Raman and X-ray diffraction study of pressure-induced phase transition in synthetic Mg$_2$TiO$_4$

Ching-Pao Wang$^{1*}$, Sean R. Shieh$^{1,2*}$, Anthony C. Withers$^{1,3}$, Xi Liu$^{4,5}$, Dongzhou Zhang$^{6}$, Sergey N. Tkachev$^{7}$, Abd-Erraouf Djirar$^{1}$, Tianqi Xie$^{1}$ & Justin D. Rumney$^{1}$

Synthetic Mg$_2$TiO$_4$ qandilite was investigated to 50 and 40.4 GPa at room temperature using Raman spectroscopy and X-ray diffraction, respectively. The Raman measurements showed that cubic Mg$_2$TiO$_4$ spinel transforms to a high pressure tetragonal (I4$_1$/amd, No.141) phase at 14.7 GPa. Owing to sluggish kinetics at room temperature, the spinel phase coexists with the tetragonal phase between 14.7 and 24.3 GPa. In the X-ray diffraction experiment, transformation of the cubic Mg$_2$TiO$_4$ to the tetragonal structure was complete by 29.2 GPa, ~5 GPa higher than the transition pressure obtained by Raman measurements, owing to slow kinetics. The obtained isothermal bulk modulus of Mg$_2$TiO$_4$ spinel is $K_{T0} = 148(3)$ GPa when $K_{T0}' = 6.6$, or $K_{T0} = 166(1)$ GPa when $K_{T0}'$ is fixed at 4. The isothermal bulk modulus of the high-pressure tetragonal phase is calculated to be 209(2) GPa and $V_0 = 270(2)$ Å$^3$ when $K_{T0}'$ is fixed at 4, and the volume reduction on change from cubic to tetragonal phase is about 9%. The calculated thermal Grüneisen parameters ($\gamma_{th}$) of cubic and tetragonal Mg$_2$TiO$_4$ phases are 1.01 and 0.63. Based on the radii ratio of spinel cations, a simple model is proposed to predict post-spinel structures.

Mg$_2$TiO$_4$ (qandilite) is an oxospinel with excellent dielectric properties that are widely used in satellite communications, mobile phones and wireless communication systems$^{1,2}$. In addition, Mg$_2$TiO$_4$ spinel can form a high-temperature superconducting epitaxial thin film$^{10}$, and is a good candidate for thin film phosphor in optoelectronic applications due to its red emission at high temperature$^{1}$. Natural Mg$_2$TiO$_4$ was discovered in the Kangerdlugssuaq region of East Greenland$^{8}$ and named qandilite after the Qandil Group of metamorphic rocks at Qala-Dizeh region of Iraq$^{7}$. At ambient pressure, Mg$_2$TiO$_4$ exhibits as a tetragonal structure below 660 °C but as a cubic structure above 660 °C$^{8,9}$. The cubic phase breaks down to MgTiO$_3$ (geikielite) and MgO (periclase) with increasing pressure$^{10}$. Synthetic Mg$_2$TiO$_4$ qandilite has inverse spinel structure T(Mg$^{2+}$)$^{2}$O$^4$°(Mg$^{2+}$, Ti$^{4+}$)O$_4$$^{9,11,12}$, which means that Mg$^{2+}$ cations occupy both tetrahedral (T) and octahedral (O) sites, while Ti$^{4+}$ cations are present only in octahedral sites. The isothermal bulk modulus of cubic qandilite was reported to be 169 GPa, based on empirical calculations$^{13}$, and 175 GPa in a diamond anvil cell study$^{14}$, whereas the adiabatic bulk modulus of qandilite was determined to be 152 GPa by ultrasonic measurements$^{15}$. However, no phase transition was found in previous studies, even though three major post-spinel structures, namely CaTi$_2$O$_4$ (CT; space group Cmcm), CaMn$_2$O$_4$ (CM; space group Pbcm), and CaFe$_2$O$_4$ (CF; space group Pnma) have been proposed to be stable under high pressure environments$^{16}$. Unlike CM and CF structures, most CT phases have not been discovered at room temperature but instead under higher temperatures$^{17–19}$. The tetragonal structure (space group I4$_1$/amd) was reported for post-spinel phases at high pressure conditions as an intermediate phase$^{20–25}$. The post-spinel structures attract considerable attention because they are isostuctural with ringwoodite, which is the most abundant phase, comprising approximately 50–60% by volume, in the Earth’s transition zone (400–600 km in depth)$^{26}$. Furthermore, knowledge of the post-spinel phase may have important implications for structure and dynamics of the interior of the exoplanets. Because of the geological and material importance of Mg$_2$TiO$_4$ phases, high pressure measurements of phase stability, structure determination, and

---

1Department of Earth Sciences, University of Western Ontario, London, Ontario, N6A 5B7, Canada. 2Department of Physics and Astronomy, University of Western Ontario, London, Ontario, N6A 5B7, Canada. 3Bayerisches Geoinstitut, Universitat Bayreuth, Bayreuth, Germany. 4Key Laboratory of Orogenic Belts and Crustal Evolution, MOE, Peking University, Beijing, 100871, China. 5School of Earth and Space Sciences, Peking University, Beijing, 100871, China. 6School of Ocean and Earth Science and Technology, Key Laboratory of Oceanic Sciences and Geoplanetology, University of Hawaii at Manoa, Honolulu, HI, 96822, United States. 7Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, Germany. 8Department of Physics and Astronomy, University of Western Ontario, London, Ontario, N6A 5B7, Canada. *email: jinbaow@gmail.com; sshieh@uwo.ca
thermodynamic properties are needed in the Mg$_2$TiO$_4$ system. In this study, in situ high-pressure Raman measurements and equations of states of both spinel and post-spinel structures of synthetic Mg$_2$TiO$_4$ qandilite were investigated at room temperature. The post-spinel phase was identified and a model for prediction of post-spinel structure is also reported.

