Equations of state of Co\textsubscript{2}TiO\textsubscript{4}-Sp, Co\textsubscript{2}TiO\textsubscript{4}-CM, and Co\textsubscript{2}TiO\textsubscript{4}-CT, and their phase transitions: an experimental and theoretical study

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Abstract

Co\textsubscript{2}TiO\textsubscript{4} spinel (Co\textsubscript{2}TiO\textsubscript{4}-Sp) was synthesized at 1573 K and room P by heating in an argon atmosphere for 72 h, and quasi-hydrostatically compressed to ~24 GPa using a diamond-anvil cell in conjunction with a synchrotron X-ray radiation (ambient \(T\)). We found that the Co\textsubscript{2}TiO\textsubscript{4}-Sp was stable up to ~21 GPa and transformed to a new phase at higher \(P\). With some theoretical simulations, we revealed that this new phase adopted the CaMn\textsubscript{2}O\textsubscript{4}-type structure (Co\textsubscript{2}TiO\textsubscript{4}-CM), which might further transform to the CaTi\textsubscript{2}O\textsubscript{4}-type structure (Co\textsubscript{2}TiO\textsubscript{4}-CT) at ~35 GPa. The isothermal bulk modulus (\(K_T\)) was experimentally obtained as 175.5(36) GPa for the Co\textsubscript{2}TiO\textsubscript{4}-Sp and 161(7) GPa for the Co\textsubscript{2}TiO\textsubscript{4}-CM, with its first pressure derivative \(K'_T\) as 2.8(5) and 7.3(8), respectively. Furthermore, the \(K_T\) was theoretically constrained (the GGA method) as 138(3) GPa for the Co\textsubscript{2}TiO\textsubscript{4}-CM and 196.8(14) GPa for the Co\textsubscript{2}TiO\textsubscript{4}-CT, with the \(K'_T\) as 7.6(3) and 5.0(1), respectively. Consequently, the Co\textsubscript{2}TiO\textsubscript{4}-CM is ~12.3% denser than the Co\textsubscript{2}TiO\textsubscript{4}-Sp at ~21 GPa, whereas the Co\textsubscript{2}TiO\textsubscript{4}-CT is just ~0.8% denser than the Co\textsubscript{2}TiO\textsubscript{4}-CM at ~35 GPa. The spinel and post-spinel phase assemblages for the Co\textsubscript{2}TiO\textsubscript{4} composition at some high \(T\) have been tentatively deduced as Co\textsubscript{2}TiO\textsubscript{4}-Sp, CoO-B1 (NaCl-type structure) + CoTiO\textsubscript{3}-Ilm (ilmenite-type structure), 2CoO-B1 + TiO\textsubscript{2}-α-PbO\textsubscript{2} (α-PbO\textsubscript{2}-type structure), Co\textsubscript{2}TiO\textsubscript{4}-CM and Co\textsubscript{2}TiO\textsubscript{4}-CT, as \(P\) increases.

Keywords Co\textsubscript{2}TiO\textsubscript{4}-CM · Co\textsubscript{2}TiO\textsubscript{4}-CT · Co\textsubscript{2}TiO\textsubscript{4}-Sp · DFT calculation · Diamond-anvil cell · Equation of state · High-\(P\) phase transition · Synchrotron X-ray diffraction

Introduction

The Co\textsubscript{2}TiO\textsubscript{4} composition commonly crystallizes to a 4–2 inverse spinel (Co\textsubscript{2}TiO\textsubscript{4}-Sp; Romeijn 1953), which has interesting and useful electrical, magnetic, and electronic properties (Sakamoto 1962; Dube and Darshane 1991; Prosnikov et al. 2016). In Earth sciences, titanate spinels (A\textsubscript{2}TiO\textsubscript{4}-Sp) include Mg\textsubscript{2}TiO\textsubscript{4}-Sp, Mn\textsubscript{2}TiO\textsubscript{4}-Sp, Fe\textsubscript{2}TiO\textsubscript{4}-Sp, Co\textsubscript{2}TiO\textsubscript{4}-Sp and Zn\textsubscript{2}TiO\textsubscript{4}-Sp, which usually attain the inverse spinel structure at ambient conditions.
and found that this phase should adopt the CaMn$_2$O$_4$-type structure (space group $Fd\bar{3}m$, $Z = 8$; structurally written as $(\text{A}^{2+})(\text{A}^{2+}\text{Ti}^{4+})\text{O}_4$; e.g., Verwey and Heilmann (1947), Sakamoto (1962), Hagenmuller et al. (1966), Wechsler and Von Dreele (1989), Dube and Darshane (1991), Sedler et al. (1994), Millard et al. (1995), Yamanaka et al. (2013)). A large number of phase transitions have been reported for the A$_2$TiO$_4$-Sp. For example, the Fe$_2$TiO$_4$-Sp transforms to an Fe$_2$TiO$_4$-TDS phase (tetragonal distorted structure) at ~9 GPa, which further transforms to a Fe$_2$TiO$_4$-CT phase (CaTi$_2$O$_4$-type structure) at ~16 GPa (ambient $T$; Yamanaka et al. 2009, 2013). Similarly, extensive experimental investigations with different techniques have been conducted to establish the equation of state of the A$_2$TiO$_4$-Sp at high pressure [ambient $T$; e.g., Liebermann et al. (1977), Wang et al. (2002), Yamanaka et al. (2009), Yamanaka et al. (2013), Xiong et al. (2015), Lv et al. (2016), Zhang et al. (2017)].

