Equation of State of a Natural Chromian Spinel at Ambient Temperature

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Abstract: A natural chromian spinel with the composition $(\text{Mg}_{0.48(3)}\text{Fe}_{0.52(3)})\text{(Fe}_{0.06(1)}\text{Al}_{0.28(1)}\text{Cr}_{0.66(2)})_2\text{O}_4$ was investigated up to 15 GPa via synchrotron X-ray diffraction with a diamond-anvil cell at room temperature. No phase transition was clearly observed up to the maximum experimental pressure. The pressure–volume data fitted to the third-order Birch–Murnaghan equation of state yielded an isothermal bulk modulus ($K_{T0}$) of 207(5) GPa and its first pressure derivative ($K_{T0}'$) of 3.2(7), or $K_{T0} = 202(2)$ GPa with $K_{T0}'$ fixed as 4. With this new experimental result and the results on some natural chromian spinels in the literature, a simple algorithm describing the relation between the $K_{T0}$ and the compositions of the natural chromian spinels was proposed. To examine this algorithm further, more compression experiments should be performed on natural chromian spinels with different chemical compositions.

Keywords: chemical composition; diamond anvil-cell; equation of state; natural chromian spinel

1. Introduction

The 2-3 spinel oxides, with the general chemical formula $\text{AB}_2\text{O}_4$ ($\text{A} = 2+$ and $\text{B} = 3+$), as well as the so-called 4-2 spinel oxides ($\text{A} = 4+$ and $\text{B} = 2+$; ringwoodite ($\text{Mg,Fe}_2\text{SiO}_4$-spinel for example), are geologically important minerals, and are frequently found in different types of rocks in different geological settings [1]. They all have the cubic $Fd\bar{3}m$ structure, but show wide compositional variation [2]. Due to their compositional diversity, they have been used as key petrogenetic indicators of many geological processes [2–4] and played important roles in constraining pressure, temperature, oxygen fugacity, and other quantities [5–7].

The only major mineral source for metal chromium is the 2-3 natural chromian spinels (termed as Spss hereafter) [8]. These chromian spinels are also among the most common mineral inclusions found in cratonic diamonds and therefore can be used to estimate the formation $P$ and $T$ of the diamonds. To achieve this goal of the $P$–$T$ estimation, the isothermal bulk moduli ($K_{T0}$) of the natural chromian spinels and their compositional dependence should be accurately known. To date, there have been very limited experimental studies on the $K_{T0}$ of the Spss [9–11]. Considering the complicated correlations between the $K_{T0}$ and compositions of the solid solution series of some minerals [12–14], more experimental investigations should be conducted to determine the $K_{T0}$ of the Spss with different compositions.
In this study, the $K_{\text{f0}}$ of an Spss was determined by performing compression experiments at room $T$ using a diamond-anvil cell (DAC) coupled with synchrotron X-ray radiation. Comparing this new result with the results in the literature, the correlation between the $K_{\text{f0}}$ and the compositions of the Spss is tentatively discussed.

2. Experimental Method

The Spss-bearing sample was sourced from the Big Daddy Deposit, Sudbury, ON, Canada [15]. The spinel crystals were black and exhibited good octahedral shape (grain size up to ~400 μm). Nineteen electron microprobe analyses were done with a JEOL JXA-8100 at the School of Earth and Space Sciences, Peking University and gave out the following compositional data, FeO 23.20 wt %, MgO 10.04 wt %, Cr$_2$O$_3$ 51.49 wt %, and Al$_2$O$_3$ 14.86 wt %, leading to the chemical formula of (Mg$_{0.48(3)}$Fe$_{0.52(3)}$)(Fe$_{0.06(1)}$Al$_{0.28(1)}$Cr$_{0.66(2)}$)$_2$O$_4$. Some spinel crystals were picked up and ground into a fine powder, which was then loaded into a DAC. In the DAC experiments, we used a rhenium gasket and a Neon pressure medium, which was loaded by employing the GSECARS high-pressure gas-loading system. A flake of gold (~20 μm in diameter) was placed on the top of the sample to serve as pressure standard and position marker. In-situ high-pressure synchrotron X-ray diffraction experiments with the loaded DAC were performed up to ~15.00 GPa at the beamline 16-ID-B of HPCAT, the Advanced Photon Source of the Argonne National Laboratory. The sample was probed with a monochromatic X-ray beam (beam size $3 \times 3$ μm$^2$, wavelength 0.37379 Å) and the data were collected with a 2-dimensional CCD detector. The sample-to-detector distance and orientation of the detector were calibrated by using a CeO$_2$ powder standard.