**Result and Discussion**

Two Raman measurements were conducted at pressure to 24.5 GPa and 50 GPa, respectively. Group theory predicts that for normal spinels at the $\Gamma$ point of the Brillouin zone:

$$\Gamma = A_{1g}(R) + E_g(R) + T_{1g} + 3T_{2g}(R) + 2A_u + E_u + 4T_{1u} + T_{1u} + 2T_{2u}$$

where R denotes Raman-active modes and u denotes infrared-active modes. Therefore, five Raman bands are predicted for the normal spinels. However, cation disorder in the inverse spinel is expected to cause splitting of the $A_{1g}$ mode. In this study, two $A_{1g}$, one $E_g$ and three $T_{2g}$ were observed for Mg$_2$TiO$_4$ spinel, and, in addition, two weak peaks at the shoulders of $T_{2g}$ (432 and 546 cm$^{-1}$) were present (blue arrows in Fig. 1). The higher frequency peaks of $A_{1g}$ modes are assigned to stretching of the MgO$_4$ tetrahedron and the split $A_{1g}$ mode is found at about 596 cm$^{-1}$ in our measurements. The $E_g$ mode corresponds to a symmetric bending vibration of the oxygens within tetragonal units. The $T_{2g}$ near 506 cm$^{-1}$ is caused by an asymmetric bending of O-Mg-O bonds and the other $T_{2g}$ near 281 cm$^{-1}$ is assigned to the translation between TiO$_6$ octahedron and Mg cation. The $T_{2g}$ near 385 cm$^{-1}$ arises from the opposing translations between cations and oxygens along one direction of the lattice. The two different shoulders of $T_{2g}$ are likely related to cation substitutions. When Mg$_2$TiO$_4$ spinel was compressed to 14.7 GPa, a new peak appeared close to 595 cm$^{-1}$. Upon further compression to 24.5 GPa, four additional new peaks were observed, strongly suggesting a new phase. To test whether the new high-pressure phase can be quenchable, the sample was gradually decompressed to ambient pressure, after which a shoulder of high frequency $A_{1g}$ from the high pressure phase was retained, suggesting that the new phase did not fully back-transform and some amount of the new phase coexisted with the spinel phase (Fig. 1). The second Raman measurements were conducted to 50 GPa and the results are shown in Fig. 2. Phase transition again occurred near 15 GPa, marked by the appearance of a single new peak. The full spectrum of the new phase was evident at 24.3 GPa, in agreement with the first run, and the new phase persisted to 50 GPa. However, upon decompression the high-pressure phase was retained to about 18.7 GPa and most of the features were diminished with further decompression, except for the broad $A_{1g}$ peak near 700–800 cm$^{-1}$. Minor MgTiO$_3$ impurity was also observed during the second Raman measurement at 8.8 and 12.2 GPa, giving rise to the weak feature marked by an asterisk in the second set of Raman measurements. A previous Raman study of MgTiO$_3$ showed no phase change at pressure to 27 GPa, suggesting that even if there is minor MgTiO$_3$ impurity, it should not have any contribution to the transition pressure.

**Figure 1.** Raman spectra of Mg$_2$TiO$_4$ at pressure to 24.5 GPa and room temperature. A new Raman peak appeared at 14.7 GPa and four additional modes of the high-pressure phase appeared at 24.5 GPa. Red: compression, blue: decompression. Blue and black arrows indicate the Raman modes of spinel and tetragonal phases, respectively.
To better understand the phase transition boundary, the frequency shifts as a function of pressure are plotted in Fig. 3. A single new peak observed at slightly higher frequency near 595 cm$^{-1}$ at about 14.7 GPa and is assigned to the new phase. A discontinuity was clearly observed near 24.3 GPa, as evidenced by four additional modes near 413, 558, 737, and 836 cm$^{-1}$. Our Raman data suggest that the new phase only partially transformed at about 14.7 GPa, and that the transformation is very sluggish. A two-phase mixture therefore persists between 14.7 and 24.3 GPa. The decompression results showed that the high-pressure phase was partly quenchable, and both spinel and high-pressure phases coexisted to ambient pressure. Four high-pressure modes and six cubic bands were found in the quenched Raman spectra based on two sets of Raman measurements, but the peak at about 500 cm$^{-1}$, which coincides with the position of a peak in compression data, appeared only below 4 GPa. Since this is a first-order phase transition for Mg$_2$TiO$_4$, we were then able to obtain the slopes of pressure dependence $d\nu_i/dP$ values based on two different datasets of curve fits.