In this study, we focused on the high-$P$ behavior of the Co$_2$TiO$_4$-Sp. We synthesized the Co$_2$TiO$_4$-Sp using a solid-state reaction method (ambient $P$), and compressed this material to ~24 GPa using a diamond-anvil cell (DAC) in conjunction with a synchrotron X-ray radiation (ambient $T$). The compression experiments indicated a new phase stable at $P$ > ~21 GPa. To determine the structure of this high-$P$ phase, we conducted some theoretical simulations and found that this phase should adopt the CaMn$_2$O$_4$-type structure (Co$_2$TiO$_4$-CM). Our simulation also suggested that the Co$_2$TiO$_4$-CM would further transform to a Co$_2$TiO$_4$-CT phase at ~35 GPa. In addition, the compressional behaviors of the Co$_2$TiO$_4$-Sp, Co$_2$TiO$_4$-CM, Co$_2$TiO$_4$-CT were investigated and compared, and the sequence of the phase assemblages for the Co$_2$TiO$_4$ composition at high $P$-$T$ conditions was tentatively deduced.

Experimental and simulating methods

The Co$_2$TiO$_4$-Sp was synthesized by a solid-state reaction method. We used the chemicals CoO (99.99% purity; Alfa Aesar) and TiO$_2$ (99.99% purity; Alfa Aesar) to prepare the starting material for the synthesizing experiment. We first dried these chemicals at 1 atm and 1373 K for 36 h under an argon environment; second weighed them according to the stoichiometry of the Co$_2$TiO$_4$-Sp and homogenized them into a mixture with an agate mortar under acetone, and third pressed this mixture into a pellet. The resulting pellet was placed in a platinum crucible and sintered with a muffle furnace, which was continuously flushed with argon. The sample was heated at 1573 K for 72 h and then slowly cooled to room $T$ at the rate of ~5 K/min. According to Sakamoto (1962), our synthetic product was expected to be pure Co$_2$TiO$_4$-Sp.

One small portion of the synthetic sample from the high-$T$ synthesizing experiment was processed and characterized using a scanning electron microscope (Quantum 650 FEG) and an electron microprobe (EMP; JEOL JXA-8100). The rest of the sample was slowly ground down to a fine powder, which was first checked with a powder X-ray diffractometer (X’Pert Pro MPD system) at ambient $P$-$T$ conditions, and later used in our high-$P$ synchrotron X-ray diffraction experiments.

With a symmetrical DAC, we conducted the high-$P$ synchrotron X-ray diffraction experiments (ambient $T$) at the beamline 13-ID-D of the GSECARS, Advanced Photon Source (APS), Argonne National Laboratory. The experimental techniques were similar to those used in our previous studies (e.g., Liu et al. 2011; He et al. 2012; Zhang et al. 2017). The powder sample was mixed with a trace amount of Au powder, and loaded into a rhenium gasket with a hole of 100 µm in diameter. We used neon as the pressure medium, a ruby sphere as the pressure marker (the ruby fluorescence method; Mao et al. 1978), and an incident synchrotron radiation beam of the wavelength of 0.3344 Å and the size of ~3 × 4 µm$^2$. Due to the small X-ray beam size and the small amount of admixed Au, the XRD peaks of the gold were not usually detected and not very useful for pressure determination (see later discussion). The sample-to-detector distance (246.4524 mm) and the orientation of the detector were calibrated using LaB$_6$. Each X-ray diffraction image was collected for about 30–120 s using an online CCD detector, and later integrated to derive the one-dimensional X-ray diffraction pattern using the Dioptas program (Presscher and Prakapenka 2015). We processed the XRD data using the PeakFit V4.12 software (SPSS Inc.), and derived the unit-cell parameters using the UnitCell program (Holland and Redfern 1997).

