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Pressure-volume equation of state for chromite and magnesiochromite: a single-crystal X-ray diffraction investigation

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ABSTRACT

The pressure-volume equation of state for the two spinel end-member compositions chromite FeCr_2O_4 and magnesiochromite MgCr_2O_4 was determined for flux-grown synthetic single crystals at room temperature up to 8.2 and 9.2 GPa, respectively, by single-crystal X-ray diffraction using a diamond-anvil cell. The pressure-volume data show that the linear volume compressibility (here used only for purpose of comparison), calculated as $\beta_V = [(\Delta V/V_0)/\Delta P]$, is 0.00468 and 0.00470 GPa^{-1} , for chromite and magnesiochromite, respectively, with a negligible difference below 0.5%. The experimental data were fitted to a 3rd-order Birch-Murnaghan equation of state (BM3) allowing a simultaneous refining of the following coefficients: $V_0 = 588.47(4) \text{ \AA}^3$, $K_{T0} = 184.8(1.7) \text{ GPa}$ and $K' = 6.1(5)$ for chromite and $V_0 = 579.30(4) \text{ \AA}^3$, $K_{T0} = 182.5(1.4) \text{ GPa}$ and $K' = 5.8(4)$ for magnesiochromite.

The difference in K_{T0} is reduced to less than 1.5% going from Fe to Mg end-member composition, whereas the first pressure derivative seems not to be affected by the chemical variability. The limited difference in the equation of state coefficients recorded for FeCr_2O_4 and MgCr_2O_4 allowed us to fit the pressure-volume data of both to a single BM3 equation, resulting in a $K_{T0} = 184.4(2.2) \text{ GPa}$ and $K' = 5.7(6)$.

INTRODUCTION

Spinel belonging to the chromite-magnesiochromite (FeCr_2O_4 - MgCr_2O_4) solid solution series are among the most common inclusions found in diamonds (Stachel and Harris 2008), and because of that this work represents a contribution to a wider project focused on minerals found as inclusions in diamonds (ERC Starting Grant 2012, 307322). As demonstrated by

39 Nestola et al. (2011a) studying olivine micro-crystals included in diamond, it is crucial to
40 obtain accurate and precise thermo-elastic parameters in order to apply the so called “elastic
41 method” capable to determine the pressure of formation of the diamond-inclusion pair. Thus,
42 this study aims at being an important starting point in terms of available thermodynamic data
43 to help in determining the pressure of spinel formation in diamond.

44 Spinel minerals present a wide range of solid solutions with a chemistry reflecting igneous
45 processes and superimposed metamorphic effects (Perinelli et al. 2012 and references therein).
46 In particular, chromite-magnesiochromite spinels are frequent in ultramafic and mafic rocks
47 originated from primitive, mantle-derived magmas (Barnes and Roeder 2001). Chromium-
48 spinels are typically only accessories phases but widely recognized as important petrogenetic
49 indicators (e.g., Irvine 1965, 1967; Evans and Frost 1975; Sack and Ghiorso 1991; Bosi et al.
50 2008) because they present compositional variations and order-disorder modifications related
51 to the petrologic processes in which they are involved (e.g., Perinelli et al. 2014). Chromium-
52 spinels are stable over a wide range of temperatures and pressures in the Earth upper mantle
53 and therefore the determination of their thermoelastic properties becomes fundamental to
54 better define the thermodynamic modeling of Cr-bearing minerals in mantle assemblages.
55 Besides Cr, the equilibrium inter-crystalline exchange of Mg and Fe²⁺ cations has been
56 intensely analyzed, and revealed its great potential to be used as geothermometer in rocks
57 containing the paragenesis olivine-spinel (Fabries 1979; Ballhaus 1990), as geobarometer in
58 rocks containing olivine, garnet and pyroxene (O'Neill 1981; O'Neill and Wall 1987), and as
59 oxygen barometer in rocks containing olivine-orthopyroxene-spinel (Ballhaus 1991). Finally,
60 adopting the “elastic method” as in Nestola et al. (2011a), spinels can represent an important
61 potential geobarometer for the diamond formation.