The high-pressure phase of Mg$_2$TiO$_4$ could have a tetragonal structure, based on the splitting of MgO$_4$ modes. Previous studies on ZnGa$_2$O$_4$ and MgCr$_2$O$_4$ also suggested a cubic to tetragonal transition at high pressure and room temperature. Our X-ray diffraction analyses (see below) suggest that the high-pressure phase is a tetragonal spinel (I4$_1$/amd, No.141). The new peak at 413 cm$^{-1}$ splits from Eg at 24.3 GPa due to the different bending vibration of oxygen at tetrahedral units, and the other new peak at 558 cm$^{-1}$ appeared at high pressure in the tetragonal phase because of the change of O-Mg-O bending from original higher-frequency T$_2g$. The cubic spinel A$_{1g}$ peak at 737 cm$^{-1}$ split into two peaks at 809 and 836 cm$^{-1}$, which can be attributed to differences in the shortening of bond lengths of the MgO$_4$ tetrahedron. As a result, the observed Raman-mode frequencies ($\nu_i$), pressure dependencies ($d\nu_i/dP$), and mode Grüneisen parameters ($\gamma_i$) for spinel and for the high-pressure phase are listed in Table 1. The pressure dependencies $d\nu_i/dP$ of Mg$_2$TiO$_4$ spinel indicate that two higher-frequency T$_2g$ and one A$_{1g}$ are more compressible, and the lowest-frequency T$_{2g}$ are stiffer. The lowest-frequency E$_g$ of the high-pressure phase is stiffer than the other Raman modes. Mode Grüneisen parameters ($\gamma_i$) are calculated from the equation $\gamma_i = \frac{\kappa_T}{\nu_i} \frac{d\nu_i}{dP}$, where isothermal bulk moduli $K_T$ of spinel and tetragonal phase are both obtained from this study (see below). The thermal Grüneisen parameter ($\gamma_{th}$) can be calculated as the weighted average of the mode Grüneisen parameters ($\gamma_i$), which are listed in Table 1. The thermal Grüneisen parameter is given by $\gamma_{th} = \sum_{\nu_i} \gamma_i \frac{C_{\nu_i} V_{\nu_i}}{\sum_{\nu} C_{\nu} V_{\nu}}$, and the harmonic heat capacity $C_V$ was estimated from the Einstein function:

$$C_V = \kappa \frac{h\nu}{kT} \left[ \exp \left( \frac{h\nu}{kT} \right) - 1 \right]^{-2}$$
where temperature $T$ is 300 kelvins, $h$ is the Plank constant, and $\kappa$ is the Boltzmann constant. Our results show that the thermal Grüneisen parameter is 1.01 for the spinel phase and 0.63 for the tetragonal phase.

No MgTiO$_3$ contaminant was observed during any of the X-ray diffraction measurements and the ambient-pressure unit-cell lattice parameters of synthetic Mg$_2$TiO$_4$ spinel collected at both 13-BM-D and 13-BM-C were confirmed to be the pure phase. The ambient-pressure unit-cell parameters of the synthetic Mg$_2$TiO$_4$ spinel are $a_0 = 8.4464(2)$ Å and $V_0 = 602.59(5)$ Å$^3$, both of which are comparable with previous studies$^{9,11,14,36}$.

In-situ high-pressure X-ray diffraction patterns of Mg$_2$TiO$_4$ to 27.4 GPa collected at beamline 13-BM-D (Run 1) are shown in Fig. 4a. Our two-dimensional images displayed a new feature at 15.7 GPa which could be the high-pressure tetragonal phase T101 (Fig. 4b). At pressure above 22.8 GPa, additional new peaks were observed, allowing us to determine that the structure of the high-pressure phase is tetragonal I41/amd (No. 141). Note that the spinel structure was found to coexist with this high-pressure tetragonal phase, but its diffraction peaks became weaker above 27.4 GPa. As a consequence, no further data at higher pressures were collected from Run 1. Upon decompression, spinel and the tetragonal phases were found to coexist at all pressures to ambient conditions. For Run 2, the pressure was increased directly from 2.7 to 22 GPa and then gradually compressed to 34 GPa within 3 hours (Fig. 5a). Again, the high-pressure tetragonal phase coexisted with Mg$_2$TiO$_4$ spinel from 22 to 34 GPa and the refined structure at 34 GPa is shown in Fig. 5c. However, the tetragonal phase T101 appeared at 32 GPa, which

**Table 1.** Observed Raman-mode frequencies (ν), pressure dependences (dν/dP), and calculated mode Grüneisen parameters (γi) for Mg$_2$TiO$_4$ at pressure to 50 GPa. The high-pressure tetragonal phase was collected from 24.3 GPa to 50 GPa.

| Mode | ν (cm$^{-1}$) | dν/dP (cm$^{-1}$/GPa) | γi | ν (cm$^{-1}$) | dν/dP (cm$^{-1}$/GPa) | γi |
|------|-------------|-----------------------|----|-------------|-----------------------|----|
| T$_{2g}$ | 281 | 2.15 | 1.13 | 325 | 1.08 | 0.70 |
| E$_g$ | 326 | 2.24 | 1.02 | 373 | 0.83 | 0.49 |
| T$_{2g}$ | 413 | 1.20 | 0.65 | |
| T$_{2g}$ | 385 | 3.22 | 1.24 | 464 | 1.47 | 0.72 |
| E$_g$ | 432 | 2.90 | 0.99 | 504 | 1.22 | 0.53 |
| T$_{2g}$ | 506 | 4.08 | 1.19 | 558 | 1.71 | 0.68 |
| A$_{1g}$ | 546 | 2.17 | 0.59 | 617 | 2.04 | 0.75 |
| A$_{1g}$ | 596 | 4.54 | 1.13 | 737 | 2.18 | 0.67 |
| A$_{1g}$ | 728 | 3.77 | 0.77 | 809 | 1.71 | 0.47 |
| A$_{1g}$ | 836 | 2.50 | 0.67 | |
was about 18 GPa higher than Run 1, and another new peak T220 appeared at 34 GPa (Fig. 5b). For Run 3, the pressure was gently increased from 1 bar to 40.4 GPa over 9 hours (Fig. 6). At 29.2 GPa the cubic spinel had fully transformed to the tetragonal phase. After decompression, both spinel and high-pressure tetragonal phases were retained and persisted for at least 24 h after decompression to ambient conditions. The tetragonal phase T220 is critical for the structure determination but it is actually very weak. We checked all our 2D images and found the new peak T101 observed above 15.7 GPa.

