	339.2	1.11	0.767
v6										
v7										
v8					384.7	1.43	0.909	389.8	1.23	0.654
v9								428.9	0.38	0.846
v10	341.4	348.2	4.83	0.963	381.4	2.40	0.963	427.6	0.83	0.868
v11	378.9	376.5	4.11	0.984						
v12	400.8	405.8	3.58	0.948	435.2	1.23	0.870	442.7	0.90	0.646
v13	416.9	417.0	2.40	0.985	404.7	3.60	0.962	505.6	0.05	0.005
v14										
v15	442.4	442.7	2.74	0.996	442.5	2.67	0.983	501.6	0.77	0.598
v16										
v17										
v18					441.7	4.05	0.968	541.9	0.59	0.081
v19	525.8	524.3	2.82	0.955	518.2	3.36	0.988	545.6	2.24	0.941
v20	539.0	540.0	1.78	0.944	525.9	3.59	0.980	548.6	2.54	0.982
v21	549.4	549.9	3.17	0.984						
v22										
v23	663.1	664.1	3.28	0.995						
v24	684.5	686.9	2.99	0.978	683.6	2.84	0.981	751.4	0.65	0.613
v25					696.2	3.38	0.993	774.7	0.73	0.565
v26	750.8	751.0	3.59	0.996	732.7	3.58	0.990			
v27					819.7	2.75	0.994	886.4	0.59	0.437
v28	858.1	851.8	2.92	0.964	848.8	3.94	0.990	901.1	2.03	0.759
v29	937.7	930.0	3.41	0.972	941.9	2.52	0.981	976.4	1.15	0.786
v30		938.3	6.34	0.965						
v31										
v32	1011.2	1016.1	3.79	0.981	1020.4	3.64	0.990	1068.1	1.86	0.806
v33	1028.9	1032.7	4.89	0.991	1043.6	4.11	0.988	1087.7	2.35	0.815

467
468 v_i, v_0, and Δv are in cm^{-1}, P in GPa, and the constant, a has the corresponding units. v_i is the frequency measured at
469 ambient conditions. R^2 is the correlation coefficient.
470

471 **TABLE 3.** Regression constants of $En_{86}Fs_{11}$ for Raman modes determined in $\Delta v = v_0 + aP$ at
472 high pressures and 300 K.

		α-orthopyroxene			β-orthopyroxene			γ-orthopyroxene		
	v_i	v_0	a	R^2	v_0	a	R^2	v_0	a	R^2
v1	236.0	240.8	0.90	0.814	237.1	0.93	0.955	251.1	0.33	0.411
v2					292.4	0.14	0.409	301.3	-0.11	0.601
v3		288.4	0.99	0.955	295.7	0.53	0.658	325.1	-0.32	0.638
v4	297.3	297.2	1.51	0.938	288.8	1.90	0.959	328.4	0.25	0.644
v5					315.6	1.63	0.947	339.5	0.80	0.853
v6	321.7	324.0	3.27	0.991						
v7										
v8					370.7	1.85	0.896	394.0	1.04	0.757
v9										
v10	340.8	347.2	4.37	0.985	367.9	2.85	0.918	432.5	0.56	0.664
v11	380.6	379.7	3.25	0.986						
v12	399.6	399.6	4.27	0.952	414.9	1.67	0.964	446.6	0.62	0.688
v13	414.4	411.9	2.41	0.960	427.4	1.61	0.345			
v14										
v15	441.6	441.4	2.44	0.981	449.5	1.81	0.932			
v16										
v17								492.6	1.39	0.835
v18	465.1	464.7	2.80	0.986	450.0	3.34	0.957			
v19	521.8	522.2	2.50	0.986	544.5	0.65	0.208			
v20	538.6	537.4	1.58	0.973	537.5	2.21	0.980			
v21	549.5	548.6	2.50	0.995						
v22		575.6	1.95	0.998						
v23	662.2	663.0	3.16	0.998						
v24	683.8	685.3	2.93	0.996	665.3	3.48	0.961	731.3	1.03	0.723
v25					678.5	3.78	0.902	736.2	1.57	0.870
v26										
v27					834.1	2.16	0.834	864.9	1.31	0.651
v28	857.7	850.2	2.18	0.951	833.5	3.89	0.965	903.4	1.42	0.657
v29	936.0	932.2	3.41	0.979	937.7	2.79	0.804	1055.5	-1.02	0.779
v30	938.2	940.9	4.73	0.986						
v31					1005.5	3.83	0.947	1122.6	-0.28	0.685
v32	1009.8	1011.9	5.15	0.993	1026.4	3.86	0.931	1127.7	0.43	0.892
v33	1029.8	1030.5	4.86	0.997	1041.5	3.98	0.902	1172.0	-0.19	0.732

473

474 v_i, v_0, and Δv are in cm^{-1}, P in GPa, and the constant, a has the corresponding units. v_i is the frequency measured at
475 ambient conditions. R^2 is the correlation coefficient.