62 Spinel has general formula AB₂O₄, and their cation distribution is represented as ^{IV}(A<sub>1-
63 x</sub>B_x)^{VI}(B_{2-x}A_x)O₄, where commonly A = Mg, Fe²⁺, Zn, Mn²⁺ and B = Al, Fe³⁺, Cr³⁺, and IV
64 and VI represents tetrahedrally coordinated T sites and octahedrally coordinated M sites,
65 respectively. *Normal* spinels have $x = 0$ and *inverse* spinels have $x = 1$; however, intermediate
66 ($0 < x < 1$) disordered cation distributions are possible between the two extremes (e.g.,
67 O'Neill and Navrotsky 1983; Andreozzi and Lucchesi 2002; Martignago et al. 2006;
68 Hålenius et al. 2011; Bosi et al. 2012). The chromite-magnesiochromite series exhibits an
69 ordered ^{IV}A^{VI}B₂O₄ cation distribution at room temperature with Cr³⁺ cation completely
70 ordered at the M site and both Fe²⁺ and Mg ordered at the T site (Navrotsky and Kleppa 1967;
71 O'Neill and Dollase 1994). The detailed crystal chemistry of the MgCr₂O₄-FeCr₂O₄ series is
72 reported in Lenaz et al. (2004), where the influence of Fe²⁺-Mg substitution on spinel

73 structural parameters was investigated by single-crystal X-ray diffraction, electron
74 microprobe analyses, optical absorption, infrared and Mössbauer spectroscopies. The T-O
75 bond lengths are strongly affected by the presence of Fe^{2+} and/or Mg at the T site, and
76 significantly increase as a function of increasing Fe^{2+} , namely chromite content (Lenaz et al.
77 2004). Furthermore, both the cell edge a_0 and the oxygen positional parameter u also increase
78 with chromite content.

79 The study of comparative compressibility between ordered and disordered MgAl_2O_4 spinel
80 sensu stricto (s.s.) was carried out by Nestola et al. (2007). In spite of quite different cation
81 distributions, the results obtained indicate that the cation disorder has practically no effect on
82 spinel s.s. elastic behavior. The influence of Fe^{2+} substitution on the elastic properties of the
83 silicate Fe_2SiO_4 phase with the ringwoodite spinel structure has been recently investigated by
84 Nestola et al. (2010) who determined a bulk modulus value of $K_{T0} = 187(2)$ GPa, comparable
85 to the average value of $K_{T0} = 184$ GPa obtained for Mg_2SiO_4 by Hazen (1993), Jackson et al.
86 (2000) and Li (2003). Provided that the behavior along the Fe-Mg series may be considered
87 linear (and this is far to be undisputed), this result may be considered as a strong indication
88 that Mg- Fe^{2+} substitution has little or no effect on the elastic properties of ringwoodite. For
89 oxide spinels, the influence of pressure on chromite and magnesiochromite end members has
90 been recently investigated by Kyono et al. (2012) and Yong et al. (2012), respectively. The
91 former authors studied synthetic chromite by single-crystal X-ray diffraction and found a bulk
92 modulus of $K_{T0} = 209(13)$ GPa and K' fixed to 4. The latter authors investigated synthetic
93 magnesiochromite powders by *in situ* X-ray powder diffraction and Raman spectroscopy and
94 obtained a bulk modulus of $K_{T0} = 189(2)$ GPa, together with its first derivative $K' = 7.2(3)$
95 GPa. An intermediate value of bulk modulus was obtained by Matsukage et al. (2010) on a
96 natural Cr-spinel with composition $[(\text{Mg}_{0.77}\text{Fe}^{2+}_{0.23})(\text{Cr}_{0.46}\text{Al}_{0.50}\text{Fe}^{3+}_{0.04})\text{O}_4]$ by powder X-ray
97 diffraction using synchrotron radiation with $K_{T0} = 192(7)$ GPa, its pressure derivative of $K' =$
98 $4(1)$.

99 In the present study, new equation of state (EoS) parameters (both K_{T0} and K') are obtained for
100 synthetic chromite and magnesiochromite single crystals by using *in situ* high-pressure single-
101 crystal X-ray diffraction. The compression data were acquired following the same
102 experimental procedure for both samples, with the aim to obtain accurate comparison of
103 chromite and magnesiochromite elastic properties.