Figure 4. (a) Representative X-ray diffraction patterns of Mg₂TiO₄ collected in Run 1. A new peak 101 belongs to the high-pressure phase that coexisted with spinel from 15.7 to 27.4 GPa, and is also present in the decompressed pattern. Red: compression patterns, blue: decompression pattern. (b) 2D cake images show the new peak T101 observed above 15.7 GPa.
The tetragonal phase by doubling the c-axis to 5.446 Å at 25.9 GPa in Run 3. In summary, our X-ray diffraction results suggest that the tetragonal phase transformation started at 15.7 GPa and completed at 29.2 GPa. In addition, in all three runs, the coexistences of spinel and tetragonal phases over variable ranges of pressure are likely to be a result of sluggish kinetics. Our X-ray diffraction data showed both spinel and tetragonal phases were present between 15.7 GPa and 29.2 GPa.

Figure 5. (a) Representative X-ray diffraction patterns of Mg₂TiO₄ collected in Run 2. The high-pressure tetragonal phase coexisted with low pressure phase at 22–34 GPa, but the T101 of high-pressure phase appeared from 32 GPa and T220 appeared at 34 GPa. (b) 2D cake image showing the new T220 pattern at 34 GPa. (c) Le Bail refinement of X-ray diffraction pattern at 34 GPa. The ticks represent three calculated structures: Tetra – high-pressure tetrahedral phase, Sp- ambient pressure cubic phase and Ne – pressure medium.
Figure 6. Representative X-ray diffraction patterns of Mg$_2$TiO$_4$ collected in Run 3. Cubic Mg$_2$TiO$_4$ spinel fully transforms to tetragonal structure at 29.2 GPa. Upon decompression, both low- and high-pressure phases were present at ambient pressure. The room-pressure pattern was collected after 24 hours of decompression. (Red: compression patterns; blue: decompression patterns).

Table 2. Unit-cell lattice parameters of Mg$_2$TiO$_4$ for spinel and tetragonal phase obtained at high pressures. Numbers within parenthesis showed uncertainty of the last digit.
15.7 and 29.2 GPa, but in the Raman measurements the mixture of phases is limited to a smaller pressure range. We postulate that this is owing to longer collection time in Raman measurements than in the X-ray diffraction measurements and perhaps because local atomic bonding distortions and variations detected by Raman scattering are more sensitive than the bulk structural changes measured using the X-ray diffraction method.

The unit-cell lattice parameters and volume data of Mg$_2$TiO$_4$ at pressure to 40.4 GPa are summarized in Table 3. The Mg$_2$TiO$_4$ volume data with respect to pressures were fitted with a third-order Birch-Murnaghan equation of state, with all volume data expressed as molar volumes (Fig. 7). The obtained isothermal bulk modulus of Mg$_2$TiO$_4$ spinel is $K_{T_0} = 148(3)$ GPa when $K'_{T_0} = 6.6$, and $K_{T_0} = 166(1)$ GPa when $K'_{T_0}$ is fixed at 4, in agreement with previous studies\cite{13,14}. The volume change between spinel and tetragonal phase is about 9%. The unit-cell lattice parameters of tetragonal phase obtained from this study are also listed in Table 2. The bulk modulus $K_{T_0}$ of the tetragonal phase is obtained as 209(2) GPa and $V_0 = 270(2)$ Å$^3$ when $K'_{T_0}$ is fixed at 4, based on the trend of Eulerian strain-normalized pressure plot\cite{37}.

To evaluate the post-spinel structure for the orthotitanates, we compare several spinel phases and their post-spinel structures such as CT\cite{38}, CM\cite{39–42}, CF\cite{20,41,43,44}, and intermediate phases\cite{20–23,45,46} (Table 3). The CF phase of AB$_2$O$_4$ post-spinel was limited by the radius ratio $r_B/r_A$. In general, CF phase can be found in the range of 0.53 to

---

**Table 3.** Comparison of the radii of cations, volumes, unit-cell parameters, and bulk moduli of different spinels.

| Compound     | $r_A$ (Å) | $r_B$ (Å) | V(Å$^3$) | a (Å)   | $K_0$ (GPa) | $K'_0$ | HP Phase   | Reference |
|--------------|-----------|-----------|----------|---------|-------------|--------|------------|-----------|
| FeCr$_2$O$_4$| 0.78      | 0.615     | 588      | 8.378   | 209         | 4.0    | I4$_1$/amd | \cite{21} |
| Fe$_3$O$_4$  | 0.78      | 0.645     | 591.4    | 8.394   | 182         | 3.6    | Pbcm       | \cite{54} |
| Fe$_5$Ti$_3$O$_8$ | 0.605     | 0.645     | 624.3    | 8.530   | 250.8       | 4.0    | Cmcm       | \cite{38} |
| MgAl$_2$O$_4$| 0.72      | 0.535     | 507.8    | 7.978   | 212         | 6.3    | Pnma       | \cite{55} |
| MgCr$_2$O$_4$| 0.72      | 0.615     | 578.7    | 8.333   | 189         | 7.2    | I4$_1$/amd | \cite{22} |
| Mg$_2$TiO$_4$| 0.605     | 0.72      | 602.6    | 8.466   | 166         | 4      | I4$_1$/amd | This Study |
| MgFe$_2$O$_4$| 0.72      | 0.645     | 589.9    | 8.387   | 195         | 4      | Pbcm       | \cite{40} |
| MnFe$_2$O$_4$| 0.83      | 0.645     | 617.5    | 8.5157  | 169.7       | 2.87   | Pbcm       | \cite{42} |
| NiMn$_2$O$_4$| 0.69      | 0.645     | 590.6    | 8.390   | 206         | 4      | 14$_1$/amd | \cite{54} |
| ZnAl$_2$O$_4$| 0.74      | 0.535     | 529.7    | 8.091   | 201.7       | 7.62   | Pnma       | \cite{56} |
| ZnGa$_2$O$_4$| 0.74      | 0.62      | 580.1    | 8.340   | 233         | 8.3    | I4$_1$/amd | \cite{57} |
| Zn$_3$Ti$_2$O$_7$ | 0.605     | 0.74      | 608.2    | 8.472   | 154.6       | 4      | I4$_1$/amd | \cite{48} |
| Co$_2$TiO$_4$| 0.605     | 0.75      | 604.38   | 8.454   | 167.2       | 4      | Pbcm       | \cite{58} |

