1   **Revision 1**

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3   ***In situ* observation of the pyroxene-majorite transition in Na$_2$MgSi$_5$O$_{12}$ using**

4   **synchrotron radiation and Raman spectroscopy of Na-majorite**

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14   **Abstract**

15   In situ X-ray diffraction study of the pyroxene to majorite transition in Na$_2$MgSi$_5$O$_{12}$ was

16   carried out in Kawai-type high-pressure apparatus coupled with synchrotron radiation. The phase

17   boundary between Na-pyroxene and Na-majorite was determined over the temperature interval

18   of 1073–1973 K and was described by a linear equation P (GPa) = 12.39 + 0.0018×T (K). The

19   Clapeyron slope (dP/dT) determined in this study is similar to the one predicted by computer

20   simulations (Vinograd et al., 2011) but smoother than the one obtained by quenched experiments

21   (Dymshits et al., 2010). The presence of sodium in the system lowers the pressure of pyroxene-

22   to-majorite transformation. For the first time Na-majorite was characterized using Raman

23   spectroscopy. Raman peaks of Na-majorite are broader than pyrope due to the substitution of

24   Mg^{2+} for Na$^+$ at the X site. Both Si-O symmetric stretching (A_{1g}-ν$_1$) and O-Si-O symmetric

25   bending (A_{1g}-ν$_2$) modes of Na-majorite are significantly shifted to higher frequencies relative to

26   corresponding bands of pyrope. In contrast the A_{1g}-R (SiO$_4$) mode of Na-majorite (342 cm^{-1})

27   displays a lower frequency than that of pyrope (365 cm^{-1}). Obtained results enable further

28   understanding of mechanisms responsible for phase transformations in the Earth's transition

29   zone and lower mantle.

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30   **Keywords** Na-pyroxene, Na-majorite, Phase transition, *In situ* Experiment, Diamond, Mantle

31   **Introduction**

32   An important mechanism for phase transformation of silicate minerals in the Earth's

33   mantle is the change of Si coordination from four (tetrahedral) to six (octahedral) with an

34   increase in pressure. The particular interest of this change is the formation of mixed-coordination

35   phases with Si substitution cations in the octahedral position. Pyroxene with the composition of

36    $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ (Na-px) was first obtained by Angel et al. (1988) and contained Si in

37   tetrahedral and octahedral positions. A high-pressure analogue of Na-px with a denser structure

38   was originally proposed by Gasparik (1989) as Na-majorite (Na-maj), $(Na_2MgSi_2(SiO_4)$.

39   Garnets with significant sodium concentration (> 1 wt.% Na_2O) have been found as

40   inclusions in diamonds and mantle xenoliths in many locations worldwide (e.g., Kiseeva et al.,

41   2013; Shatskii et al., 2010; Sobolev et al., 1991; Sobolev and Lavrent'ev, 1971; Sobolev et al.,

42   2004; Stachel, 2001). Rarely found in peridotitic paragenesis, Na-rich garnets are quite common

43   for eclogitic assemblage (Fig. 1). Figure 1 shows a clear correlation between Na and Si contents

44   in eclogitic garnets, which is the evidence of Na-maj incorporation into the garnet structure.

45   Sobolev and Lavrent'ev (1971) first supposed that pressure controls Na admixture in the

46   dodecahedral positions of garnet, and that Na in dodecahedral sites is connected to a silicon

47   excess in octahedral site. Later, this pressure dependence was confirmed experimentally in

48   model and natural eclogitic systems (Bobrov et al., 2009; Dymshits et al., 2013; Hirose and Fei,

49   2002; Litasov and Ohtani, 2005; Okamoto and Maruyama, 2004). Therefore, revealed pressure

50   dependence of Na-maj content in garnet may be taken into account in the calculation of

51   geobarometers for sodium bearing garnet assemblages.