3. Result and Discussion

In total, 26 X-ray diffraction (XRD) patterns were collected at pressures from 0.90 to 15.00 GPa (Table 1), with the pressures determined using the Au equation of state (EoS) from Fei et al. [16]. Some XRD patterns are shown in Figure 1. As pressure increases, all XRD peaks shift continuously toward higher 2θ angles. No apparent peak-splitting or new peak has been observed, indicating no phase transition for this spinel up to the maximum experimental pressure. However, several XRD peaks such as the 311 and 511 peaks show slight peak-broadening, potentially implying a structural instability which was somehow kinetically hindered due to the low experimental temperature. The used pressure medium neon can maintain a good hydrostatic experimental condition up to ~15 GPa [17], and should not be the major reason for the observed minor peak-broadening. To ensure a high accuracy in the unit-cell volume refinement, we excluded the peaks 311 and 511 because of their slight broadening.

![Figure 1. Some X-ray diffraction patterns of the natural chromian spinel (cubic Fd$ar{3}$m) at 1.4, 4.4, 8.2, 12.4, and 15.0 GPa. All major peaks can be assigned to the structures of our 2-3 natural chromian spinels (Spss) and Au (marked with asterisks).](image-url)
Table 1. Unit-cell parameters of chromium spinel at high pressures.

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>a (Å)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90(7)</td>
<td>8.284(1)</td>
<td>568.57(14)</td>
</tr>
<tr>
<td>1.37(1)</td>
<td>8.281(1)</td>
<td>567.76(11)</td>
</tr>
<tr>
<td>1.46(2)</td>
<td>8.283(2)</td>
<td>567.76(38)</td>
</tr>
<tr>
<td>1.78(3)</td>
<td>8.275(2)</td>
<td>566.70(38)</td>
</tr>
<tr>
<td>2.07(1)</td>
<td>8.270(1)</td>
<td>565.59(26)</td>
</tr>
<tr>
<td>2.17(2)</td>
<td>8.283(2)</td>
<td>567.76(38)</td>
</tr>
<tr>
<td>1.78(3)</td>
<td>8.275(2)</td>
<td>566.70(38)</td>
</tr>
<tr>
<td>2.07(1)</td>
<td>8.270(1)</td>
<td>565.59(26)</td>
</tr>
<tr>
<td>2.17(2)</td>
<td>8.270(1)</td>
<td>565.59(26)</td>
</tr>
</tbody>
</table>

*a* Numbers in parentheses represent one standard deviation.

The P–V data are summarized in Table 1 and shown in Figure 2. They were fitted to the third-order Birch–Murnaghan equation of state (BM-EoS; [18]):

\[
P = \frac{3}{2} K_{T0} \left[ \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - \left( \frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} K'_{T0} - 4 \left( \frac{V_0}{V} \right)^{\frac{4}{3}} - 1 \right\},
\]

(1)

where P is the pressure (GPa), \( K_{T0} \) the isothermal bulk modulus (GPa), \( K'_{T0} \) the first pressure derivative of the \( K_{T0} \), \( V_0 \) the volume at zero pressure, and \( V \) the volume at high pressure. Using the software EosFit 5.2 [19], we obtained \( K_{T0} = 207(5) \) GPa, \( K'_{T0} = 3.2(7) \), and \( V_0 = 571.69(15) \) Å³, or \( K_{T0} = 202(2) \) GPa with \( K'_{T0} \) fixed to 4 and \( V_0 = 571.79(10) \) Å³.