**Figure 7.** The molar volume as a function of pressure for Mg$_2$TiO$_4$ to 40 GPa. Solid circles represent volumes of cubic phase and solid squares are from high-pressure tetragonal phase. The solid and dashed curves are best-fit third-order Birch-Murnaghan equations of state. The error bars of all data points are smaller than the symbols. The Eulerian strain-normalized pressure plot shows that $K'_{T_0}$ of the high-pressure phase is close to 4.
0.89, but not in the case of $r_B/r_A < 0.53$. The radius ratio $r_B/r_A$ of Mg$_2$TiO$_4$ is around 1.19 which is larger than the range of CF phase but very close to Zn$_2$TiO$_4$ with radius ratio $r_B/r_A$ of 1.22. The post-spinel structure of Zn$_2$TiO$_4$ was suggested to be CT phase with an intermediate tetragonal phase. The radii of cations in tetrahedral and octahedral sites could be a determining factor in the structure of AB$_2$O$_4$ spinel. Normal spinel has the formula $A^+B^{2+}O_4$, where $A$ cations sit in tetrahedral sites and $B$ cations sit in octahedral ones. If the radius of $A$ cations is too big, they are unlikely to remain in tetrahedral sites. The formula of inverse spinel can be expressed as $B^+(A^+, B^{2+})O_4$, where $A$ cations do not sit in tetrahedral sites anymore and the size limit for $B$ cations is smaller as they have to fit into tetrahedral sites. Nevertheless, whether in normal or inverse spinels, $A$ cations are usually larger than $B$ cations under ambient conditions. Figure 8 shows the radius ratio $r_A/r_O$ with respect to $r_B/r_O$ for several different spinels at ambient conditions, and two distinct trends of CM and CF are observed. Intermediate tetragonal and CT phases lie mostly between CM and CF curves. The $A$ cations (Ti$^{4+}$) of Mg$_2$TiO$_4$, Zn$_2$TiO$_4$, and Co$_2$TiO$_4$ inverse spinels are the same and the radii of $B$ cations (Mg$^{2+}$, Zn$^{2+}$, and Co$^{2+}$) are very similar. However, they have different post-spinel structures within the area $r_A/r_O < 0.45$ and $r_B/r_O > 0.5$. The possible explanation is that when $r_A$ is smaller than $r_B$, not only $B$ cations can sit in both tetrahedron and octahedron but also $A$ cations. With the exception of the CF phase, the trends of all post spinels are located within the area where radius ratio $r_B/r_A$ is smaller than 1.

**Conclusion**

Two sets of Raman measurements were performed at pressure to 24.5 GPa and 50 GPa in this study. Our Raman results demonstrated that a phase transformation occurred at 14.7 GPa, and a two-phase mixture persisted at pressure up to 24.3 GPa. The cubic Mg$_2$TiO$_4$ spinel fully transformed to a tetragonal phase above 24.3 GPa and the new phase persisted to 50 GPa. On decompression, the high-pressure phase was observable from 50 to about 18.7 GPa, and most Raman features were diminished with further decompression except the broad A$_{1g}$ peak near 700–800 cm$^{-1}$. The high-pressure phase was partly quenchable below 18.7 GPa, and both spinel and high-pressure phases coexisted to ambient pressure. Our X-ray diffraction data suggest that the tetragonal phase transformation started at 15.7 GPa and completed at 29.2 GPa. The coexisting cubic and tetragonal phases are also shown on our decompression X-ray diffraction patterns at ambient pressure. Comparing our three X-ray diffraction runs, the coexistence of spinel and tetragonal phases extends over three different pressure ranges, and the full phase transformation pressure is ~5 GPa higher than Raman measurements, which is likely the result of slow kinetics. The obtained isothermal bulk modulus of Mg$_2$TiO$_4$ spinel is $K_B = 148(3)$ GPa when $K_B' = 6.6$, or $K_B = 166(1)$ GPa when $K_B'$ is fixed at 4. The isothermal bulk modulus of high-pressure tetragonal phase is calculated as 209(2) GPa and $V_0 = 270(2)$ Å$^3$ when $K_B'$ is fixed at 4, and the volume reduction from cubic to tetragonal phase is about 9%. Grüneisen parameters ($\gamma_B$) calculated from the isothermal bulk moduli $K_B$ of spinel and tetragonal phases obtained from this study are 1.01 and 0.63. A simple model to predict post-spinel structures is proposed based on the radii ratio of spinel cations and our model shows the tetragonal phases located in between the CM and CF trends.
Experimental Methods