52   Increasing interest in Na-maj and Na-px is related to a growing number of reports of

53   sodium-bearing mineral inclusions from a "super-deep" diamonds (e.g., Harte and Hudson, 2013;

54   Plá Cid et al., 2014). An unusual mineral inclusion with garnet structure and composition (16

55   mol. % Na-maj and 84 mol. % majorite (Maj) $Mg_4Si_4O_{12}$) was found in diamond from Liaoning

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56 province, China (Gasparik and Hutchison, 2000; Wang and Sueno, 1996). First attempts to

57 estimate the pressure of this inclusion on the basis of pyroxene–majorite transition was made by

58 Gasparik and Hutchison (2000). According to their experiment, pyroxene with such composition

59 transforms into garnet at a minimum pressure of 16.5 GPa and temperature of 1923 K that

60 corresponds to mantle transition zone (MTZ). Recently, Piá Cid et al. (2014) found unusual

61 mineral inclusion containing 40 mol. % Na-maj in the diamond from Juina province, Brazil. The

62 formation pressure of such alkali-rich inclusion can be estimated based on Na-px–Na-maj

63 transition.

64   The Na-px–Na-maj phase boundary was investigated by static high-pressure experiments

65 using quenching method (Dymshits et al., 2010) and *ab initio* computations (Vinograd et al.,

66 2011). Experimentally estimated value of dP/dT for this transition has five times more positive

67 slope (5.0 MPa/K) than the value determined from the numerical simulations (1.0 MPa/K).

68   In this study, we established the phase boundary of Na-px–Na-maj transition by *in situ* X-

69 ray diffraction experiments using pressure scale for Au (Dorogokupets and Dewaele, 2007) and

70 investigated the effect of Na on pyroxene–majorite transition at the mantle conditions.

71 Additionally, this is the first report of Na-maj structure by Raman spectroscopy.

Experimental methods

73   We conducted three *in situ* X-ray diffraction experiments. Runs #P187 and #P210 were

74 carried out at the Photon Factory (Tsukuba, Japan) using a 700-tons Kawai-type multi-anvil

75 apparatus "MAX-III" installed at a bending magnet beam line NE7A. We used 22 mm WC

76 anvils (Tungaloy F-grade) with a truncated edge length of 3.5 mm. Run #S2683 was conducted

77 at SPring-8 synchrotron radiation facility (Hyogo, Japan) using a Kawai-type multi-anvil

78 apparatus 'SPEED-1500' installed at a bending magnet beam line BL04B1. The high-pressure

79 systems are combined with a synchrotron radiation source and the energy-dispersive X-ray

80 diffraction system. In details the experimental techniques are explained in Litasov et al. (2013).

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81   Experimental starting materials were prepared using the nitrate gelling method (Hamilton

82   and Henderson, 1968) with Au admixture used as a pressure marker. As starting material the

83   mixture of $Na_2MgSi_5O_{12} + 3SiO_2$ was used. Excess silica did not change the phase relations and

84   was used for simultaneous studies of stishovite equation of state (EoS). Experimental assembly

85   was essentially the same with that used in Dymshits et al. (2014). An octahedron of ZrO_2 with

86   MgO-insert (for X-ray transparency) was used as a pressure medium. A sample enclosed in a BN

87   capsule was placed in a cylindrical lanthanum chromite heater. Temperature was monitored by a

88      $W_{97\%}Re_{3\%}$- $W_{75\%}Re_{3\%}$ thermocouple with a junction located at nearly the same position as where

89   the X-ray path through the sample. This allowed to minimize the effect on temperature gradient

90   across the sample chamber.

91   Experimental pressures at high temperatures were calculated from the unit cell volume of

92   Au using the EOS from Dorogokupets and Dewaele (2007). The uncertainties of unit cell volume

93   of Au, determined by a least-square method, are typically less than 0.1 GPa uncertainty in

94   pressure. Refinement of peaks positions and determination of the unit cell parameters were

95   achieved using the XRayAnalysis software provided by the BL04B1 beam line. Typically 4–5

96   diffraction lines of Au [(111), (200), (220), (311), and (222)] were used to calculate the pressure.