The quality of our derived BM-EoS can be evaluated by a linear fitting of the normalized pressure (F) as a function of the Eulerian strain (\( f_E \)) (i.e., the \( f_E-F \) plot) [20]. The two variables, F and \( f_E \), are defined as:

\[
F = \frac{P}{3 f_E (1 + 2 f_E)^{\frac{7}{2}}}
\]

(2)

and

\[
f_E = \frac{1}{2} \left[ \left( \frac{V_0}{V} \right)^{\frac{4}{3}} - 1 \right].
\]

(3)

The third-order BM-EoS can then be rewritten as:

\[
F = \frac{3}{2} K_{T0} (K'_{T0} - 4) f_E + K_{T0},
\]

(4)

where the slope of the line defined by the experimental data is equal to \( 3/2 K_{T0}(K'_{T0} - 4) \), and the intercept value is the \( K_{T0} \). Accordingly, a slope of zero means \( K'_{T0} = 4 \), a negative slope \( K'_{T0} < 4 \), and a
positive slope $K_{T0}' > 4$. Figure 3 clearly shows that the $K_{T0}'$ of our $Sp_{ss}$ should be close to 4, supporting a 2nd-order truncation of the BM-EoS fit.

The third-order BM-EoS can then be rewritten as:

$$V_0 = 571.79(10) \text{ Å}^3$$

$$K_{T0} = 202(2) \text{ GPa}$$

$$K_{T0}' = 4$$

**Figure 2.** Effect of pressure on the volume of some $Sp_{ss}$ (300 K). Note that most experimental data points have error bars approximate to or smaller than the symbols. Shu et al. [9], (Mn$_{0.02}$Mg$_{0.30}$Fe$_{0.68}$) (Al$_{0.07}$Fe$_{0.10}$Cr$_{0.83}$)$_2$O$_4$; Fan et al. [10], (Na$_{0.01}$Mg$_{0.68}$Fe$_{0.28}$)$_{0.97}$(Cr$_{1.49}$Al$_{0.51}$)$_{2.03}$O$_4$; Matsukage et al. [11], (Mg$_{0.77}$Fe$_{0.23}$)(Cr$_{0.46}$Al$_{0.5}$Fe$_{0.04}$)$_2$O$_4$. The curves are drawn using the second-order Birch–Murnaghan equation of state, as listed in Table 2. The equations in red are for the natural chromian spinel, (Mg$_{0.48}$Fe$_{0.52}$)(Fe$_{0.06}$Al$_{0.29}$Cr$_{0.68}$)$_2$O$_4$, investigated in this study.

Following Matsukage et al. [11], our $Sp_{ss}$ can be viewed as a complicated solid solution made of the following six end-members, spinel (Sp, MgAl$_2$O$_4$), hercynite (He, FeAl$_2$O$_4$), magnesiocromite (Mg-Ch, MgCr$_2$O$_4$), chromite (Ch, FeCr$_2$O$_4$), magnesioferrite (Mg-Fe, MgFe$_2$O$_4$), and magnetite (Ma, Fe$_3$O$_4$), with their mole percentages calculated as 13.44%, 14.56%, 31.68%, 34.32%, 2.88%, and 3.12%, respectively. The $K_{T0}$ values of these six end-members were experimentally constrained, and are summarized in Table 2. On the assumption of $K_{T0}' = 4$ for all spinel oxides, as proposed by
Liu et al. [13,14], the $K_{T_0}$ of our Sp$_{ss}$ (Sp$_{13}$He$_{15}$Mg-CH$_{32}$CH$_3$Mg-Fe$_3$Ma$_3$) was approximated as 193.4(7) GPa with the following simple algorithm:

$$K_{T_0 - Sp_{ss}} = \sum x_i K_{T_0 - i},$$

where $K_{T_0 - Sp_{ss}}$ denotes the $K_{T_0}$ of the Sp$_{ss}$, $x_i$ the mole fraction of the $i$-th end-member, and $K_{T_0 - i}$ the $K_{T_0}$ of the $i$-th end-member. The absolute difference and relative difference between the approximated bulk modulus and our experimentally measured value were only ~9 GPa and ~4.5%, respectively.

