

1 **Revised 2**

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3 **Structural and chemical characterization of Mg[(Cr,Mg)(Si,Mg)]O₄, a new**
4 **post-spinel phase with six-fold coordinated silicon**

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21 **ABSTRACT**

22 The crystal structure and chemical composition of a crystal of Mg(Mg,Cr,Si)₂O₄ post-
23 spinel phase synthesized in the model system MgCr₂O₄–Mg₂SiO₄ at 16 GPa and 1600 °C
24 have been investigated. The compound was found to crystallize with a distorted orthorhombic
25 calcium-titanate (CaTi₂O₄) structure type, space group *Cmc*2₁, with lattice parameters *a* =
26 2.8482(1), *b* = 9.4592(5), *c* = 9.6353(5) Å, *V* = 259.59(1) Å³, and *Z* = 4. The structure was
27 refined to *R*₁ = 0.018 using 345 independent reflections. The loss of the inversion center is
28 due to the ordering of cations at the octahedral sites: Cr is mainly hosted at the M1 site
29 whereas Si at the M2 site. Such an ordered distribution induces a distortion thus provoking a
30 change in coordination of Mg, which becomes sevenfold-coordinated instead of the usually
31 eightfold-coordination observed in post-spinel phases. Electron microprobe analysis gave the
32 Mg[(Cr_{0.792}Mg_{0.208})(Si_{0.603}Mg_{0.397})]O₄ stoichiometry for the studied phase. The successful
33 synthesis of this phase can provide new constraints on thermobarometry of
34 wadsleyite/ringwoodite-bearing assemblages.

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36 **Keywords:** calcium titanate structure, chromium, spinel, post-spinel phases, crystal structure,
37 microprobe analysis, synthesis

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INTRODUCTION

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Spinel-group minerals exhibit the formula AB_2O_4 and crystallize predominantly with the cubic $Fd\bar{3}m$ structure (Biagioni and Pasero 2014). Such minerals are important from a geophysical point of view since they exhibit high-pressure structural phase transitions either to perovskite-type ABO_3 + rock salt-type BO (and then to post-perovskite) or to one of the orthorhombic CaM_2O_4 modifications ($M = Mn$, space group $Pbcm$; $M = Fe$, space group $Pnma$; $M = Ti$, space group $Cmcm$), depending on composition (Yamanaka et al. 2008). The $CaFe_2O_4$ structure, first reported at a pressure of about 25 GPa for the $MgAl_2O_4$ composition by Irifune et al. (1991), exhibits tunnel-like cation sites and for this reason it was hypothesized that it could host alkali elements in the Earth's deep mantle.

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Among the several natural-occurring spinels, magnesiochromite ($MgCr_2O_4$), is usually found with nearly end-member composition as accessory mineral in magmatic rocks and also as inclusions in diamonds (Lenaz et al. 2009). It was also described in natural UHP chromitites in the Luobusa ophiolite, Tibet (Yang et al. 2007; Yamamoto et al. 2009; Dobrzhinetskaya et al. 2009). For the reasons mentioned above, the high-pressure modifications of $MgCr_2O_4$ have been recently deeply studied by several authors (Wang et al. 2002; Yong et al. 2012; Bindi et al. 2014; Ishii et al. 2015). It was observed that the spinel-type $MgCr_2O_4$ dissociates in $MgO + Cr_2O_3$ at temperatures lower than 1000 °C and to a $MgCr_2O_4$ with a calcium-titanate structure (via $Mg_2Cr_2O_5 + Cr_2O_3$) at higher temperatures (Ishii et al. 2015).

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To study the effect of the entry of silicon in the $MgCr_2O_4$ structure, we studied the phase relations in the model system $MgCr_2O_4$ - Mg_2SiO_4 at 10–24 GPa and 1600 °C. The run product synthesized at $P = 16$ GPa revealed the presence of crystalline materials having a mixed $Mg(Mg,Cr,Si)_2O_4$ composition and exhibiting a distorted calcium-titanate ($CaTi_2O_4$) structure type. Here we report the first structural study by means of single-crystal X-ray diffraction together with chemical data of such a synthetic compound.