In situ high-pressure and room-temperature Raman and X-ray diffraction measurements on Mg₂TiO₄ qandilite were performed at pressure to 50 and 40.4 GPa, respectively, using symmetric diamond anvil cells. Mg₂TiO₄ qandilite starting material was synthesized at 1673 K for 52 h from a mixture of MgO and TiO₂. The product was examined by electron probe microanalysis and conventional X-ray diffraction. The results show Mg₂TiO₄ with less than 5% of MgTiO₃. We used a pair of 300-μm diamond culets for both Raman and X-ray diffraction measurements in the high-pressure diamond anvil cell study. Rhenum gaskets were pre-indented to 35–40 μm thickness and a 150-μm hole was drilled to create a sample chamber. Neon was used as a pressure-transmitting medium, together with 1 or 2 ruby spheres for both Raman and X-ray diffraction experiments. A small piece of 10–15 μm gold foil was also loaded in the sample chamber as a pressure marker for the synchrotron X-ray study. Pressure was monitored by the ruby fluorescence method and/or equation of state of gold.

Raman spectra were collected at the University of Western Ontario using a custom-built system. An argon-ion laser with a wavelength of 514.5 nm was used as an excitation source. The Raman signals were collected by a spectrometer with a 500-mm focal length and equipped with a liquid nitrogen-cooled CCD detector. The spectrometer was calibrated by a neon lamp and a silicon chip. The uncertainty in Raman shift measurements did not exceed 1 cm⁻¹. Two different in situ Raman measurements were carried out to 24.5 and 50 GPa, respectively. The pressure was measured by the shift of ruby R₁ emission peak before and after Raman measurements. The collection time of each spectrum was 240 seconds at lower pressure and then increased to 420 seconds at pressure above 24 GPa. The reported spectrum was the average of five spectra at each pressure step. Peakfit software (SPSS Inc., Chicago) was used for Raman peak curve-fitting.

In situ high-pressure angular-dispersive X-ray diffraction experiments were carried out at beamline 13-BM-C and 13-BM-D, sectors of GSECARS, Advanced Photon Source. At both beamlines LaB₆ was used for sample-to-detector distance calibration. The purity of the Mg₂TiO₄ spinel phase was confirmed by X-ray diffraction before the high-pressure experiments. One run (Run 1) at pressure to 27.4 GPa was performed at 13-BM-D. The wavelength of the monochromatic X-ray beam at 13-BM-D was 0.3344 Å, and the beam size was focused to 3 × 7 μm. Two runs (Run 2 and 3) at pressures to 34 and 40.4 GPa were conducted at 13-BM-C. The wavelength of the monochromatic X-ray beam at 13-BM-C was 0.434 Å and beam size was focused to 12 × 18 μm. X-ray diffraction patterns were collected by two-dimensional MAR CCD at 13-BM-C and the exposure time of each pattern was 90–120 seconds with sample rotation angle from 80 to 100 degrees. The exposure time of a two-dimensional image was the average of 20 patterns to enhance the signal-to-noise ratio. Two-dimensional images were integrated and reduced to one-dimensional patterns using Dioptas software. The powder X-ray diffraction data were processed using the software PeakFit V4.12 (SPSS Inc.) and the unit cell parameters were calculated by the program UnitCell. Experimental powder diffraction results are compared to theoretical values calculated using CRYSTALLDIFFRACT software and Le Bail refinement by GSAS (Fig. 5c).