Our electronic structure calculations were carried out with the CASTEP code using the density functional theory (DFT; Hohenberg and Kohn 1964; Kohn and Sham 1965) and planewave pseudopotential technique (Payne et al. 1992). Taking into account the potential order–disorder phenomenon in the spinel structure, we constructed the initial structural model of the Co$_2$TiO$_4$-Sp according to Rankin et al. (2008), and the resulting structural model was similar to that for the Zn$_2$TiO$_4$-Sp depicted in Fig. 6b of Zhang et al. (2017). In addition, the initial structural model of the Co$_2$TiO$_4$-CT (space group $Bbmm$; $Z = 4$), Co$_2$TiO$_4$-CM (space group $Pbem$; $Z = 4$), and Co$_2$TiO$_4$-CF (CaFe$_2$O$_4$-type structure; space group $Pnma$; $Z = 4$) were from Bertaut and Blum (1956), Giesber et al. (2001), and Decker and Kasper (1957), respectively. To consider the magnetic ordering of these phases, we carried out spin-polarized calculations with initial ferromagnetic and antiferromagnetic structures (labeled as Sp-fm, CT-fm, CM-fm and CF-fm, and Sp-afm, CT-afm, CM-afm and CF-afm, respectively).
We treated the exchange–correlation interaction by the
generalized gradient approximation (GGA) with the Per-
dew–Burker–Ernzerhof functional (PBE; Perdew et al. 1996),
and used a convergence criterion of \(10^{-6}\) eV/atom on the total
energy in the self-consistent field calculations. The GGA + \(U\)
method (Dudarev et al. 1998) was employed to deal with the
strong correlation effect of the \(\text{Co}^{2+}\) electrons, and the value
of the Hubbard \(U\) for the on-site Coulomb interaction in the
localized \(d\) orbitals was set as 2.5 eV; the effects of different
\(U\) values on the energies, lattice parameters, magnetic and
electronic properties of the \(\text{Co}_2\text{TiO}_4\)-Sp can be found in the
Supplementary Material. Subject to the unavailability of any
experimental measurements to facilitate comparisons, it was
assumed that a Hubbard \(U\) of 2.5 in combination with the
GGA method would work well for all other \(\text{Co}_2\text{TiO}_4\) phases.
We employed the ultrasoft pseudopotentials for the O, Co,
and Ti in the CASTEP’s internal libraries of pseudopoten-
tials to model the ion–electron interaction, and the planewave
basis set with an energy cutoff of 380 eV to expand the elec-
tronic wave functions (Vanderbilt 1990; Kresse and Hafner
1994). The cutoff core radii were 0.70 Å for the O atom
in the electronic configuration \(2s^22p^4\), 1.70 Å for the Co atom
in the electronic configuration \(3d^74s^2\), and 1.50 Å for the Ti
atom in the electronic configuration \(3s^23p^63d^24s^2\). We set a
\(k\)-point separation as 0.07 Å\(^{-1}\) for all the phases so that the
initial \(k\)-point grids were automatically generated as \(2 \times 2 \times 2,
2 \times 5 \times 1, 5 \times 1 \times 1,\) and \(1 \times 1 \times 5\) (Monkhorst and Pack
1976) for the \(\text{Co}_2\text{TiO}_4\)-Sp, \(\text{Co}_2\text{TiO}_4\)-CF, \(\text{Co}_2\text{TiO}_4\)-CM and
\(\text{Co}_2\text{TiO}_4\)-CT, respectively. The effects of using larger energy
cutoff and denser \(k\)-point meshes on the calculated proper-
ties were tested and found as negligible. By minimizing the
Hellmann–Feynman force on the atoms and simultaneously
matching the stress on the unit cell to the target stress, the
equilibrium lattice parameters and internal coordinates were
fully relaxed until the total energy was minimized.

**Result and discussion**

**Synthetic \(\text{Co}_2\text{TiO}_4\)-Sp**

The electron back-scatter images of our synthetic product
suggest that there is only one crystalline phase, with grain
sizes ranging from a few micrometers to a few dozens of
micrometers (Fig. 1). The ambient powder X-ray diffraction
data indicate no impurity and confirm the expected cubic
spinel structure. The EMP analyses (4 analyses) performed
on our synthetic product suggest a chemical formula of
\(\text{Co}_{2.01(2)}\text{Ti}_{1.00(0)}\text{O}_{4.00}\), which is essentially identical to the
ideal chemical formula of the \(\text{Co}_2\text{TiO}_4\)-Sp. The powder
X-ray diffraction data at ambient conditions give out the
unit-cell parameters of our \(\text{Co}_2\text{TiO}_4\)-Sp as \(a_0 = 8.454(0)\)
Å and \(V_0 = 604.28(8)\) Å\(^3\), in good agreement with those
from Sakamoto (1962; \(a_0 = 8.44\) Å) and Hirota et al. (1990;
\(a_0 = 8.443\) Å).

**Equation of state of \(\text{Co}_2\text{TiO}_4\)-Sp**

Our DAC experiments (ambient \(T\)) were conducted up to \(\sim 24\)
GPa. The X-ray diffraction patterns obtained at pressures up
to \(\sim 20.6\) GPa do not show any apparent peak-broadening,
peak-splitting, or new peak (Fig. 2), suggesting no phase
transition up to this pressure. However, the X-ray diffraction
patterns collected at pressures higher than \(\sim 22\) GPa show
significant peak-broadening and attained some new peaks
which cannot be attributed to the cubic spinel structure. It fol-
low that there must have been a phase transition somewhere
between \(\sim 20.6\) and 22 GPa. On the other hand, the major
peaks of the X-ray diffraction pattern collected at \(\sim 24\) GPa
can be confidently assigned to the \(\text{Co}_2\text{TiO}_4\)-Sp still, indicat-
ing an incompletion of the phase transition. The new peaks
can also be observed on decompression to 1 atm (Fig. 2).
The unit-cell parameters of the \(\text{Co}_2\text{TiO}_4\)-Sp at different
pressures obtained during both compression and decompres-
sion are summarized in Table 1 and shown in Fig. 3a. Dur-
ing compression, the data obtained at \(P > \sim 17\) GPa show
some deviation from the trend defined by the data at lower
pressures (Fig. 3a). Since the magnitude of this deviation
is positively correlated with the nominal experimental \(P\),
we tentatively ascribe it to the progressive development of a non-hydrostatic
environment at $P \sim 15$ GPa. Nevertheless, the volume data obtained from the compression and decompression experiments are well mixed, suggesting that the pressure status in our experiments was almost quasi-hydrostatic, and the elastic behavior of the $\text{Co}_2\text{TiO}_4$-$\text{Sp}$ was fully reversible after compression to $\sim 24$ GPa.