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EXPERIMENTAL DETAILS

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Synthesis

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The experiment that produced the run 2629-40 was carried out at $P = 16$ GPa and $T = 1600$ °C using a 2000-t Kawai-type multianvil apparatus installed at the Ehime University (Matsuyama, Japan). The samples were compressed by eight cubic tungsten carbide anvils with 2.5-mm truncation edge lengths. Heating of the sample was performed by a tubular $LaCrO_3$ heater. The samples were loaded into platinum capsules isolated from the heater by a MgO insulator (Sirotkina et al. 2015). Approximate sample volumes after experiments were

75 1.0 mm³. Mixtures of MgO, SiO₂ and Cr₂O₃ in stoichiometric proportions were used as
76 starting materials and prepared for the composition magnesiochromite (Sp - MgCr₂O₄) –
77 forsterite (Fo - Mg₂SiO₄) Sp₄₀Fo₆₀ (mol %). Temperature was measured by a W₉₇Re₃-W₇₅Re₂₅
78 thermocouple. The pressure was calibrated at room temperature using the semiconductor-
79 metal transitions of Bi, ZnS and GaAs (Irifune et al. 2004). The effect of temperature on
80 pressure was further corrected using the α - β and β - γ phase transitions of olivine (Katsura and
81 Ito 1989; Yamada et al. 2004). In the run product, Mg[(Cr,Mg)(Si,Mg)]O₄ was associated to
82 Mg₂Si₂O₅ and eskolaite (Fig. 1)

83 Data collection and crystal-structure refinement

84 A small crystal (35 × 42 × 48 μ m), hand-picked under a reflected light microscope from
85 the run product 2629-40 (Fig. 1), was preliminarily examined with a Bruker-Enraf MACH3
86 single-crystal diffractometer using graphite-monochromatized MoK α radiation. The data
87 collection was then done with an Oxford Diffraction Xcalibur 3 diffractometer (X-ray MoK α
88 radiation, $\lambda = 0.71073$ Å) equipped with a Sapphire 2 CCD detector (see Table 1 for details).
89 Intensity integration and standard Lorentz-polarization corrections were performed with the
90 *CrysAlis* RED (Oxford Diffraction 2006) software package. The program ABSPACK of the
91 *CrysAlis* RED package (Oxford Diffraction 2006) was used for the absorption correction.

92 Reflection conditions (hkl : $h + k = 2n$; $0kl$: $k = 2n$; $h0l$: $h, l = 2n$; $hk0$: $h + k = 2n$; $h00$: h
93 $= 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$) were consistent with the space groups *Cmcm* and *Cmc2*₁, the
94 first being the space group typically observed in post-spinel phases exhibiting a calcium-
95 titanate structure type (e.g., Yamanaka et al. 2008). Although the statistical tests on the
96 distribution of $|E|$ values strongly indicate the absence of an inversion centre ($|E^2 - 1| = 0.803$),
97 preliminary refinements using the full-matrix least-squares program SHELXL-97 (Sheldrick
98 2008), were carried out in the space group *Cmcm* starting from the atomic coordinates
99 reported for the post-spinel phase of MgCr₂O₄ (Bindi et al. 2014). The structural model
100 obtained ($R = 0.20$) indicated a large spread of the electron density around the octahedral site,
101 and the displacement parameters of two of the three oxygen atoms showed non-positive
102 values. At this point, a thorough analysis of the structure (essentially based upon the
103 observation of the displacement parameters for particular atoms) suggested that the mirror
104 symmetry perpendicular to the *c*-axis of the *Cmcm* space group should be removed. The
105 reflection and atomic position data sets were then adapted to the *Cmc2*₁ space group and the
106 structure refined. The unique octahedral site in the *Cmcm* space group splits in two octahedra
107 (hereafter M1 and M2) in the non-centrosymmetric *Cmc2*₁ space group. Site-scattering values
108 were refined using scattering curves for neutral species (Ibers and Hamilton 1974) as follows:
109 Mg vs. Cr for the eightfold-coordinated Mg site, Cr vs. and Si vs. for the M1 and M2

110 sites, respectively, and O vs. for the anion sites. The Mg and O sites were found to be fully
111 occupied, and the occupancy factors were then fixed to 1.00. The refined mean electron
112 numbers at the M1 and M2 sites were found to be 21.65(6) and 12.99(6), respectively, thus
113 indicating an ordering of the smaller light species (i.e., Si) at the M2 site. Such a distribution
114 is also in agreement with the observed sites geometry (see below). Successive cycles were run
115 introducing anisotropic temperature factors for all the atoms leading to $R_1 = 0.0182$ for 219
116 observed reflections [$F_o > 4\sigma(F_o)$] and $R_1 = 0.0188$ for all 345 independent reflections. The
117 Flack parameter of 0.01(2) (Flack 1983) indicated the orientation to be correct. Given the
118 non-centrosymmetric nature of the structure, the possible effect of anomalous dispersion of
119 X-ray was taken into account. For this purpose, a new data collection was carried out using a
120 Oxford Diffraction Excalibur PX Ultra diffractometer equipped with a 165 mm diagonal
121 Onyx CCD detector at 2.5:1 demagnification operating with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).
122 The refinement results were nearly identical to those obtained using $\text{MoK}\alpha$ radiation either in
123 electron densities at the structural sites and atom coordinates. In the present article, we
124 decided to present data obtained using $\text{MoK}\alpha$ radiation.