<table>
<thead>
<tr>
<th>Spinel</th>
<th>$V_0$</th>
<th>$K_{T_0}$</th>
<th>$K_{T_0}$</th>
<th>Experimental Details$^a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp$_{ss}$</td>
<td>571.71(1)</td>
<td>207(5)</td>
<td>3.2(7)</td>
<td>0–15; Gold; Ne; Powder</td>
<td>This study</td>
</tr>
<tr>
<td>Sp$_{ss}$</td>
<td>571.8(1)</td>
<td>202(2)</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sp$_{ss}$</td>
<td>579.69(9)</td>
<td>179(10)</td>
<td>3.9(9)</td>
<td>0–29; Ruby; He; SC</td>
<td>[9]</td>
</tr>
<tr>
<td>Sp$_{ss}$</td>
<td>579.69(9)</td>
<td>179(1)</td>
<td>4 c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sp$_{ss}$</td>
<td>557.86</td>
<td>209(9)</td>
<td>7(1)</td>
<td>0–26.8; Mo; MEW; Powder</td>
<td>[10]</td>
</tr>
<tr>
<td>Sp$_{ss}$</td>
<td>556.58(8)</td>
<td>242(7)</td>
<td>4 c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sp$_{ss}$</td>
<td>560.62</td>
<td>192(7)</td>
<td>4(1)</td>
<td>0–10.19; Ruby; ME; Powder</td>
<td>[11]</td>
</tr>
<tr>
<td>Sp$_{ss}$</td>
<td>560.62(2)</td>
<td>192(7)</td>
<td>3.6(13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All compression experiments were done with the diamond-anvil cell (DAC), with some of the experimental details listed in the following order: $P$ range (GPa), pressure scale, pressure medium, and XRD method. Gold, pressure scale of gold from Fei et al. [16] or Heinz and Jeanloz [21]; Ruby, pressure scale of ruby from Mao et al. [27]; Mo, pressure scale of Zhao et al. [28]; Quartz, pressure scale of quartz from Angel et al. [29]. Ne, pressure medium of neon; He, pressure medium of helium; MEW, pressure medium of a 16:3:1 methanol–ethanol–water mixture; ME, pressure medium of a 4:1 methanol–ethanol mixture. Powder, powder XRD; SC, single-crystal XRD.atab Numbers in parentheses represent one standard deviation. $^c$ If the reference did not provide the value of $K_{T_0}$ at $K'_{T_0} = 4$, we calculated it from the $P$–$V$ data.

Matsukage et al. [11] compressed another Sp$_{ss}$ (Sp$_{38}$He$_{13}$Mg-CH$_{32}$CH$_3$Mg-Fe$_3$Ma$_3$) with the chemical formula (Mg$_{0.7}$Fe$_{0.23}$)(Cr$_{0.46}$Al$_{0.5}$Fe$_{0.04}$)$_2$O$_4$ using similar experimental techniques (Table 2; Figure 2). The experimentally-obtained $K_{T_0}$ was 192 GPa, and the approximated $K_{T_0}$ with the above algorithm was 195 GPa, suggesting a relative difference of only 1.5%. Shu et al. [9] studied another Sp$_{ss}$ (Sp$_{25}$He$_{25}$Mg-CH$_{32}$CH$_3$Mg-Fe$_3$Ma$_3$; Mn standing for manganochromite, MnCr$_2$O$_4$) with the chemical formula (Mg$_{0.02}$Mg$_{0.3}$Fe$_{0.68}$)(Al$_{0.07}$Fe$_{0.1}$Cr$_{0.83}$)$_2$O$_4$. The experimentally-obtained $K_{T_0}$ was 179 GPa (Table 2) and the approximated $K_{T_0}$ was 193 GPa, suggesting a large relative difference of 8%, which was presumably caused by the limited and scattering data points (seven data as shown in Figure 2). Fan et al. [10] investigated another Sp$_{ss}$ (Sp$_{19}$He$_{19}$Mg-CH$_{31}$Ch$_{22}$) with the chemical formula (Na$_{0.01}$Mg$_{0.68}$Fe$_{0.28}$)$_3$(Cr$_{1.49}$Al$_{0.54}$)$_2$O$_4$ (Figure 2). Fitting their $P$–$V$ data at room $T$ to Equation (1), we obtained $K_{T_0} = 242(7)$ GPa as $K_{T_0}$ fixed at 4 or $K_{T_0} = 194(17)$ GPa with $K'_{T_0} = 9(2)$. In comparison, the approximated $K_{T_0}$ was only 192 GPa, being 50 GPa smaller than the experimentally-obtained value (with a large relative difference of ~21%); $K'_{T_0}$ fixed at 4. As pointed out by Fan et al. [10], the 16:3:1
methanol–ethanol–water mixture pressure medium used in their experiments resulted in somewhat non-hydrostatic experimental condition at \( P > 10 \) GPa, which in turn should have led to the nominally much larger \( K_{T_0} \) [30].