To accurately determine the isothermal bulk modulus ($K_{IT}$) of the $\text{Co}_2\text{TiO}_4$-$\text{Sp}$, we have only fitted the $P$--$V$ data from the compression experiments collected at pressures from 1 atm to 17 GPa with the third-order Birch–Murnaghan equation of state (BM-EoS; Birch 1947) by a least-squares method:

$$P = \left(\frac{3}{2}\right)K_{IT} \left[ \left(\frac{V_0}{V}\right)^\frac{7}{2} - \left(\frac{V_0}{V}\right)^{\frac{3}{2}} \right]$$

$$\times \left\{ 1 + \frac{3}{4} (K'_{IT} - 4) \left[ \left(\frac{V_0}{V}\right)^\frac{7}{2} - 1 \right] \right\}, \quad (1)$$

**Table 1** Experimentally determined unit-cell parameters of $\text{Co}_2\text{TiO}_4$-$\text{Sp}$ at various pressures (room $T$)

<table>
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<th>$P$ (GPa)</th>
<th>$a$ (Å)</th>
<th>$V$ (Å$^3$)</th>
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<tr>
<td>0.0001</td>
<td>8.454(0)$^a$</td>
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</tr>
<tr>
<td>0.9(1)$^b$</td>
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<td>1.7(1)</td>
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<tr>
<td>2.0(1)</td>
<td>8.427(1)</td>
<td>598.50(26)</td>
</tr>
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<td>8.459(2)</td>
<td>605.33(35)</td>
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</table>

$^a$Numbers in parentheses representing one standard deviation

$^b$Pressure determined by averaging the values measured before and after collection of synchrotron data; uncertainty of the $P$ measurement in the high-$P$ experiments assumed as 0.1 GPa
The decompressional data are represented by empty circles; the solid black curve is drawn according to our third-order BM-EoS (see text for the details). The compressional data collected at pressures up to ~17 GPa and at pressures higher than ~17 GPa are represented by filled squares and filled diamonds, respectively. The solid line represents the fit of our third-order BM-EoS for Co$_2$TiO$_4$-Sp (Fig. 3b). The Eulerian definition of the finite strain $f_E$ is $f_E = 4$, a positive slope $K'_T > 4$, and a negative slope $K'_T < 4$. Figure 3b shows that the slope of the fitted line for the data at lower pressures, suggesting that the data at higher pressures are significantly deviated from the fitted line.

The quality of the derived third-order BM-EoS for the Co$_2$TiO$_4$-Sp can be evaluated using the $f_E-F$ plot (Fig. 3b). The Eulerian definition of the finite strain $f_E$ is $f_E \equiv [(V/V_0)^{2/3} -1]/2$, and the normalized pressure $F$ is $F \equiv P/[3f_E/(1 + 2f_E)^{3/2}]$. Using $F$, the third-order BM-EoS can be rewritten as:

$$F = K_T + 3/2K'_T(K'_T - 4)f_E,$$

so that the slope of the line defined by the experimental data should be equal to $3/2K'_T(K'_T - 4)$, and the intercept value is the isothermal bulk modulus. Accordingly, a slope of zero implies $K'_T = 4$, a positive slope $K'_T > 4$, and a negative slope $K'_T < 4$. Figure 3b shows that the slope of the fitted line for the data in the $P$ range from 1 atm to ~17 GPa is negative so that the value of the $K'_T$ should be smaller than 4, confirming our EoS fit. Further, Fig. 3b shows that the data at $P > ~17$ GPa gradually deviate away from the line with negative slope defined by the data at lower pressures, suggesting that the spinel structure was increasingly strained indeed due to the progressive development of the non-hydrostatic pressure environment in our DAC experiments at $P > ~17$ GPa (Klotz et al. 2009).

Table 2: Isothermal bulk moduli (GPa) of Co$_2$TiO$_4$-Sp, Co$_2$TiO$_4$-CM and Co$_2$TiO$_4$-CT

<table>
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<tr>
<th>Phase</th>
<th>$K_T$</th>
<th>$K'_T$</th>
<th>Method*</th>
<th>References</th>
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<td>Sp</td>
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<td>2.8(5)</td>
<td>Exp/SX/Ne</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>167.2(12)</td>
<td>4(fixed)</td>
<td>Exp/SX/Ne</td>
<td>This study</td>
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<tr>
<td></td>
<td>162(9)</td>
<td>-</td>
<td>Exp/US</td>
<td>Liebermann et al. (1977)</td>
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<tr>
<td>CM</td>
<td>161(7)</td>
<td>7.3(8)</td>
<td>Exp/SX/Ne</td>
<td>This study</td>
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<td></td>
<td>192.1(44)</td>
<td>4(fixed)</td>
<td>Exp/SX/Ne</td>
<td>This study</td>
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<tr>
<td></td>
<td>138(3)</td>
<td>7.6(3)</td>
<td>Cal/DFT/GGA + PBE/usp</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>184(3)</td>
<td>4(fixed)</td>
<td>Cal/DFT/GGA + PBE/usp</td>
<td>This study</td>
</tr>
<tr>
<td>CT</td>
<td>196.8(14)</td>
<td>5.0(1)</td>
<td>Cal/DFT/GGA + PBE/usp</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>219.6(26)</td>
<td>4(fixed)</td>
<td>Cal/DFT/GGA + PBE/usp</td>
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</tbody>
</table>