476

477 **TABLE 4.** Regression constants of $En_{74}Fs_{21}$ for Raman modes determined in $\Delta v = v_0 + aP$ at
478 high pressures and 300 K.

	v_i	α-orthopyroxene			β-orthopyroxene			γ-orthopyroxene		
		v_0	a	R^2	v_0	a	R^2	v_0	a	R^2
v1	231.6	236.1	1.11	0.940	232.44	1.23	0.963	239.0	0.94	0.937
v2										
v3										
v4	294.7	292.9	1.66	0.930						
v5										
v6	312.3	309.8	4.18	0.966						
v7										
v8					373.58	1.61	0.942	313.0	3.52	0.792
v9										
v10	337.4	346.5	4.02	0.973	363.59	2.76	0.981	307.7	4.45	0.877
v11	371.2	366.5	2.69	0.952						
v12	397.6	401.6	3.18	0.981	430.78	0.95	0.790			
v13					411.58	2.58	0.920			
v14										
v15		436.7	2.66	0.967	447.98	1.77	0.937	507.5	0.02	0.801
v16										
v17										
v18										
v19	517.9	517.8	2.69	0.987	481.42	5.10	0.981			
v20	532.0	531.8	1.97	0.966	484.84	5.30	0.988	630.3	0.20	0.777
v21	543.9	545.2	2.82	0.982						
v22		570.9	3.72	0.988	589.48	2.32	0.943	650.2	0.51	0.417
v23	656.7	658.7	3.16	0.986	655.50	3.15	0.997			
v24	678.8	682.1	3.01	0.989	684.93	2.46	0.929	770.7	-0.16	0.827
v25					698.81	2.81	0.951	804.4	-0.45	0.719
v26	748.5	749.2	3.05	0.991						
v27					830.74	2.54	0.970	849.8	2.03	0.691
v28	850.7	848.9	2.97	0.963	819.66	4.77	0.980			
v29	936.3	937.3	2.98	0.940	945.05	2.73	0.944			
v30		952.2	3.61	0.994						
v31										
v32	1002.6	1007.6	5.02	0.995	1005.46	3.65	0.964	1095.3	0.76	0.670
v33	1020.1	1028.4	4.16	0.974	1021.91	4.29	0.962	1119.7	1.06	0.662