97   Recovered samples were examined with an electron microprobe (JEOL Superprobe JXA-

98   8800) at Tohoku University. Acceleration voltage of 15 kV and 10 nA specimen current were

99   used for an analysis. The average composition of the obtained phases (wt %, SiO_2 74.8; MgO 9.8;

100   Na_2O 14.8; formula $Na_{0.966}Mg_{0.492}Si_{2.512}O_6$) was quite close to ideal Na-px.

101   Raman spectroscopy measurements were performed using a Horiba Jobin Yvon Lab

102   RAM HR800 Raman microspectrometer with the 514 nm line of Ar-ion laser and Olympus

103   BX41 microscope at IGM SB RAS (Novosibirsk, Russia). Olympus MPlan 100×/0.90 ∞/0/FN22

104   objective was used to focus the laser beam onto the sample and to collect Raman signal. Spectra

105   were recorded at room temperature in backscattering geometry with the laser power of about 40

106   mW and spectral resolution of approximately 2 cm^{-1}. Spectra were calibrated using the 520.6 cm^{-}

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107   ^{1} line of a silicon wafer. We also examined pyrope (Prp)–Na-maj solid solutions with

108   composition $(Na_{0.72}Mg_{2.28})(Al_{1.28}Si_{0.72})Si_3O_{12}$ ($Prp_{64}Na$-maj_{36}) synthesized at 20 GPa and 2373

109   K.

110   **Results**

111   In the run #S2683, the sample was first compressed up to 14.3 GPa, and then temperature

112   was increased. At 1273 K and 14.4 GPa peaks of Na-px and stishovite appeared (Fig. 2a). Then

113   we increased the temperature to 1473 K, which caused simultaneous pressure increase to 15.4

114   GPa. No significant changes in the diffraction pattern were detected (Fig. 2b). However, during

115   exposure at the constant temperature new peaks of Na-maj have appeared (Fig. 2c). After 10 min

116   annealing the Na-px peaks disappeared completely. No significant changes were observed by the

117   further temperature increase to 1673 K and simultaneous pressure increase to 16.2 GPa (Fig. 3).

118   Then we decreased press load at the constant temperature of 1673 K. At 1673 K and 15.5 GPa,

119   Na-maj still remained, while at 1673 and 15.0 GPa the peaks of Na-px have appeared (Fig. 3c).

120   After repeated the cycle of changing the *P-T* conditions two another forward and backward

121   transformations were observed (Table 1). It is important to note that stishovite has crystallized at

122   the very beginning of the experiment due to the SiO_2 admixture in the starting material.

123   Stishovite peaks were observed during all experimental period at the all diffractions. The

124   intensities of peaks did not changed during obtained forward and backward transformations (Fig.

125   2 and 3) so it is reasonable to suggest that stishovite does not react either with Na-maj or with

126   Na-px.

127   In the run #P187 we compressed sample to 14.6 GPa and then heated it to 1273 K. At

128   1273 K and 14.8 GPa peaks of Na-maj were recognized. Further temperature increase to 1473 K

129   caused appearance of Na-px peaks at 14.4 GPa. This means that the stability of Na-maj ranges

130   between 14.8 GPa and 14.4 GPa transforming into Na-px at lower lower pressures.

131   In the run #P210, sample was compressed to 19.4 GPa at room temperature and then

132   heated to 1273 K. During heating pressure dropped to 15.9 GPa. At these conditions Na-maj was

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133   observed. No significant changes occurred with further temperature and pressure increase to

134   1973 K and 17.6 GPa. Then we maintained temperature at 1973 K and gradually decreased press

135   load. The Na-px peaks appeared at 15.1 GPa. To observe reverse transformation we decreased

136   temperature to 1773 K, where only peaks of Na-px were observed at 14.3 GPa. With increasing

137   pressure the Na-maj peaks appeared at 16.6 GPa. The results of this run suggest that

138   transformation from Na-maj to Na-px occurs at 1973 K and 15.1 GPa and the reverse

139   transformation occurs at 1773 GPa and 16.0 GPa.