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106 **EXPERIMENTAL METHODS**

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109 **Samples**

110 Spinel single-crystals of MgCr_2O_4 and FeCr_2O_4 composition were synthesized by a flux-
111 growth method in the laboratory of Sapienza University of Rome following the conditions
112 reported in Andreozzi (1999) and Quintiliani et al. (2011). Analytical grade MgO , Fe_2O_3 and
113 Cr_2O_3 were dehydrated and dried at $900\text{ }^\circ\text{C}$ for 1 hour before mixing with $\text{Na}_2\text{B}_4\text{O}_7$, used as
114 flux compound. The flux/nutrients ratio of each composition was determined by trial and
115 error, as no specific literature data was found. About 2 g of starting material were thoroughly
116 ground and mixed under acetone in an agate mortar and then transferred to a Yttrium-
117 stabilized 10-cc Pt/Au (5%) crucible. The latter was suspended inside a vertical furnace
118 whose heating elements guarantee a homogeneous temperature zone of 30 cm. The furnace is
119 equipped with a multi-step temperature controller and an oxygen fugacity control system,
120 which uses a binary gas mixture ($\text{CO}_2\text{-H}_2$). For both compositions thermal runs consisted of a
121 rather steep increment of temperature up to $1200\text{ }^\circ\text{C}$, then the temperature was kept constant
122 for 24 hours and linearly decreased down to $900\text{ }^\circ\text{C}$ with $4\text{ }^\circ\text{C/h}$ cooling rate. During the
123 synthesis of chromite, to keep iron in the Fe^{2+} oxidation state, the ratio CO_2/H_2 was kept
124 constant at 58/2 and oxygen fugacity ranged from 10^{-8} to 10^{-13} bars at 1200 and $900\text{ }^\circ\text{C}$,
125 respectively. During thermal runs, both T and $f\text{O}_2$ were monitored by sensors close to the
126 crucible, and recorded by a computer software. At the end of thermal runs the heating
127 elements were switched off and crucibles were allowed to rapidly cool down. Visual
128 inspection revealed that products consisted of an intergrowth of octahedral spinel crystals and
129 elongated, prismatic Fe-Mg-borate crystals embedded in minor Na-borate glass. The products
130 were immersed in hot, dilute hydrochloric acid for few days to dissolve glass and borates.
131 Hundreds of octahedral to sub-octahedral spinel crystals ~ 0.3 mm large were handpicked
132 under a binocular microscope, and gem-quality inclusion-free perfect octahedral single
133 crystals were selected for X-ray diffraction and high-pressure experiments.

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136 **X-ray diffraction at ambient conditions**

137 X-ray diffraction measurements were performed at Earth Sciences Department, Sapienza
138 University of Rome, with a Bruker KAPPA APEX-II single-crystal diffractometer, equipped
139 with CCD area detector ($6.2 \times 6.2\text{ cm}^2$ active detection area, 512×512 pixels) and a graphite
140 crystal monochromator, using $\text{MoK}\alpha$ radiation from a fine-focus sealed X-ray tube. The

141 sample-to-detector distance was 4 cm. A total of about 5000 exposures per sample (step =
142 0.2°, time/step = 10 s) covering a full reciprocal sphere were collected. The orientation of the
143 crystal lattice was determined from 500 to 1000 strong reflections ($I > 100 \sigma_I$) evenly
144 distributed in the reciprocal space, and used for subsequent integration of all recorded
145 intensities. Final unit-cell parameters were refined by means of the Bruker AXS SAINT
146 program from ca. 2500 recorded reflections with $I > 10 \sigma_I$ in the range $8^\circ < 2\theta < 90^\circ$. The
147 intensity data were processed and corrected for Lorentz, polarization and background effects
148 with APEX2 software program of Bruker AXS. The data were corrected for absorption using
149 multi-scan method (SADABS). The absorption correction led to a significant improvement in
150 R_{int} . No violation of $Fd\bar{3}m$ symmetry was noted. Sporadic appearance of forbidden space-
151 group reflections was recognized as double reflections.

152 Structural refinements were done with the SHELXL program (Sheldrick 2008). Setting the
153 origin at $\bar{3}m$, initial atomic positions for oxygen atoms were taken from the structure of
154 spinel (Bosi et al. 2010). Variable parameters were overall scale factor, extinction coefficient,
155 atomic coordinates and atomic displacement factors. No chemical constraint was applied
156 during the refinement. To obtain the best values of statistical indexes ($R1$ and $wR2$) the
157 oxygen site was modeled with neutral vs. full ionized oxygen scattering curves, while neutral
158 curves were used for the cation sites. In detail, the T site was modeled considering the
159 presence of Fe (for the chromite) and Mg (for the magnesiochromite) scattering factors,
160 whereas the M site was modeled by Cr scattering factor. Both the cation sites were modeled
161 with a fixed occupancy of 1.000, because refinement with unconstrained T- and M-
162 occupancies showed no significant deviations. Three full-matrix refinement cycles with
163 isotropic displacement parameters for all atoms were followed by anisotropic cycles until
164 convergence was attained, that is, when the shifts in all refined parameters were less than their
165 estimated standard deviations. Correlations over 0.7 were observed for chromite (among U^{11}
166 of Cr, overall scale factor and extinction coefficient) and for the magnesiochromite (between
167 U^{11} of Cr and overall scale factor) at the end of refinement. Table 1 summarizes structural
168 parameters and refinement details.