479

480 v_i, v_0, and Δv are in cm^{-1}, P in GPa, and the constant, a has the corresponding units. v_i is the frequency measured at
481 ambient conditions. R^2 is the correlation coefficient.
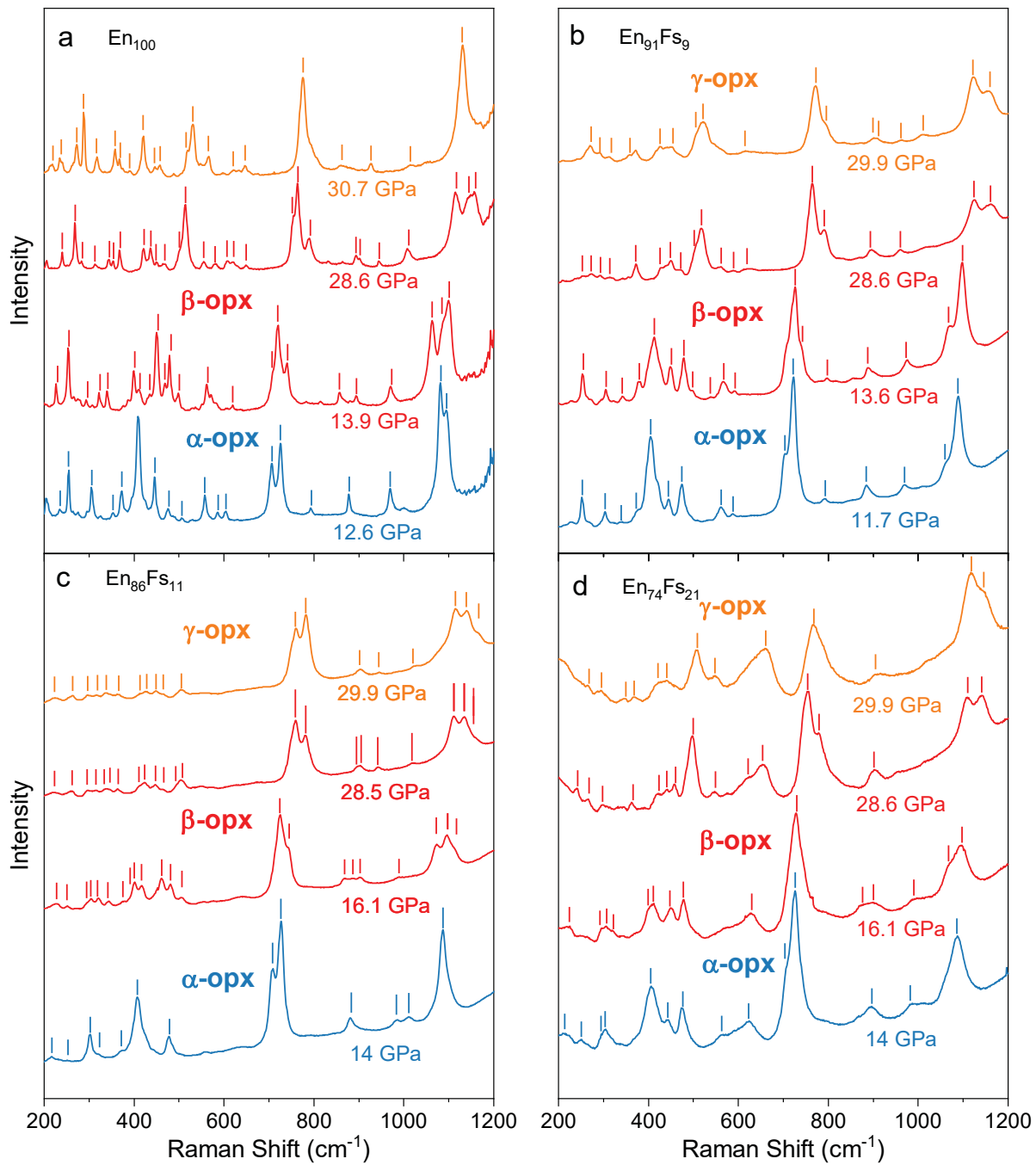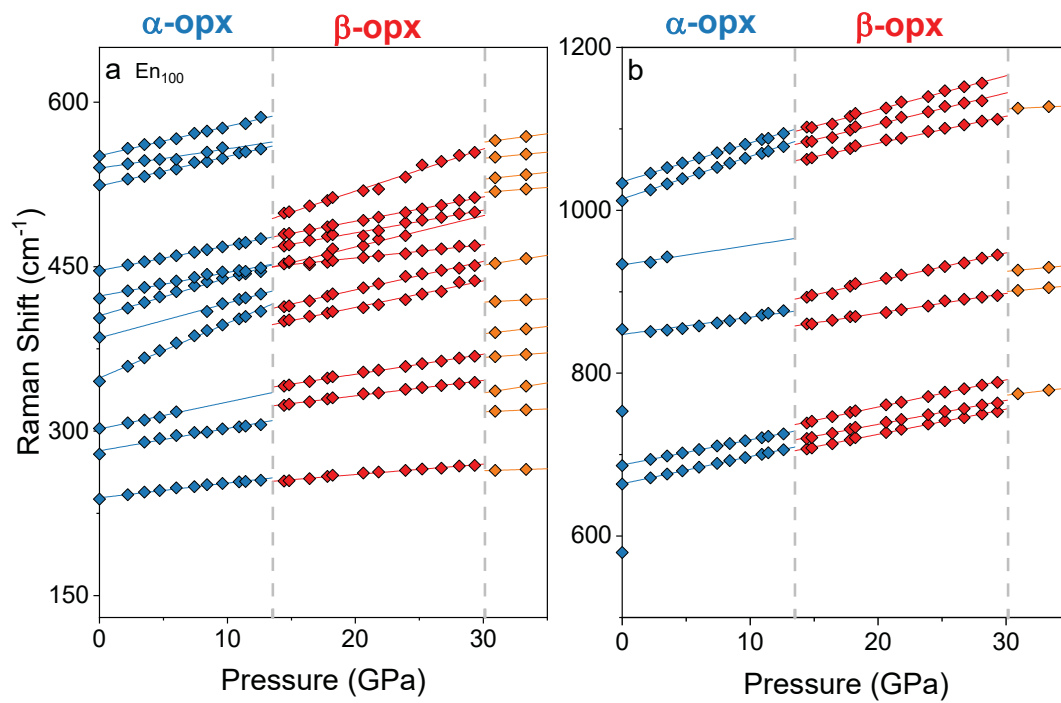