140   In this study we changed P-T conditions several times during each run while observing

141   forward and backward transformation between Na-px and Na-maj. The results are plotted on the

142   P-T diagram in Fig. 4. It is known that the phase transformations in such heating cycles are

143   influenced by sluggish kinetics near the phase boundary in equilibrium phase, especially at lower

144   temperatures. The critical data points that constrain the phase boundary in present work were

145   obtained at relatively high temperatures: 14.4 GPa and 1273 K, and 15.0 GPa and 1653 K (Na-px

146   stability field), and 14.8 GPa and 1273 K, and 16.0 GPa and 1773 K (Na-maj stability field). On

147   Based on the positions of the critical points, we determined two limited boundaries were

148   determined (Fig. 4a). The first dashed line corresponds to the lowest pressures of Na-maj

149   stability and Na-maj + Na-px growth. The second dashed line corresponds to the upper value of

150   Na-px stability and Na-px + Na-maj growth. Crossing of the lower and upper boundaries

151   matches to the average value of phase transition from Na-px to Na-maj. The phase boundary

152   between Na-px and Na-maj can be expressed by linear relationship P (GPa) = 12.39 + 0.0018×T

153   (K). The Clapeyron slope can be between 0.5 and 3.2 MPa/K with the average near 1.8 MPa/K.

154   Due to their little effect on the boundary position, in these estimations the uncertainties of

155   pressure and temperature were not taken into account.

156   The Raman spectrum of Na-px is almost identical to that reported by Yang et al. (2009b)

157   (Fig. 5). Comparison of the Raman spectrum of Na-maj and Prp from the RRUFF database

158   (http://rruff.info/R080060) and Li-majorite (Li-maj), $(Li_2Mg)Si_2(SiO_4)_3$ (Yang et al., 2009a) is

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159   shown in Figure 6. Based on previous studies on Prp, majoritic garnets and other silicate garnets

160   (Hofmeister and Chopelas, 1991; Hofmeister et al., 2004; Yang et al., 2009a) we made

161   assignments of observed Raman modes for Na-maj (Table 2) grouped into three distinct regions:

162   the bands in the high (850-1200 cm^{-1}) and middle-frequency (500-850 cm^{-1}) regions are

163   attributed to internal modes of the SiO_4 unit, whereas the bands in the low-frequency (150-450

164   cm^{-1}) region include the rotational or translational modes of SiO_4 tetrahedra, as well as the X-

165   cation motions. Basically, Li-maj and Na-maj have similar Raman patterns (Fig. 6), and thus

166   they may be considered as analogues, even though Li-maj is cubic with space group $Ia\overline{3}d$

167   (Yang et al., 2009a) while Na-maj is tetragonal with space group $I4_1/acd$ (Bindi et al., 2011).

168   Additionally Na-maj spectrum has well attended O-Si-O asymmetric bending (T_{2g}-v_4) mode (827

169   cm^{-1}) typical for tetragonal majoritic garnets (Hofmeister et al., 2004). Raman peaks of Na-maj

170   and Li-maj are broader than those of Prp, due to the local structural heterogeneities or atomic

171   positional disorder caused by the size and charge differences between Mg^{2+} and Na^+ or Li^+ at the

172   X site. Both Si-O symmetric stretching (A_{1g}-v_1) and O-Si-O symmetric bending (A_{1g}-v_2) modes

173   of Na-maj significantly shift to higher frequencies relative to the corresponding bands of Prp and

174   a lower frequencies relative to the corresponding bands of Li-maj. In contrast A_{1g}-R (SiO_4) mode

175   of Na-maj (342 cm^{-1}) displays a lower frequency than mode of Prp (365 cm^{-1}) and a higher

176   frequency than mode of Li-maj (316 cm^{-1}).