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171 **X-ray diffraction at high pressure**

172 Dark brownish-color crystals of chromite ($130 \times 100 \times 40 \mu\text{m}$) and magnesiochromite ($100 \times$
173 $87 \times 40 \mu\text{m}$) were used for high-pressure unit-cell parameter determination by means of high-

174 pressure single-crystal diffraction experiments. The crystals were selected on the basis of their
175 crystal size, lack of twinning and sharpness of diffraction profiles. High-pressure single-
176 crystal diffraction measurements were performed in an ETH-type diamond-anvil cell (DAC)
177 equipped with Be-backing plates (Miletich et al. 2000). Two separate sets of data were
178 acquired for each end-member compositions, loading each crystal sample in a DAC together
179 with a single-crystal of quartz used as an internal pressure standard (Angel et al. 1997).
180 Stainless steel gaskets pre-indented to a thickness of 90 μm and with a spark eroded hole of
181 250 μm in diameter were used. A mixture of methanol and ethanol (4:1) was used as a
182 pressure-transmitting medium. The data were acquired using $\text{MoK}\alpha$ radiation at 50 kV and 40
183 mA. The measurements of the unit-cell edge and volume were carried out on a four-circle
184 STOE STADI-IV single-crystal diffractometer at the Dipartimento di Geoscienze of the
185 University of Padua (Italy), equipped with a point detector and controlled by the SINGLE
186 software (Angel and Finger 2011). Unit-cell edge and volume were determined from the
187 centering of at least 16 reflections for each high-pressure measurements, in the 2θ range
188 between 8° and 28° . Typical half-widths of reflections were between 0.08° and 0.1° in ω . Full
189 details of the instrument and the peak-centering algorithms are provided in Angel et al. (2000).
190 During the centering procedure the effects of crystal offsets and diffractometer aberrations
191 were eliminated from the refined peak positions using the eight-position centering method
192 (King and Finger 1979). Unconstrained unit-cell parameters, obtained by vector least-squares
193 (Ralph and Finger 1982), were measured for chromite at 11 pressures up to 8.241(9) and for
194 magnesiocromite at 13 different pressures from room pressure up to 8.046(12) GPa. The
195 experiments for both compositions were stopped at the maximum pressure reached before
196 damaging due to the gasket failure.

197

198 **RESULTS**

199 **Crystal structure at room pressure**

200 The crystal structure of FeCr_2O_4 and MgCr_2O_4 were collected with the crystals in air in order
201 to thoroughly characterize the material before high pressure investigation. The structures of
202 FeCr_2O_4 and MgCr_2O_4 are fully consistent with the space group $Fd\bar{3}m$. The refined
203 occupancies show no cation vacancy, which could affect the high-pressure data (see Nestola
204 et al. 2009). Although Sickafus et al. (1999, and references therein) suggested that a reduction
205 in symmetry would apply to spinel with the M site dominated by Cr, the present results
206 provide no evidence of lower symmetry in the X-ray diffraction data. Structural refinement

207 results show that FeCr_2O_4 and MgCr_2O_4 are normal spinel with Fe^{2+} and Mg ordered at the T
208 site and Cr^{3+} ordered at the M site. The measured tetrahedral bond distances are ${}^{\text{T}}\text{Fe}^{2+}\text{-O} =$
209 1.998 \AA and ${}^{\text{T}}\text{Mg-O} = 1.967 \text{ \AA}$, and the octahedral bond distance is ${}^{\text{M}}\text{Cr-O} = 1.994 \text{ \AA}$ (Table
210 1), in excellent agreement with results of Lenaz et al. (2004).