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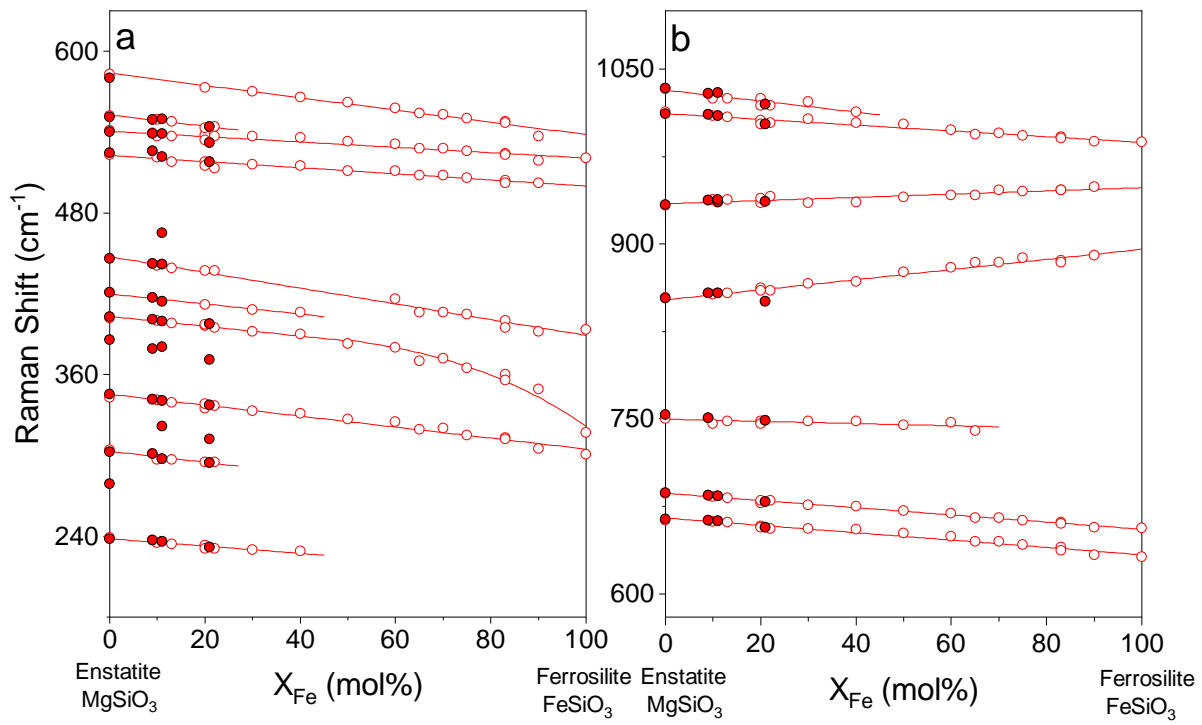
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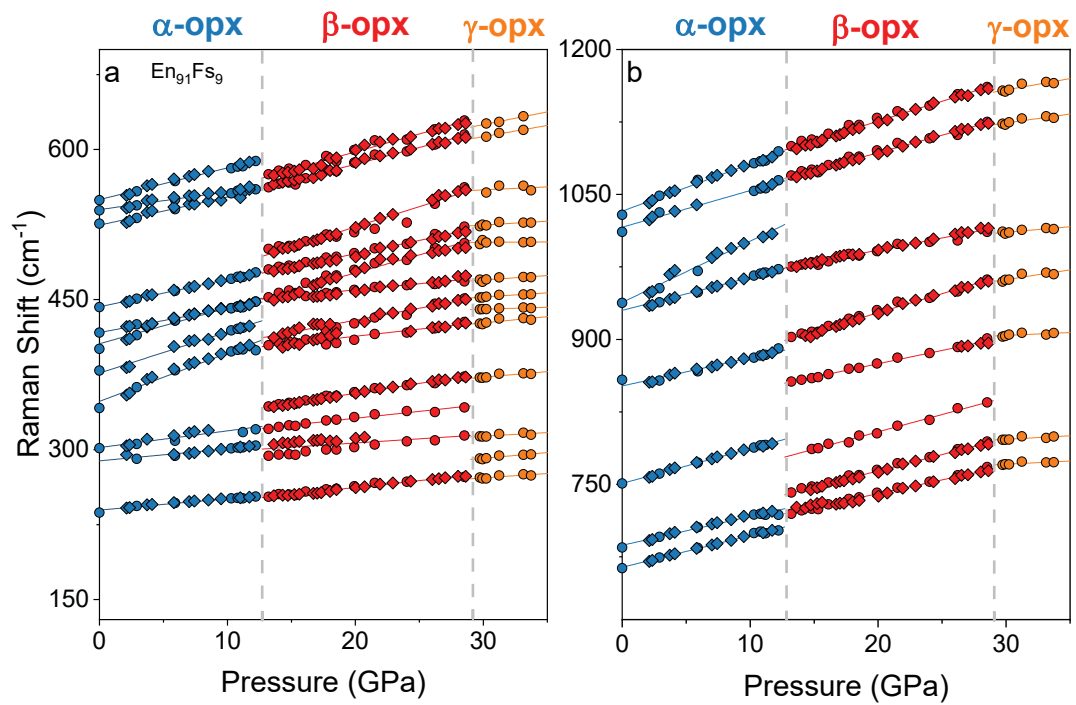
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