177   To obtain how Raman spectra of Prp–Na-maj solid solutions change with increasing Na-

178   maj content we compared Prp, Na-maj$_{36}$Prp$_{64}$ and Na-maj spectra (Fig.6). With increasing

179   amount of Na-maj the A_{1g}-v_1 and A_{1g}-v_2 the modes of garnets shift to the higher frequencies.

180   Similar modes shift to the higher frequencies were also observed by Hofmeister et al. (2004) for

181   Prp–Maj solid solutions when garnet becomes more majoritic. In contrast the frequency of the

182   A_{1g}-R(SiO_4) mode is gradually reduced with increasing Na-maj content. The additional mode at a

183   frequency of 825 cm^{-1} is observed in the garnet with composition Prp$_{64}$Na-maj$_{36}$ similar for

184   tetragonal Prp-Maj garnets with more than of 39 mol. % Maj (Hofmeister et al., 2004). This

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185   feature may indicate a transition from the cubic to tetragonal symmetry in Prp–Na-maj solid

186   solutions already at 36 mol.% Na-maj. However, using X-ray diffraction Bindi et al. (2011)

187   showed that in the system Prp–Na-maj garnet transforms from the cubic to tetragonal structure at

188   60-80 mol.% of Na-maj.

189   **Discussion**

190   Comparison of results from this and previous studies is shown in Fig. 4. Our results are in

191   a good agreement with *ab initio* calculations made by Vinograd et al. (2011). Close consistency

192   of numerical study and *in situ* experiments allows further theoretical works for prediction of

193   mixing thermodynamic properties for silicates and in particular for garnets of a broader

194   compositional range.

195   The obtained dP/dT of phase boundary is twice lower than that determined from quench

196   experiments (Dymshits et al., 2010), where pressure was calibrated at room temperature based

197   on changes in electrical resistance in Bi, ZnS and at high temperature based on graphite–

198   diamond transition. Dymshits et al. (2010) fitted phase boundary by linear equation P(GPa) =

199   6.14 + 0.0050×T (K). On the other hand, inspection of original experimental data of Dymshits et

200   al. (2010) demonstrates that the critical points are consistent with the linear relationship obtained

201   by *in situ* experiments.

202   Phase transition from pyroxene to majorite in $Na_2MgSi_5O_{12}$ system occurs at lower

203   pressures relative to $MgSiO_3$ system (Fig. 4c). Sawamoto (1987) obtained the positive slope of

204   the pyroxene–majorite transition in $MgSiO_3$ system whereas Presnall and Gasparik (1990) found

205   the negative slope. In both studies pressure calibration at high temperature was done on the basis

206   of the coesite–stishovite transition. Thermodynamically calculated boundary (Yusa et al., 1993)

207   is consistent with the slope suggested by Presnall and Gasparik (1990). Comparing our results

208   with $MgSiO_3$ system demonstrated that adding Na in the system lowers the pressure of

209   pyroxene–majorite transformation from 0.8 to 1.3 GPa (Presnall and Gasparik, 1990; Yusa et al.,

210   1993) and 1.2 GPa (Sawamoto, 1987) at ambient mantle temperature (Fig. 4c). In hot mantle

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211   (e.g., Iceland plume geotherm) the difference between our boundary and the one obtained by

212   Presnall and Gasparik (1990) is 0.5 GPa (Fig. 4c). Maj is a high-temperature phase in $MgSiO_3$

213   system. At the temperature lower than 1873–1923 K (at ~17 GPa) it transforms to the beta phase

214   of Mg_2SiO_4 + stishovite (e.g. Yusa et al., 1993). In case of $Na_2MgSi_5O_{12}$ system Na-maj is stable

215   over the entire temperature range.