211

212 **Volume equation of state**

213 The unit-cell edge and volume measured at different pressures for chromite and
214 magnesiochromite are reported in Table 2. The unit-cell volume for both end-member
215 compositions decreases continuously as a function of pressure, with no evidence of phase
216 transitions up to the maximum pressure (Fig. 1). The decreasing volume trend is nearly
217 parallel for the two samples investigated, showing a linear volume compressibility (e.g. we
218 here use a linear expression only for comparison with previous works) $\beta_V = 0.00468(6)$ and
219 $0.00470(5) \text{ GPa}^{-1}$, for FeCr_2O_4 and MgCr_2O_4 , respectively (with $\beta_V = [(\Delta V/V_0)/\Delta P]$). The F_E -
220 f_E plot, where f_E is defined as the Eulerian strain $[(V_0/V)^{2/3} - 1]/2$ and F_E the normalized
221 stress $[P/(3f_E) \times (1 + 2f_E)^{5/2}]$ (Angel 2000), was obtained from the P - V data of the two end-
222 member compositions (Fig. 2). The plot in Figure 2 is a useful visual tool to define which is
223 the best equation of state capable to describe adequately the unit-cell volume compression
224 trends: the high-pressure data on the F_E - f_E plot fall on a positive straight line indicating that a
225 third-order Birch-Murnaghan equation of state (BM3-EoS; Birch 1947) properly represents
226 the experimental P - V data of both end-members. Thus, the P - V data sets for the two end-
227 members were fitted to a BM3-EoS, refining simultaneously the unit-cell volume (V_0), the
228 bulk modulus (K_{T0}) and its first derivative (K'). By using the EoSFIT5.2 software (Angel
229 2000), we refined the following coefficients: $V_0 = 588.47(4) \text{ \AA}^3$, $K_{\text{T0}} = 184.8(1.7) \text{ GPa}$ and $K' =$
230 $6.1(5)$ for chromite and $V_0 = 579.30(4) \text{ \AA}^3$, $K_{\text{T0}} = 182.5(1.4) \text{ GPa}$ and $K' = 5.8(4)$ for
231 magnesiochromite (Table 3). In the F_E - f_E plot, the intercept line on the F_E -axis line gives the
232 value of bulk modulus, whereas the slope is equal to $3K_{\text{T0}}(K' - 4)/2$ (Angel 2000). The K_{T0} and
233 K' values obtained from F_E - f_E plot displayed in Figure 2 are comparable, within standard
234 uncertainties, with those obtained from the least-squares refinement using a BM3-EoS,
235 indicating the high accuracy of present P - V data. The positive slope of the linear regression of
236 the F_E - f_E data confirms that K' is greater than 4 and, therefore, according to Angel (2000), the
237 BM3-EoS well describes our P - V data for both investigated samples.

238 The values of the two refined variables K_{T0} and K' are strongly correlated (usually comprised
239 between -90% and -95% ; Angel 2000), and this must be taken into consideration when

240 comparing a set of EoS parameters determined by least-square refinement, as done in this
241 study. In such a refinement indeed the K_{T0} and K' values are independently determined,
242 resulting generally in an underestimation of their standard uncertainties. Therefore, in order to
243 visualize the correlation between these parameters, it is usual to make use of a series of
244 confidence ellipses in the parameter space whose axes x and y represent values of K_{T0} and K'
245 (e.g., Bass et al. 1981). This approach was followed in the present case, and Figure 3 displays
246 the confidence ellipses of chromite and magnesiochromite corresponding to 68.3% and 90%
247 of confidence level, obtained from a matrix which consists of variance and covariance of K_{T0}
248 and K' calculated from the least-square procedure (see Angel 2000 for details). With the
249 purpose of comparison, the confidence ellipses are also constructed for the spinel s.s.
250 $MgAl_2O_4$, using the elastic parameters obtained for the ordered cation distribution by Nestola
251 et al. (2007) (Table 3). The ellipses created for chromite and magnesiochromite, as well as
252 that of the spinel s.s., are strongly elongated with a negative slope, reflecting the negative
253 correlation between K_{T0} and K' parameters (Fig. 3). For all the compositions the inner ellipse
254 represents an area in K_{T0} and K' parameter space with 68.3% confidence level (e.g., the
255 probability of the true values of K_{T0} and K' to lie in that area), and the outer one is for a
256 confidence level of 90%. For the chromite end member, considering the 90% confidence
257 ellipse, the K_{T0} values can vary in the range 181.1-188.5 GPa. Such an interval overlaps
258 almost entirely the K_{T0} variation range for magnesiochromite, spanning 179.4-185.6 GPa. The
259 K' values range obtained for chromite from the ellipses within the 90% of confidence level is
260 5.1-7.1, practically including the whole range of the K' parameter obtained for
261 magnesiochromite ($K' = 5.1-6.5$). Therefore, from the ellipses construction (Fig. 3) the K'
262 value falls for both the compositions chromite and magnesiochromite practically in the same
263 range, while the K_{T0} is minimally affected by the Mg-Fe²⁺ substitution. The comparison with
264 the confidence ellipses for spinel s.s. highlights a stronger influence of the chemical
265 composition on K_{T0} . In fact, even though the K' range ($K' = 4.8-6.2$) for spinel s.s. remains
266 comparable to those obtained for chromite and magnesiochromite, the K_{T0} values within the
267 90% confidence level are quite higher ($K_{T0} = 190.6-195.4$ GPa).