where $K'_T$ is the first pressure derivative of the $K_T$, and $V_0$ is the volume at zero pressure whereas $V$ is the volume at high pressure. When the $K'_T$ is set as 4, we obtain $K_T = 167.2$ (12) GPa, and $V_0 = 605.13$ (13) Å$^3$ for the Co$_2$TiO$_4$-Sp (Table 2). If the $K'_T$ is not fixed, we obtain $K_T = 175.5(36)$ GPa, $K'_T = 2.8(5)$ and $V_0 = 604.85(16)$ Å$^3$ (Table 2).
compression data from 1 atm to ~17 GPa. The ellipses strongly elongate with negative slopes, indicating a negative correlation between the $K_T$ and $K_T^*$ parameters. This observation implies that the experimental data can be fitted almost equally well by decreasing the value of $K_T$ and increasing the value of $K_T^*$, or vice versa. In Fig. 3c, the area enclosed by the dashed line or solid line represents a 68.3% or 90% probability (or confidence level; Angel 2000) that the true values of $K_T$ and $K_T^*$ lie in such an area, respectively. If we consider the 90% confidence ellipse, the $K_T$ value can vary in the range from ~168 to ~183 GPa with the $K_T^*$ value from ~3.8 to ~1.9, which then verifies our data fitting process.

The adiabatic bulk modulus ($K_S$) of the Co$_2$TiO$_4$-Sp was once determined as 162(9) GPa using an ultrasonic pulse echo method (Table 2; Liebermann et al. 1977), about 7.7% smaller than our $K_T$ value. According to Liu et al. (2016a), the $K_S$ should be ~4 GPa larger than the $K_T$ in any 4–2 spinel. The primary reason for the relatively small $K_S$ is that the velocity data were taken at pressures up to 0.75 GPa only. As illustrated by Rigden et al. (1988) and Rigden and Jackson (1991), this magnitude of experimental pressure would have led to some underestimation of the porosity of the polycrystalline specimen, then some underestimation of the velocities, and eventually some underestimation of the $K_S$.

**Structures of post-spinel phases**

Our compression experiments have suggested that for the Co$_2$TiO$_4$ composition, a phase transition from the Co$_2$TiO$_4$-Sp to a new phase initiates at ~21 GPa. Since our compression experiments were conducted up to ~24 GPa only, where all the major XRD peaks belonged to the Co$_2$TiO$_4$-Sp, and only a few relatively weak XRD peaks were not attributable to the Co$_2$TiO$_4$-Sp (Fig. 2), the exact structure of this new phase could not be practically constrained by the experimental data. According to previous experimental studies (Errandonea 2014, and references therein), a number of structures such as the CM, CF, CT, TDS and ε-MgAl$_2$O$_4$ types are potential candidates. Using the most intense X-ray lines from the new phase [for example, the peak at ~7.1° (1 atm) or at ~7.4° (24 GPa)], we could narrow down the potential candidates to the following three types, the CM, CF and CT structures, but could not tell which one is the correct answer. These three structures have very similar powder XRD patterns (Yamanaka et al. 2008).

Theoretical simulation has been proved to be an effective method for determining the relative stabilities of different polymorphs (e.g., Zhang et al. 2017), and thus employed in this study. The calculated enthalpies of the Sp-fm, CM-fm, CF-fm, CT-fm, Sp-afm, CM-afm, CF-afm and CT-afm structures relative to that of the CF-afm structure for the $P$ range of 0–50 GPa are shown in Fig. 4. Obviously, the Sp-afm has the lowest enthalpy from 0 to ~22 GPa, whereas the CM-afm has the lowest enthalpy from ~22 to ~35 GPa. It follows that the new phase observed in our high-$P$ experiments highly possibly adopts the CM structure. The experimentally observed XRD peaks for the new phase at 5.3 GPa, as summarized in Table 3, support the assignment of the CM structure to the new high-$P$ phase, and the calculated transition $P$ agrees well with the experimental observation. Moreover, the CT-afm attains the lowest enthalpy at $P$ > ~35 GPa, meaning that the CM-afm might further transform to the CT-afm at a pressure somewhere close to ~35 GPa. This structural transition from the CM to CT phase is consistent with Yamanaka et al. (2008). Furthermore, the CF structure never attains the lowest enthalpy at any $P$, implying an insignificant role in the high-$P$ behavior of the Co$_2$TiO$_4$ composition.

**Pressure-induced magnetic transitions**

A pressure-induced magnetic transition is usually accompanied by a volume reduction (e.g., Lin et al. 2013). For the Co$_2$TiO$_4$-Sp, no discernable volume reduction has been confidently observed in our room-$T$ compression experiments (Fig. 3), implying no pressure-induced magnetic transition for this material. This conclusion has been substantiated by
our DFT calculation results; for the $P$ interval from 0 to at least 35 GPa, the enthalpy of the Sp-$\text{afm}$ is always lower than that of the Sp-fm (Fig. 4). We infer, therefore, that no pressure-induced magnetic transition may occur to the $\text{Co}_2\text{TiO}_4$-$\text{Sp}$ material.

On the other hand, the enthalpy of the CM-fm phase is lower than that of the CM-afm phase at $P < \sim 3$ GPa, but higher at higher $P$; the enthalpy of the CT-fm phase is lower than that of the CT-afm phase at $P < \sim 10$ GPa, but higher at higher $P$ (Fig. 4). As a result, pressure-induced magnetic transition might occur to the CM and CT structures. Our preliminary volume data experimentally obtained for the $\text{Co}_2\text{TiO}_4$-$\text{CM}$ (to be shown in the next section), however, do not show any clear evidence of volume variation when the experimental $P$ is decreased from higher than $\sim 3$ GPa to lower than $\sim 3$ GPa, probably suggesting no pressure-induced magnetic transition. Further experimentation is thus highly desirable to resolve this discrepancy.