216   The composition of sodium-rich garnet inclusion from Chinese diamond is closer to Maj

217   composition (Gasparik and Hutchison, 2000; Wang and Sueno, 1996). Gasparik and Hutchison

218   (2000) assumed that the value of pressure formation for this garnet inclusion would be the same

219   as for pure Maj and corresponds to 16.5 GPa. Real pressure of this garnet inclusion containing

220   18 mol.% Na-maj would be between the Na-maj and Maj boundaries. The minimum pressure of

221   Na-maj formation is 15.5 GPa according to our phase boundary that is also corresponds to MTZ.

222   Recently, Piá Cid et al. (2014) described extremely Na- and Si-rich mineral inclusion in

223   Brazilian diamond which composition corresponds to either pyroxene or garnet stoichiometry

224   with the highest possible Si excess. Thus, the formation pressure of this inclusions can be

225   estimated based on Na-px–Na-maj transition. Unfortunately, Piá Cid et al. (2014) did not

226   determined the structure of this phase. In case of garnet structure such inclusion would originated

227   at least in MTZ. It is important to identify whether garnet or pyroxene was detected. The

228   problem of structural diagnostic for mineral inclusions exists due to their small sizes. To use the

229   X-ray diffraction as a phase diagnostic method is often inconvenient. The more appropriate

230   method is confocal Raman spectroscopy that allows to analyze very small (1-2 μm) samples

231   within the host minerals (Pearson et al., 2014; Sharygin et al., 2013; Zedgenizov et al., 2014).

232   Garnet and pyroxene structures can be easily distinguished within inclusions in deep diamonds

233   by Raman spectroscopy. Basically the Raman spectrum of Na-bearing majoritic garnets is

234   similar to other silicate garnet end-members, but former should reflect the widening of Raman

235   peaks due to local structural heterogeneities or atomic positional disorder caused by the size and

236   charge differences between Na^+ and divalent cations such as Mg^{2+} and Fe^{2+} at the X site.

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237   The structure determination of the inclusions is not the only way for pressure estimations.

238   Another possibility is to study mineral composition. A rough estimate of the formation depth is

239   usually made using Si excess (majorite component) in the garnets from inclusions in diamonds.

240   Keshav and Sen (2001) suggested a barometer for majoritic garnets using very limited number of

241   experiments dominated by the data of Irifune (1987) on ultrabasic compositions. That is not

242   entirely correct since the bulk composition of some inclusions has basic composition rather than

243   ultrabasic. Haggerty and Sautter (1990) described eclogitic xenolith from Jagersfontain

244   kimberlite that contained pyroxene inclusions oriented along (111) in the garnet. Such textural

245   relations were interpreted as an exsolution of pyroxene lamellas from Na-bearing majoritic

246   garnet during decompression. The composition of initial garnet demonstrated high silicon (3.23

247   a.p.f.u.) and sodium (0.10 a.p.f.u.) concentrations. Based on Keshav and Sen (2001) barometry

248   the pressure corresponds to 11–12 GPa. However, garnet with such amount of excessive Si

249   appears at 13.3 GPa and 1923 K in experiments on the system with closely related composition

250   (Gasparik, 1989). According to the data obtained by Dymshits et al. (2013) and Gasparik (1992)

251   the same pressure corresponds to a higher amount of majoritic component in Prp–Maj system in

252   contrast with Prp–Na-maj system. Composition of Na-free garnets corresponds to 3.67 and 3.80

253   a.p.f.u. Si (red stars in Fig. 4c) at 14 and 15 GPa while alkaline garnets contain 3.31 and 3.58

254   a.p.f.u Si (yellow stars in Fig. 4c) at the same pressures. It means that in the Na-rich natural

255   systems the competing mechanisms of Maj and Na-maj incorporation in the garnet structure

256   should exist and presence of Na leads to a higher pressures of Si enrichment. Thus, the estimated

257   pressure of 13.3 GPa for the inclusions based on experiments of Gasparik (1989) seems to be

258   realistic.