It is rather interesting that the simple algorithm of Equation (5) could reproduce so well the \( K_{T_0} \) values of the Sp\(_{ss}\) established by the properly-performed experiments, but reject the \( K_{T_0} \) values of the Sp\(_{ss}\) yielded by the malfunctioned experiments (Figure 4); According to our experience, a relative difference of \(-5\%\) (or even much larger) among the \( K_{T_0} \) values determined for certain minerals using similar experimental techniques is not unusual [7,13]. If this observation is confirmed by further experimental studies on the Sp\(_{ss}\) of different compositions, Equation (5) may provide a convenient method to estimate the \( K_{T_0} \) of those Sp\(_{ss}\) inclusions hosted by the diamonds. Meanwhile, we should keep in mind that Liu et al. [14] discovered a non-monotonic correlation between the \( K_{T_0} \) and composition for the (Mg\(_{1-x}\)Mn\(_x\))\( \text{Cr}_2\text{O}_4 \) spinel solid solutions. Nevertheless, it is highly possible that the cations in the Sp\(_{ss}\) might more randomly enter the spinel structure, which should then result in a generally ideal mixing behavior, whereas the Mg and Mn cations in the (Mg\(_{1-x}\)Mn\(_x\))\( \text{Cr}_2\text{O}_4 \) spinel solid solutions can compete for the T-site only, which eventually leads to a significant deviation from an ideal mixing.

![Graph](image)

**Figure 4.** \( K_{T_0} \) vs. \( V_0 \) of some Sp\(_{ss}\) and their six end-members Sp, He, Mg-Ch, Ch, Ma, and Mg-Fe. The plotted experimental results and their sources for the six end-members, plus some experimental details, are listed in Table 2. The symbols for the Sp\(_{ss}\) are the same as those in Figure 2, with the filled symbols standing for the experimental results whereas the empty symbols represent the approximated results. Note that the Sp\(_{ss}\) from [9] can be recasted as Sp\(_{2}\)He\(_{5}\)Mg-Ch\(_{25}\)Ch\(_{56}\)Mg-Fe\(_{3}\)Ma\(_{2}\); that from [10] as Sp\(_{19}\)He\(_{5}\)Mg-Ch\(_{51}\)Ch\(_{22}\); that from [11] as Sp\(_{38}\)He\(_{12}\)Mg-Ch\(_{35}\)Ch\(_{11}\)Mg-Fe\(_{3}\)Ma\(_{1}\); and that from this study as Sp\(_{13}\)He\(_{15}\)Mg-Ch\(_{32}\)Ch\(_{34}\)Mg-Fe\(_{3}\)Ma\(_{3}\). The Sp\(_{ss}\) from [9] has 2\% managanochromite (Mn, MnCr\(_2\)O\(_4\)), which has \( K_{T_0} = 199.2(106) \) GPa with a fixed \( K'_{T_0} \) of 4 [14].

**Author Contributions:** Conceptualization, X.L. and S.R.S.; Validation, X.L.; Investigation, Z.M., W.S.; Writing—Original Draft Preparation, Z.M.; Writing—Review & Editing, X.L.; Supervision, X.L., S.R.S., L.Z.; Project Administration, X.L.; Funding Acquisition, X.L., S.R.S., L.Z. All authors discussed the results and commented on the manuscript.

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Conflicts of Interest: The authors declare no conflict of interests.

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