References

1. Bhuyan, R., Santosh Kumar, T., Perumal, A., Ravi, S. & Pamu, D. Optical properties of ambient temperature grown nanocrystalline Mg₂TiO₄ thin films. Surf. Coatings Technol. 221, 196–200 (2013).
2. Cheng, L., Liu, P., Qu, S., Cheng, L. & Zhang, H. Microwave dielectric properties of Mg₂TiO₄ ceramics synthesized via high energy ball milling method. J. Alloys Compd. 623, 238–242 (2015).
3. Haeffke, H. et al. Mg₂TiO₄ as a novel substrate for high-temperature superconducting thin films. Applied Physics Letters 61, 2359–2361 (1992).
4. Zeng, J., Wang, H., Shang, S., Wang, Z. & Lin, C. Preparation of textured Mg₂TiO₄ thin films on Si substrate by atmospheric pressure metalorganic chemical vapour deposition. J. Mater. Sci. Mater. Electron. 8, 159–162 (1997).
5. Ho, Y., Su, C. & Huang, C. Intense red photoluminescence emission of sol-gel-derived nanocrystalline Mg₂TiO₄ thin films. J. Am. Ceram. Soc. 97, 358–360 (2014).
6. Gittins, J., Fawcett, J. & Rucklidge, J. An occurrence of the spinel end-member Mg₂TiO₄ and related spinel solid solutions. Mineral. Mag. 45, 135–137 (1982).
7. Al-‘Hermezi, H. Qandilite, a new spinel end-member, Mg₂TiO₄, from the Qala-Dīzeh region, NE Iraq. Mineral. Mag. 49, 739–744 (1985).
8. Wechsler, B. & Navrotvsky, A. Thermodynamics and structural chemistry of compounds in the system MgO-TiO₂. J. Solid State Chem. 55, 165–180 (1984).
9. Millard, R., Peterson, R. & Hunter, B. Study of the cubic to tetragonal transition in Mg₂TiO₄ and Zn₂TiO₄ spinels by ¹⁷O NMR and Rietveld refinement of X-ray diffraction data. Am. Mineral. 80, 885–896 (1995).
10. Akimoto, S. & Syono, Y. High-pressure decomposition of some titanate spinels. Am. Mineral. 83, 1874–1881 (1998).
11. O’Neill, H., Redfern, S., Kesson, S. & Short, S. An in situ neutron diffraction study of cation disordering in synthetic qandilite Mg₂TiO₄ at high temperatures. Am. Mineral. 88, 860–865 (2003).
12. Kumar, S. et al. Structural and electrical properties of Mg₂TiO₄. J. Ceram. Soc. Japan 117, 689–692 (2009).
13. Hazen, R. & Yang, H. Effects of cation substitution and order–disorder on P-V-T equations of state of cubic spinels. Am. Mineral. 84, 1956–1960 (1999).
14. Lu, M. et al. Equation of state of synthetic qandilite Mg₂TiO₄ at ambient temperature. Phys. Chem. Miner. 43, 301–306 (2016).
15. Liebermann, R., Jackson, I. & Ringwood, A. Elasticity and phase-equilibria of spinel disproportionation reactions. Geophys. J. R. Astron. Soc. 50, 553–587 (1977).
16. Yamanaka, T., Uchida, A. & Nakamoto, Y. Structural transition of post-spinel phases CaMn₂O₄, CaFe₂O₄, and CaTi₂O₄ under high pressures up to 60 GPa. Am. Mineral. 93, 1874–1881 (2008).
17. Chen, M., Shu, J., Mao, H., Xie, X. & Hemley, R. J. Natural occurrence and synthesis of two new post-spinel polymorphs of chrome. Proc. Natl. Acad. Sci. U. S. A. 100, 14651–14654 (2003).
18. Ishii, T. et al. High-pressure phase transitions in FeCr₂O₄ and structure analysis of new post-spinel FeCr₂O₄ and Fe₇Cr₄O₁₉ phases with meteoritical and petrological implications. Am. Mineral. 99, 1788–1797 (2014).
19. Ishii, T. et al. High-pressure high-temperature transitions in MgCr2O4 and crystal structures of new Mg,Cr2O4 and post-spinel MgCr2O4 phases with implications for ultrahigh-pressure chemistries in ophiolites. *Am. Mineral.* **100**, 59–65 (2015).

20. López-Moreno, S. et al. Lattice dynamics of ZnAl2O4 and ZnGa2O4 under high pressure. *Ann. der Phys.* **523**, 157–167 (2011).

21. Kyono, A. et al. The influence of the Jahn–Teller effect at Fe2+ on the structure of chromite at high pressure. *Phys. Chem. Miner.* **39**, 131–141 (2012).

22. Yorg, B. Bottis, S., Shieh, S., Shi, W. & Withers, A. C. Pressure-induced phase transition study of magnesiochromite (MgCr2O4) by Raman spectroscopy and X-ray diffraction. *Phys. Earth Planet. Inter.* **196–197**, 75–82 (2012).

23. Wang, Z., Saxena, S. & Zha, C. In situ x-ray diffraction and Raman spectroscopy of pressure-induced phase transformation in spinel Zn3Ti2O6. *Phys. Rev. B* **66**, 024103 (2002).

24. Darul, J., Lathe, C. & Piszora, P. Mn3O4 under high pressure and temperature: Thermal stability, polymorphism, and elastic properties. *Phys. Chem. Chem. Phys.* **11**, 23487–23494 (2013).

25. Lv, H. & et al. Effect of grain size on pressure-induced structural transition in MnO2. *J. Phys. Chem. C* **116**, 2165–2171 (2012).

26. Frost, D. The Upper Mantle and Transition Zone. *Elements* **4**, 171–176 (2008).

27. White, W. & DeAngelis, B. Interpretation of the vibrational spectra of spinels. *Spectrochim. Acta Part A Mol. Spectros.* **23**, 985–995 (1967).

28. Cynn, H., Sharma, S., Cooney, T. & Nicol, M. High-temperature Raman investigation of order–disorder behavior in the MgAl2O4 spinel. *Phys. Rev. B* **45**, 500–502 (1992).

29. deWijs, G., Fang, C., Kresse, G. & deWith, G. First-principles calculation of the phonon spectrum of MnAl2O4 spinel. *Phys. Rev. B* **65**, 094305 (2002).

30. Chandramohan, P., Srinivasan, M., Velmurugan, S. & Narasimhan, S. Cation distribution and particle size effect on Raman spectrum of CoFe2O4. *J. Solid State Chem.* **184**, 89–96 (2011).

31. O’Horo, M., Frisillo, A. & White, W. Lattice vibrations of MgAl2O4 spinel. *J. Phys. Chem. Solids* **34**, 23–28 (1973).

32. Reynard, B. & Guyot, F. High-temperature properties of geikelite (MgTi2O4-Ilmenite) from high-temperature high-pressure Raman spectroscopy: some implications for MgSiO3-Ilmenite. *Phys. Chem. Miner.* **21**, 441–450 (1994).

33. Gillet, P., Guyot, F. & Malezieux, J. High-pressure, high-temperature Raman spectroscopy of CaGeO3 (olivine form): some insights on anharmonicity. *Phys. Earth Planet. Inter.* **58**, 141–154 (1989).

34. Chopelas, A. Thermal expansivity of lower mantle phases MgO and MgSiO2 perovskite at high pressure derived from vibrational spectroscopy. *Phys. Earth Planet. Inter.* **98**, 3–15 (1996).

35. Zhai, S. et al. High-pressure X-ray diffraction and Raman spectroscopy of CaFe2O4-type β-CaCr2O4. *Phys. Chem. Miner.* **43**, 307–314 (2016).