259   Another barometer accounting Na component was proposed by Collerson et al. (2010).

260   The method suggested by Collerson et al. (2010) incorporates combined (Si^{4+} + Ti^{4+}) and Na^{+},

261   rather than just Si^{4+}. However, for some eclogitic experimental systems (e.g. Litasov and Ohtani,

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262   2010; Okamoto and Maruyama, 2004) it gives lower pressures that should be further studied. It

263   is obvious that barometry needs more thermodynamic basis.

Implications

265   The most important finding of this study is that the presence of sodium in the majorite-

266   garnet system decreases the pressure of the pyroxene–majorite transformation. In alkali-rich

267   systems the higher pressures are needed for Si enrichment in the garnets due to the competing

268   incorporation of two silica-rich phases (Na-maj and Maj) in the structure. Thus, estimating the

269   pressure of natural samples (e.g., "super-deep" diamonds) from garnet with high amounts of Na

270   should be with respect to Na-maj component. Moreover, the obtained data is essential for

271   thermodynamic calculations. The enthalpy and the entropy of Na-maj near the Na-px–Na-maj

272   transition line can be obtained from the Clapeyron equation. We have already reported P-V-T

273   EoS of Na-maj (Dymshits et al., 2014) and are going to obtain the P-V-T data for Na-px in

274   further studies in order to calculate thermodynamic constants of Na-maj.

Acknowledgments

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415   **Figure captions**

416   **Fig. 1.** Si-Na ratio of the majoritic garnets from the natural and experimental samples.

417   Experimental garnets obtained in the Na-rich systems (Bobrov et al., 2009; Dymshits et al.,

418   2013; Hirose and Fei, 2002; Litasov and Ohtani, 2005; Okamoto and Maruyama, 2004).

419   Compositions of the natural samples are summarized in the Kiseeva et al. (2013).

420

421   **Fig. 2.** X-ray diffraction patterns of run #S2683, where occurrence of the transformation from

422   the Na-px to Na-maj was confirmed. (a) The diffraction profile collected in the Na-px stability

423   field (the critical *P-T* point where Na-px was synthesized from starting material). (b) and (c) are

424   diffraction profiles collected in *P-T* points between which growth of the Na-maj from Na-px

425   occurred (obtained by increasing pressure). (c) Critical *P-T* point were growth of the Na-px

426   peaks was first detected. Px - Na-px, Gt - Na-maj, St - stishovite, Au - gold pressure marker, X -

427   unidentified peaks.

428

429   **Fig. 3.** Diffraction profiles of run #S2683, where occurrence of the transformation from the Na-

430   maj to Na-px was confirmed. (a) The diffraction profile collected in the Na-maj stability field.

431   (b) and (c) are diffraction profiles collected in *P-T* point between which growth of the Na-px

432   from Na-maj occurred (obtained by decreasing pressure). (c) Critical *P-T* point were growth of

433   the Na-maj peaks was detected. Abbreviations are as in Figure 1.

434

435   **Fig. 4.** (a) Data points plotted in a *P-T* diagram to illustrate the phase boundary between Na-px

436   and Na-maj (solid line). Na-px + Na-maj growth and Na-maj + Na-px growth indicates first

437   appearance of peaks of Na-maj or Na-px, respectively. Arrows shows *P-T* path during

438   experiments. The possible range of boundary locations are shown by the dashed lines. (b)

439   Comparison of phase boundaries between Na-px and Na-maj obtained by different methods: *in*

440   *situ* study using different pressure scales Doro07 (Dorogokupets and Dewaele, 2007) and And89

441   (Anderson et al., 1989), quench experiments (Dymshits et al., 2013; Dymshits et al., 2010) and

15

442   *ab initio* calculation (Vinograd et al., 2011) (c) Conditions of pyroxene–majorite transformations

443   in the Earth's mantle. Data for MgSiO$_3$ are from (Yusa et al., 1993)(Sawamoto, 1987). Red and

444   yellow stars corresponds to Si in f.u. in the garnets from Na-free (Gasparik, 1992) and Na-

445   bearing systems (Dymshits et al., 2013). More details in the text. Ol – olivine and Wad –

446   wadsleyite (Katsura et al., 2004) En – enstatite. Mid ocean ridge adiabat and Iceland plume

447   adiabat are after Putirka et al. (2007). The hot subduction geotherm is after Bina et al. (2001).