**Equation of state of $\text{Co}_2\text{TiO}_4$-$\text{CM}$ and $\text{Co}_2\text{TiO}_4$-$\text{CT}$**

The high-$P$ unit-cell parameters of the $\text{Co}_2\text{TiO}_4$-$\text{CM}$ obtained by our compression and decompression experiments are listed in Table 4 and shown in Fig. 5. It appears that the data collected during compression and decompression are well mixed, suggesting that the elastic behavior of the $\text{Co}_2\text{TiO}_4$-$\text{CM}$ is by and large reversible, similar to the elastic behavior of the $\text{Co}_2\text{TiO}_4$-$\text{Sp}$. Further, all the unit-cell parameters vary non-linearly with $P$ for the investigated $P$ range from $\sim 0.6$ to 24 GPa, with the $a$-axis decreasing from 2.837(1) to 2.768(2) Å (by 2.4(1) %), the $b$-axis decreasing from 9.358(8) to 9.120(10) Å (by 2.5(1) %), the $c$-axis decreasing from 9.868(3) to 9.433(3) Å (by 4.76(4) %), and the volume decreasing from 261.93(16) to 237.22(17) Å$^3$ (by 9.4(1) %).

The experimental $P-V$ data for the $\text{Co}_2\text{TiO}_4$-$\text{CM}$ have been fitted to Eq. (1), yielding $V_0 = 263.0(3)$ Å$^3$, $K_T = 161(7)$ GPa and $K'_{\text{CM}} = 7.3(8)$, or $V_0 = 262.2(3)$ Å$^3$ and $K_T = 192(4)$ GPa if $K'_{\text{CM}}$ is fixed as 4 (Table 2). A linearized third-order BM-EoS (Angel 2000) have been used to obtain the parameters of the equations of state for the crystallographic axes, yielding $a_0 = 2.840(1)$ Å and $K_{\text{CM}} = 266(8)$ GPa for the $a$-axis, $b_0 = 9.362(6)$ Å and $K_{\text{CM}} = 257(12)$ GPa for the $b$-axis, and $c_0 = 9.868(11)$ Å and $K_{\text{CM}} = 119(5)$ GPa for the $c$-axis, if the $K'_{\text{CM}}$ are fixed as 4. It follows that the $\text{Co}_2\text{TiO}_4$-$\text{CM}$ has a prominent elastic anisotropy ($K'_{\text{CM}} < K'_{\text{Sp}}$), with the $c$-axis as the most compressible axis. The compressibility of the $a$-axis is somewhat very similar to that of the $b$-axis.

The calculated $P-V$ data for the antiferromagnetic $\text{Co}_2\text{TiO}_4$-$\text{CM}$ have been fitted to Eq. (1) as well, yielding $V_0 = 270.6(2)$ Å$^3$, $K_T = 138(3)$ GPa and $K'_{\text{CM}} = 7.6(3)$, or $V_0 = 268.9(4)$ Å$^3$ and $K_T = 184(3)$ GPa with $K'_{\text{CM}}$ fixed as 4 (Table 2). These EoS parameters are in good agreement with our experimentally determined results if the uncertainty of the GGA method is considered (Zhang et al. 2016, 2017). The $K'_{\text{CM}}$ value of the $\text{Co}_2\text{TiO}_4$-$\text{CM}$ is significantly larger than 4, indicating that the $\text{Co}_2\text{TiO}_4$-$\text{CM}$ phase quickly attains large bulk modulus and becomes highly incompressible as $P$ increases.

The calculated $P-V$ data for the antiferromagnetic $\text{Co}_2\text{TiO}_4$-$\text{CT}$ have been fitted to Eq. (1), yielding $V_0 = 264.6(1)$ Å$^3$, $K_T = 196.8(14)$ GPa and $K'_{\text{CT}} = 5.0(1)$, or $V_0 = 263.6(3)$ Å$^3$ and $K_T = 219.6(26)$ GPa if $K'_{\text{CT}}$ is fixed as 4 (Table 2).

---

**Table 3** Experimentally observed XRD peaks for $\text{Co}_2\text{TiO}_4$-$\text{CM}$ at $\sim 5.3$ GPa (room $T$)

<table>
<thead>
<tr>
<th>$h\ k\ l$</th>
<th>$d_{\text{obs}}$ (Å)</th>
<th>$d_{\text{calc}}$ (Å)</th>
<th>$d_{\text{obs}}-d_{\text{calc}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0 2</td>
<td>4.86569</td>
<td>4.86549</td>
<td>0.00021</td>
</tr>
<tr>
<td>1 1 0</td>
<td>2.70137</td>
<td>2.70178</td>
<td>$-0.00040$</td>
</tr>
<tr>
<td>0 2 3</td>
<td>2.66021</td>
<td>2.66043</td>
<td>$-0.00022$</td>
</tr>
<tr>
<td>1 1 1</td>
<td>2.60290</td>
<td>2.60330</td>
<td>$-0.00039$</td>
</tr>
<tr>
<td>1 1 2</td>
<td>2.36249</td>
<td>2.36204</td>
<td>0.00045</td>
</tr>
<tr>
<td>0 4 0</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>0 2 4</td>
<td>2.15513</td>
<td>2.15561</td>
<td>$-0.00048$</td>
</tr>
<tr>
<td>1 3 0</td>
<td>2.08766</td>
<td>2.08753</td>
<td>0.00013</td>
</tr>
<tr>
<td>1 3 1</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>1 3 2</td>
<td>1.91824</td>
<td>1.91841</td>
<td>$-0.00018$</td>
</tr>
<tr>
<td>0 0 6</td>
<td>1.62184</td>
<td>1.62183</td>
<td>0.00002</td>
</tr>
<tr>
<td>1 1 5</td>
<td>1.57909</td>
<td>1.57915</td>
<td>$-0.00006$</td>
</tr>
<tr>
<td>1 3 5</td>
<td>1.42377</td>
<td>1.42351</td>
<td>0.00026</td>
</tr>
<tr>
<td>1 5 3</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

The unit-cell parameters at 5.3 GPa were $a = 2.824(1)$ Å, $b = 9.301(9)$ Å, $c = 9.731(3)$ Å and $V = 255.55(18)$ Å$^3$.