36. Sawada, H. Electron density study of spinel: Magnesium titanium oxide (MgTi2O4). *Mater. Res. Bull.* **31**, 355–360 (1996).

37. Angel, R. J. Equations of State. *Rev. Mineral. Geochemistry* **41**, 35–59 (2000).

38. Yamanaka, T., Mine, T., Asogawa, S. & Nakamoto, Y. Jahn-Teller transition of Fe2TiO4 observed by maximum entropy method at high pressure and low temperature. *Phys. Rev. B* **80**, 134120 (2009).

39. Fei, Y., Frost, D., Mao, H., Previtt, C. & Hausermann, D. In situ structure determination of the high-pressure phase of Fe3O4. *Am. Mineral.* **84**, 203–206 (1999).

40. Andrault, D. & Bolfan-Casanova, N. High-pressure phase transformations in the MgFe2O4 and Fe2O3–MgSiO3 systems. *Phys. Chem. Miner.* **28**, 211–217 (2001).

41. Reid, A. & Ringwood, A. Newly observed high pressure polymorphs in MnO2, CaAl2O4, and ZrSiO4. *Earth Planet. Sci. Lett.* **6**, 205–208 (1969).

42. Ye, L. et al. Compressibilities of MnFe2O4 polymorphs. *Phys. Chem. Miner.* **42**, 569–577 (2015).

43. Irfan, T., Fujino, K. & Ohtani, E. A new high-pressure form of MgAl2O4. *Phys. Rev. B* **59**, 109 (1997).

44. Ono, S., Kikegawa, T. & Ohishi, Y. The stability and compressibility of MgAl2O4 high-pressure polymorphs. *Phys. Chem. Miner.* **33**, 200–206 (2006).

45. Asbrink, S., Wąskowska, A., Olsen, J. & Gerward, L. High-pressure phase of the cubic spinel NiMn2O4. *Phys. Rev. B* **57**, 4972–4974 (1998).

46. Asbrink, S., Wąskowska, A., Gerward, L., Olsen, J. & Talik, E. High-pressure phase transition and properties of spinel ZnMn2O4. *Phys. Rev. B* **60**, 12651–12656 (1999).

47. Muller-Buschbaum, H. The crystal chemistry of AMGO4 oxometallates. *J. Alloys Compd.* **349**, 49–104 (2003).

48. Zhang, Y. et al. Spinel and post-spinel phase assemblages in Zn3Ti2O6: an experimental and theoretical study. *Phys. Chem. Miner.* **44**, 109–123 (2017).

49. Shannon, R. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr.* **A32**, 751–767 (1976).

50. Mao, H., Xu, J. & Bell, P. Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *J. Geophys. Res.* **91**, 4673–4676 (1986).

51. Fei, Y. et al. Toward an internally consistent pressure scale. *Proc. Natl. Acad. Sci.* **104**, 9182–9186 (2007).

52. Prescher, C. & Prakapenka, V. DIOPtas: A program for reduction of two-dimensional X-ray diffraction data and data exploration. *High Press. Res.* **35**, 223–230 (2015).

53. Holland, T. & Redfern, S. Unit cell refinement from powder diffraction data; the use of regression diagnostics. *Mineral. Mag.* **61**, 65–77 (1997).

54. Gatta, G., Kantor, I., Boffa Ballaran, T., Dubrovinsky, L. & McCammon, C. Effect of non-hydrostatic conditions on the elastic behaviour of magnetite: In situ single-crystal X-ray diffraction study. *Phys. Chem. Miner.* **34**, 627–635 (2007).

55. Wittlinger, I., Werner, S. & Schulz, H. Pressure-induced order–disorder phase transition of spinel single crystals. *Acta Crystallogr. Sect. B Struct. Sci.* **54**, 714–721 (1998).

56. Levy, D., Pavesi, A., Sani, A. & Pischedda, V. Structure and compressibility of synthetic ZnAl2O4 (gahnite) under high-temperature conditions, from synchrotron X-ray powder diffraction. *Phys. Chem. Miner.* **28**, 612–618 (2001).

57. Errandonea, D., Kumar, R. S., Manjon, I. J., Ursaki, V. V. & Rusu, E. V. Post-spinel transformations and equation of state in ZnGa2O4: Determination at high pressure by in situ X-ray diffraction. *Phys. Rev. B - Condens. Matter Mater. Phys.* **79**, 1–6 (2009).

58. Zhang, Y. et al. Physics and Chemistry of Minerals Equations of state of Co3Ti4O12, Co3Ti4O12-CM, and Co3Ti4O12-CT, and their phase transitions: an experimental and theoretical study. (2018).

**Acknowledgements**

We acknowledge the constructive comments from two anonymous reviewers help to improve the quality of this work and the support from NSFEC for SRS and ACW. In addition, we thank the support of GeoSoilEnviroCARS (Sector 13), which is supported by the National Science Foundation - Earth Sciences (EAR-1128799), and the Department of Energy, Geosciences (DE-FG02–94ER14466). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.”
Author contributions
S. Shieh devised the project. C. Wang, S. Shieh and A. Withers wrote the manuscript. A. Djirar, T. Xie, J. Rumney, and C. Wang contributed to the experiments and data analyses. D. Zhang and S. Tkachev are the beamline scientists who helped the synchrotron X-ray diffraction experiments. X. Liu synthesized the sample. S. Shieh and A. Withers supervised the experiments and participated in data reduction.

Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to C.-P.W. or S.R.S.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2020