448

449   **Fig. 5.** Raman spectrum of Na-px. The detailed Raman data are presented in Suppl. Table 1.

450

451   **Fig. 6.** Raman spectra of Prp, Prp–Na-maj solid solution (Prp$_{64}$Na-maj$_{36}$), Na-maj and Li-maj.

452   The detailed Raman data of Prp$_{64}$Na-maj$_{36}$ and Na-maj are presented in Suppl. Table 2 and 3,

453   respectively.

454

455   **Table 1.** Representative experimental conditions

Run no.	V_{Au} (Å^3)	P_{Au} (GPa)[a]	P_{Au} (GPa)[b]	T (K)	X-ray observation
S2683*	65.10(3)	14.4(1)	14.4 (1)	1,273	Na-px growth from starting material, fig. 2a
S2683	65.15(4)	15.6(1)	15.5 (2)	1,473	Na-px → Na-maj growth, fig. 2c after 10 min of annealing Na-maj only
S2683*	65.78(2)	15.0(1)	14.9 (1)	1,673	Na-maj → Na-px growth, fig. 3c
S2683	65.29(3)	15.8(1)	15.6 (1)	1,573	Na-px → Na-maj growth
S2683	65.59(3)	14.2(1)	14.1 (2)	1,473	Na-maj → Na-px growth
P187*	64.96(4)	14.8(1)	14.6 (1)	1,273	Na-maj growth from starting material
P187	65.55(5)	14.4(2)	14.2 (2)	1,473	Na-maj → Na-px growth
P210	64.62(4)	15.9(1)	15.7 (1)	1,273	Na-maj growth from starting material
P210	66.51(5)	15.1(1)	15.1 (2)	1,973	Na-maj → Na-px growth
P210*	65.67(3)	16.0(1)	16.0 (2)	1,773	Na-px → Na-maj growth

456   [a] Based on Au scale (Dorogokupets and Dewaele, 2007); [b] Au scale by Anderson et al. (1989);

457   * Critical points used to constrain phase boundary;

458

459   **Table 2.** Observed Raman modes and assignments for Na-majorite (Na$_2$Mg)Si$_2$(SiO$_4$)$_3$

Bands (cm^{-1})	Intensity	Assignment
SiO$_4$ internal stretching modes		
1087	weak, broad	T_{2g}-ν_3 (Si-O) asymmetric stretching
973	medium, relatively broad	A_{1g}-ν_1 (Si-O) symmetric stretching
865	weak, broad	T_{2g}-ν_3 (Si-O) asymmetric stretching
SiO$_4$ internal bending modes		
827	weak, broad	T_{2g}-ν_4 (O-Si-O) asymmetric bending
670	weak	T_{2g}-ν_4 (O-Si-O) asymmetric bending
592	very strong, sharp	A_{1g}-ν_2 (O-Si-O) symmetric bending
547	weak, shoulder	T_{2g}-ν_4 (O-Si-O) asymmetric bending
Rotational/Translational modes		
393	weak, shoulder	T_{2g}-R(SiO$_4$) rotation
342	strong	A_{1g}-R(SiO$_4$) rotation
272	very weak, broad	T_{2g}-T(Na$_2$Mg) translation
192	weak, broad	E_g or T_{2g}-T(Na$_2$Mg) translation
177	very weak, broad	E_g or T_{2g}-T(Na$_2$Mg-O) translation

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