---

**Table 4** Experimentally obtained unit-cell parameters of $\text{Co}_2\text{TiO}_4$-$\text{CM}$ at various pressures (room $T$)

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.0(1)$^a$</td>
<td>2.773(2)$^b$</td>
<td>9.135(10)</td>
<td>9.419(3)</td>
<td>238.60(17)</td>
</tr>
<tr>
<td>24.0(1)</td>
<td>2.768(2)</td>
<td>9.120(10)</td>
<td>9.398(3)</td>
<td>237.22(17)</td>
</tr>
<tr>
<td>Decompression</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.7(1)</td>
<td>2.774(2)</td>
<td>9.138(9)</td>
<td>9.433(3)</td>
<td>239.08(19)</td>
</tr>
<tr>
<td>12.7(1)</td>
<td>2.799(1)</td>
<td>9.224(9)</td>
<td>9.557(3)</td>
<td>246.75(18)</td>
</tr>
<tr>
<td>10.1(1)</td>
<td>2.806(1)</td>
<td>9.245(5)</td>
<td>9.617(3)</td>
<td>249.45(15)</td>
</tr>
<tr>
<td>8.9(1)</td>
<td>2.809(1)</td>
<td>9.263(9)</td>
<td>9.652(3)</td>
<td>251.19(17)</td>
</tr>
<tr>
<td>5.3(1)</td>
<td>2.824(1)</td>
<td>9.301(9)</td>
<td>9.731(3)</td>
<td>255.55(18)</td>
</tr>
<tr>
<td>0.6(1)</td>
<td>2.837(1)</td>
<td>9.358(8)</td>
<td>9.863(3)</td>
<td>261.93(16)</td>
</tr>
</tbody>
</table>

$^a$Pressure determined by averaging the values measured before and after collection of synchrotron data; uncertainty of the $P$ measurement in the high-$P$ experiments assumed as 0.1 GPa

$^b$Numbers in parentheses representing one standard deviation
The volume changes between the Co$_2$TiO$_4$-Sp phase and the Co$_2$TiO$_4$-CM phase, and between the Co$_2$TiO$_4$-CM phase and the Co$_2$TiO$_4$-CT phase are shown in Fig. 6. As for the first phase transition, the experimentally determined volume change is ~13.3% at ambient conditions or ~12.3% at the phase transition pressure. As for the second phase transition, the theoretically determined volume change is ~2.6% at ambient conditions or ~0.8% at the phase transition pressure.

**Spinel and post-spinel phase assemblages at high P and high T**

Akimoto and Syono (1967) has experimentally demonstrated that the Co$_2$TiO$_4$-Sp decomposes to a CoO-B1 (NaCl-type structure) + CoTiO$_3$-Ilm (ilmenite-type structure) phase assemblage at $P = ~2–4$ GPa and $T = ~1073–1673$ K. Further, Ito and Matsui (1979) has experimentally indicated that the CoTiO$_3$-Ilm decomposes to a CoO-B1 + TiO$_2$-$\alpha$-PbO$_2$ ($\alpha$-PbO$_2$-type structure) phase assemblage at ~20–25 GPa and 1273 K. It follows that the phase assemblage for the Co$_2$TiO$_4$ composition at some high $T$ (1273 K for example) is presumably Co$_2$TiO$_4$-Sp ($P < ~2–3$ GPa), CoO-B1 + CoTiO$_3$-Ilm ($~2–3$ GPa < $P < 20–25$ GPa), and 2CoO-B1 + TiO$_2$-$\alpha$-PbO$_2$ ($P > 20–25$ GPa) as $P$ increases.

With the relevant data from Simons and Dachille (1967), Kidoh et al. (1984), Guo et al. (2002) and this study, the volume difference between the CoO-B1 + CoTiO$_3$-Ilm phase assemblage and the Co$_2$TiO$_4$-Sp, and between the 2CoO-B1 + TiO$_2$-$\alpha$-PbO$_2$ phase assemblage and the Co$_2$TiO$_4$-Sp (ambient $P$ and $T$) has been calculated as ~6.12 and ~8.20%, respectively.

Considering the volume difference between the Co$_2$TiO$_4$-Sp and the Co$_2$TiO$_4$-CM, ~13.3% at ambient $P$ and $T$ (Fig. 6a), the volume difference between the 2CoO-B1 + TiO$_2$-$\alpha$-PbO$_2$ phase assemblage and the Co$_2$TiO$_4$-CM should be ~5.45% (ambient $P$ and $T$). Consequently, it might be possible that at high $P$–$T$ conditions, 2CoO-B1 + TiO$_2$-$\alpha$-PbO$_2$ might recombine to form the Co$_2$TiO$_4$-CM. At still higher $P$, the Co$_2$TiO$_4$-CM might undergo a phase transition to the Co$_2$TiO$_4$-CT, as suggested by this study. It should be noted that a CT phase has been demonstrated for some A$_2$TiO$_4$-Sp including the Fe$_2$TiO$_4$-Sp and Zn$_2$TiO$_4$-Sp (Wang et al. 2002; Yamanaka et al. 2009; Zhang et al. 2017).