268 The close proximity of chromite and magnesiochromite elastic parameters is also evident
269 from the comparison of the V/V_0 relative-compression data (Fig. 4). Because the data for both
270 compositions lie on a single P - V trend, a unique equation of state can be calculated, as already
271 discovered for different olivine compositions by Nestola et al. (2011b). The dashed curve in
272 Figure 4 represents the BM3-EoS that fits all the experimental P - V data reported in Table 2,
273 and for which a $K_{T0} = 184.4(2.2)$ GPa and $K' = 5.7(6)$ are resulted by means of the EoSFit5.2

274 software (Angel 2000).

275

276 **DISCUSSION**

277 A single equation of state was obtained in this study for both chromite and magnesiochromite.
278 Negligible difference between the two end-members is observed for the bulk modulus values,
279 with the K_{T0} of chromite [184.8(1.7) GPa] being slightly higher than that for
280 magnesiochromite [182.5(1.4) GPa], and the K' values being identical within experimental
281 uncertainties. When comparing the present results with those obtained for the ordered spinel
282 s.s., no significant differences are observed for the K' value, whereas a larger difference is
283 observed for the bulk modulus, because this latter increases up to 193(1) GPa for the spinel
284 s.s. (Nestola et al. 2007). Such results would imply that the Mg-Fe²⁺ substitution at the T site
285 of Cr-spinels has a minimum effect on the elastic properties and, compared to spinel s.s.,
286 chromite and magnesiochromite present a relatively higher compressibility. A very important
287 peculiarity of the comparison between the spinel samples performed in this study is the
288 identical experimental method used for the EoS determination, e.g., based on the same single-
289 crystal diffractometer, which is the same previously adopted for spinel s.s. by Nestola et al.
290 (2007).

291 For the chromite end-member all the EoS parameters have been determined here for the first
292 time, and the refined values of K' are quite different from the fixed value of 4 assumed by
293 Kyono et al. (2012). The bulk modulus obtained by Kyono et al. (2012) by means of single-
294 crystal X-ray diffraction is 209(13) GPa. This value is significantly higher than ours, 185(2)
295 GPa, obtained by single-crystal X-ray diffraction, and is also affected by extremely larger
296 standard uncertainties. Such a difference could be due to the fact that K' was not measured but
297 fixed by Kyono et al. (2012), because as already mentioned K_{T0} and K' are strongly correlated
298 in the fit of P - V data (Angel 2000). Moreover, the large standard uncertainties for the K_{T0} in
299 Kyono et al. (2012) could be connected to the few data points used for their EoS
300 determination. For the magnesiochromite end-member, the high-pressure data previously
301 acquired by Yong et al. (2012) using X-ray powder diffraction method and Raman
302 spectroscopy were refined to a $K_{T0} = 189(2)$ GPa, a value highly consistent with the one
303 obtained in this study [183(1) GPa] and a $K' = 7.2(3)$, which is slightly higher than our 5.8(4).

304

305 **IMPLICATIONS**

306 Spinel is quite often found as inclusions in diamonds recovered from peridotitic mantle
307 source, and, in particular, frequently have magnesiochromite composition (Stachel and Harris

308 2008). The chemical analysis of spinels included in diamonds reported by Lenaz et al. (2009)
309 showed that the most abundant component is magnesiochromite followed by chromite and
310 hercynite (FeAl_2O_4)[in detail magnesiochromite + chromite reach about 90% whereas
311 hercynite is close to 6-7%]; besides, spinel s.s., magnesioferrite (MgFe_2O_4) and magnetite
312 (Fe_3O_4) were present in minor proportions (e.g. 2-3%). The P - V equation of state for
313 magnesioferrite [$K_{T0}=181.5(1.3)$ GPa and $K'=6.32(14)$] were provided by Levy et al. (2004)
314 using in situ high-pressure X-ray powder diffraction, and for magnetite [$K_{T0}=180.0(1.0)$ GPa
315 and $K'=5.2(4)$] by Reichmann and Jacobsen (2004) using single-crystal X-ray diffraction.
316 These thermoelastic parameters are comparable to those obtained for chromite and
317 magnesiochromite in this study, and the acquisition of P - V data for hercynite would allow
318 deeper understanding of high-pressure behavior of spinels included in diamonds.
319 Furthermore, the reliable equations of state obtained for the investigated compositions could
320 be applied to get very precious and highly chased information (e.g., the diamond formation
321 pressure; Izraeli et al. 1999; Sobolev et al. 2000) on diamonds with spinel inclusions using
322 non-destructive techniques, as already described for olivine and garnet inclusions (Nestola et
323 al. 2011a, 2012; Shirey et al. 2013).

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327

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330 $(\text{Mg,Fe})_2\text{TiO}_4$, $(\text{Mg,Cu})\text{Al}_2\text{O}$ e $(\text{Mg,Fe})(\text{Al,Cr})_2\text{O}_4$...” to GBA and FB.

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- 484

485 **FIGURE CAPTIONS**

486

487 **FIGURE 1** Evolution of the unit-cell volume as a function of pressure for chromite and
488 magnesiochromite studied in this work. The dashed lines represent the fit of the third-order
489 Birch-Murnaghan EoS of the P - V data. The standard uncertainties are smaller than the
490 symbols used.

491

492 **FIGURE 2** Normalized pressure F_E versus Eulerian strain f_E calculated for the P - V data of
493 chromite (closed symbol) and magnesiochromite (open symbol). The solid lines are weighted
494 linear regression through the data points and yield the intercept value $K_{T0} = 184.6(1.4)$ GPa
495 and $K_{T0} = 183.2(1.1)$ GPa, respectively for chromite and magnesiochromite. From their slope
496 the K' values can be calculated, which are 6.2(5) and 5.6(1), respectively for chromite and
497 magnesiochromite (see Angel 2000 for details).

498

499 **FIGURE 3** Confidence ellipses in K_{T0} and K' for the fit of the BM3 EoS to the chromite and
500 the magnesiochromite of this study compared with that obtained for spinel *sensu stricto*,
501 $MgAl_2O_4$, with ordered cation distribution (Nestola et al. 2007). For each composition, the
502 inner ellipse is for a 68.3% confidence level (chi-square distribution with 2 degrees of
503 freedom $\Delta = 2.30$; see Angel 2000 for details) and the outer one is for 90% confidence level
504 ($\Delta = 4.61$). The values of K_{T0} and K' determined by the least-squares refinement using the
505 software EoS fit 5.2 (Angel 2000) are also shown. Error bars correspond to $\pm 1\sigma$.

506

507 **FIGURE 4** Evolution of the V/V_0 relative compression with pressure for the chromite (blue
508 closed symbol) and magnesiochromite (red open symbol) data of this study. The dashed line
509 represents a unique fit using a third-order Birch-Murnaghan equation of state for both
510 compositions.

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514 **TABLE 1.** Selected X-ray diffraction data for synthetic chromite and magnesiochromite

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Crystal	FeCr ₂ O ₄	MgFe ₂ O ₄
Crystal size (mm)	0.26 × 0.26 × 0.21	0.17 × 0.16 × 0.14
<i>a</i> (Å)	8.3779(3)	8.3324(5)
<i>u</i>	0.26270(9)	0.26128(5)
<i>T</i> -O (Å)	1.9981(14)	1.9669(8)
<i>M</i> -O (Å)	1.9938(7)	1.9935(4)
<i>T</i> -m.a.n.	26.00	12.00
<i>M</i> -m.a.n.	24.00	24.00
<i>T</i> - <i>U</i> ¹¹ (Å ²)	0.01057(16)	0.00485(11)
<i>M</i> - <i>U</i> ¹¹ (Å ²)	0.00780(15)	0.00365(7)
<i>M</i> - <i>U</i> ¹² (Å ²)	-0.00035(4)	-0.00022(2)
O- <i>U</i> ¹¹ (Å ²)	0.0089(2)	0.00460(11)
O- <i>U</i> ¹² (Å ²)	-0.00031(18)	-0.00009(9)
ρ (g/cm)	5.057	4.416
Range for data collection, θ (°)	4.21 - 45.22	4.24 - 45.12
Reciprocal space range <i>hkl</i>	-16 ≤ <i>h</i> ≤ 16	-16 ≤ <i>h</i> ≤ 12
	-16 ≤ <i>k</i> ≤ 11	-16 ≤ <i>k</i> ≤ 12
	-8 ≤ <i>l</i> ≤ 16	-12 ≤ <i>l</i> ≤ 13
EXTI	0.155(7)	0.0094(7)
Total number of frames	5129	5139
Set of measured reflections	2675	3045
Unique reflections	146	145
<i>R</i> int. (%)	2.90	1.62
<i>R</i> 1 all (%)	1.72	1.07
<i>wR</i> 2 (%)	4.29	2.29
GooF	1.249	1.207
Diff. Peaks (e/Å ³)	-0.78; 0.49	-0.68; 0.46