The formation of a post-spinel phase (as the Co$_2$TiO$_4$-CM in this study) from the oxides (CoO-B1 and TiO$_2$-$\alpha$-PbO$_2$) resulted from the breakdown reaction of an A$_2$TiO$_4$-Sp (Co$_2$TiO$_4$-Sp) is very interesting, and leads to a tantalizing question: is there a thermodynamically stable post-spinel phase with the Mg$_2$SiO$_4$ composition in the lower mantle of the Earth? Numerous studies have suggested that under equilibrium conditions, the Mg$_2$SiO$_4$-Sp (ringwoodite) should decompose to the phase assemblage of bridgmanite (perovskite-type...
MgSiO$_3$; MgSiO$_3$-Pv) + periclase (rock salt-type structure; MgO-Rs) at the boundary between the upper and lower mantle of the Earth, which should further turn into the phase assemblage of post-perovskite (MgSiO$_3$-PPv) + MgO-Rs at the base of the lower mantle (e.g., Liu 1976; Murakami et al. 2004; Oganov and Ono 2004; Tsuchiya et al. 2004). In other words, no stable post-spinel of the Mg$_2$SiO$_4$ composition has been observed for the lower mantle so far. Considering the difficulty in performing experiments at these challenging P-T conditions, however, the fore-mentioned phase assemblages should be viewed with great caution, and further examined as the high-P experimental techniques advance with time. By performing more experiments, for example, Zhang et al. (2014) recently demonstrated for the lower mantle an Fe-rich hexagonal phase which had never been experimentally detected ever before. Moreover, some new investigations have suggested that some metastable post-spinel structures exist for the Mg$_2$SiO$_4$ composition at very low temperatures up to the ambient T (Finkelstein et al. 2014; Zhou et al. 2015). Further studies are clearly required to examine the metastability (or stability) of these post-spinel structures and their relations to other phases or phase assemblages in the vast P-T space of the lower mantle before a sound answer can be reached.

**Bulk moduli of A$_2$TiO$_4$-Sp**

The bulk moduli of some other A$_2$TiO$_4$-Sp such as the Fe$_2$TiO$_4$-Sp, Mg$_2$TiO$_4$-Sp and Zn$_2$TiO$_4$-Sp have been investigated by the DAC+synchrotron radiation experimental technique as well (e.g., Yamanaka et al. 2009, 2013; Xiong et al. 2015; Lv et al. 2016; Zhang et al. 2017). As shown in Fig. 7, a very good linear relationship is defined by the $V_0$-$K_T$ data of the Co$_2$TiO$_4$-Sp, Mg$_2$TiO$_4$-Sp and Zn$_2$TiO$_4$-Sp:

$$K_T = 2054(58) - 3.1(1)V_0,$$

where $K_T$ is in GPa and $V_0$ in Å$^3$ ($K_T$ fixed as 4). Somehow the $K_T$ of the Fe$_2$TiO$_4$-Sp obtained by Xiong et al. (2015) shows significant deviation.

All A$_2$TiO$_4$-Sp have an inverse spinel structure, (A$^{2+}$)$_{2}$(Ti$^{4+}$)$_{2}$O$_{4}$, with the A cations on the tetrahedral sites in fourfold coordination (IV) and those on the octahedral sites in sixfold coordination (VI). The correlation between the radius of the cation in the tetrahedral and octahedral sites is shown in Fig. 8. The $K_T$ values seemingly decrease linearly with the $r_{0_{-\text{tet}}}$.
where \( K'_T \) is in GPa and \( r_{0-\text{oct}} \) in Å (\( K'_T \) fixed as 4). The nearly vertical trend defined by the \( r_{0-\text{oct}}-K'_T \) data suggests a significant effect on the \( K'_T \) for the cation substitution on the octahedral sites, in good agreement with Hazen and Yang (1999), Lv et al. (2016) and Liu et al. (2016b). On the other hand, the \( r_{0-\text{tet}}-K'_T \) data demonstrate a more complicated pattern: the data for the CoO-TiO\(_4\)-Sp, Mg\(_2\)TiO\(_4\)-Sp and Zn\(_2\)TiO\(_4\)-Sp appear more or less on a straight line (with a positive slope though), but those for the Fe\(_2\)TiO\(_4\)-Sp show large deviation.

The significant deviations of the \( V'_0-K'_T \) and \( r_{0-\text{tet}}-K'_T \) data for the Fe\(_2\)TiO\(_4\)-Sp from the trends defined by those of other three A\(_2\)TiO\(_4\)-Sp might be ascribed to the Jahn–Teller effect of Fe\(^{2+}\) at the tetrahedral sites. Although the Jahn–Teller effect has been well explored on the high-P phase transition of the Fe\(_2\)TiO\(_4\)-Sp (Yamanaka et al. 2009, 2013), its influence on the \( K'_T \) of the Fe\(_2\)TiO\(_4\)-Sp is still unknown so that more investigation on the Jahn–Teller effect in the Fe\(_2\)TiO\(_4\)-Sp is deemed necessary.

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References

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