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Notes: *a* = unit-cell parameter; *u* = oxygen fractional coordinate; *T*-O and *M*-O = tetrahedral and octahedral bond lengths, respectively; *T*- and *M*-m.a.n. = *T*- and *M*-mean atomic number; *U*¹¹ = atomic displacement parameter; *U*¹¹ = *U*²² = *U*³³ and *U*¹² = *U*¹³ = *U*²³ (= 0 for *T*-site due to symmetry reasons); EXTI = extinction parameter; *R*_{int.} = merging residual value; *R*1 = discrepancy index, calculated from *F*²-data; *wR*2 = weighted discrepancy index, calculated from *F*²-data; GooF = goodness of fit; Diff. Peaks = maximum and minimum residual electron density. Radiation, Mo-Kα = 0.71073 Å. Data collection

522 temperature = 293 K. Origin fixed at $\bar{3}m$. Space group $Fd\bar{3}m$. $Z = 8$ formula units. Spinel structure
523 has cations at Wyckoff positions $8a \equiv T (1/8, 1/8, 1/8)$ and $16d \equiv M (1/2, 1/2, 1/2)$, and oxygen anions at
524 $32e (u, u, u)$.

525

526

527 **TABLE 2.** Unit-cell parameters of chromite up to 8.241 GPa and magnesiochromite up to
 528 9.200 GPa. Standard deviations in the last digits are in parentheses
 529

FeCr₂O₄			MgCr₂O₄		
<i>P</i> (GPa)	<i>a</i> (Å)	<i>V</i> (Å ³)	<i>P</i> (GPa)	<i>a</i> (Å)	<i>V</i> (Å ³)
0.00010(1)	8.3800(3)	588.48(6)	0.00010(1)	8.3361(2)	579.27(5)
0.478(5)	8.3728(3)	586.95(5)	0.663(5)*	8.3262(3)	577.22(6)
1.275(6)	8.3612(2)	584.53(4)	1.582(6)	8.3129(2)	574.45(5)
2.151(7)	8.3485(2)	581.87(5)	2.312(7)	8.3024(2)	572.29(5)
3.022(7)	8.3365(2)	579.36(5)	3.023(6)	8.2922(3)	570.17(5)
3.897(9)	8.3248(2)	576.94(5)	3.587(7)	8.2846(3)	568.61(5)
4.898(8)	8.3119(3)	574.24(6)	4.660(8)*	8.2703(3)	565.67(6)
5.989(9)	8.2975(2)	571.27(5)	4.783(9)	8.2688(3)	565.36(6)
6.533(9)	8.2909(2)	569.91(4)	6.278(9)	8.2491(2)	561.32(5)
7.868(9)	8.2745(2)	566.53(5)	6.508(8)*	8.2464(3)	560.78(6)
8.241(9)	8.2707(3)	565.76(6)	7.595(10)	8.2326(5)	557.97(9)
			8.087(10)*	8.2272(3)	556.88(6)
			9.200(11)	8.2140(3)	554.20(5)

530 *Data collected during decompression

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532

533 **Table 3.** Bulk modulus and its first pressure-derivative for chromite and magnesiochromite of
534 this study and for the spinel sensu stricto, MgAl₂O₄ (Nestola et al. 2007)

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Compound	K_{T0} (GPa)	K'
FeCr ₂ O ₄	184.8(1.7)	6.1(5)
MgCr ₂ O ₄	182.5(1.4)	5.8(4)
MgAl ₂ O ₄	193(1)	5.6(3) <i>ordered</i>
MgAl ₂ O ₄	192(1)	5.4(3) <i>disordered</i>

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