125 Fractional atomic coordinates and atomic displacement parameters are shown in Table
126 2. Table 3¹ lists the observed and calculated structure factors. Bond distances and geometric
127 parameters are reported in Table 4.

128 **Chemical composition**

129 A preliminary chemical analysis using energy dispersive spectrometry, performed on
130 the same crystal fragment used for the structural study as well as on other fragments from the
131 same run product, did not indicate the presence of elements ($Z > 9$) other than Cr, Mg and Si.
132 The chemical composition was then determined using wavelength dispersive analysis (WDS)
133 by means of a Jeol JXA-8600 electron microprobe. We used 40 s as counting time. The
134 matrix correction was performed with the Bence and Albee (1968) program as modified by
135 Albee and Ray (1970). The standards employed were forsterite (Mg, Si) and synthetic Cr_2O_3
136 (Cr). The crystal used for the X-ray study was found to be homogeneous within the analytical
137 uncertainty. The average chemical composition (six analyses on different spots) is (wt %),
138 SiO_2 22.4(2); Cr_2O_3 37.3(3); MgO 40.1(3); total 99.8(3); corresponding, on the basis of 4
139 oxygen atoms, to $\text{Mg}_{1.606(5)}\text{Cr}_{0.792(6)}\text{Si}_{0.603(5)}\text{O}_4$.

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RESULTS AND DISCUSSION

¹ For a copy of Table 3, document item, contact the Business Office of the Mineralogical Society of America.

142 Mg(Cr,Mg)(Si,Mg)O₄ crystallizes with a distorted orthorhombic calcium-titanate
143 (CaTi₂O₄) structure type (Fig. 2), space group *Cmc*2₁, with lattice parameters $a = 2.8482(1)$, b
144 $= 9.4592(5)$, $c = 9.6353(5)$ Å, $V = 259.59(2)$ Å³, and $Z = 4$. The departure from the classic
145 *Cmcm* space group is due to the ordering of the octahedral cations which is required to either
146 account for the electron density at those sites and justify the variation of the octahedral bond
147 distances (Table 4). In detail, Cr (with minor Mg) is mainly hosted at the M1 site and Si (with
148 minor Mg) is hosted at the M2 site, whereas the eightfold-coordinated site is fully occupied
149 by Mg. The linkage among the octahedra is provided by edge- and corner-sharing.

150 The bond distances of the M1 and M2 octahedra show a large anisotropy being in the
151 range 1.950-2.165 and 1.878-1.985 Å, respectively. M1, mainly occupied by Cr, exhibits a
152 mean bond distance of 2.031 Å (Table 4), which is slightly greater than that found in
153 eskolaite, Cr₂O₃ (1.988 Å; Ovsyannikov and Dubrovinsky 2011), that observed for ^{VI}Cr in
154 synthetic MgCr₂O₄ with spinel structure (1.998 Å; O'Neill and Dollase 1994) and that
155 observed for synthetic MgCr₂O₄ with post-spinel structure (1.986 Å; Bindi et al. 2014), due to
156 the presence of Mg at the site. The observed value is in excellent agreement with that
157 obtained by the sum of the ionic radii (2.037 Å; Shannon 1976). The Mg-for-Cr substitution
158 at the M1 site induces a distortion with an increase of the octahedral angle variance σ^2
159 (Robinson et al. 1971) from 15.78 in pure MgCr₂O₄ (Bindi et al. 2014) to 60.18 in the studied
160 crystal.

161 The M2 site population, derived from electron microprobe, can be written as
162 Si_{0.603}Mg_{0.397}. Such a distribution slightly differs from that derived from the structure
163 refinement (i.e., Si_{0.495}Mg_{0.505}), but it should be kept in mind that the calculated mean electron
164 numbers are very similar (13.7 vs. 13.0) and that elements having similar scattering factors
165 are present. The M2 mean bond distance of 1.940 Å is obviously greater than that observed in
166 pure MgSiO₃ (1.793 Å; Dobson and Jacobsen 2004), that observed for ^{VI}Si in synthetic
167 Na₂MgSi₅O₁₂ garnet (1.793 Å; Bindi et al. 2011) and that in stishovite (1.757 Å; Hill et al.
168 1983), due to the presence of significant amounts of Mg. Taking into account the ionic radii
169 (Shannon 1976), values of 1.927 and 1.962 Å can be calculated from the two distributions
170 (obtained by electron microprobe and from the structure refinement, respectively), which are
171 in excellent agreement with the observed value (1.940 Å).

172 The Mg-polyhedron is very distorted and coordinates seven oxygen atoms at distances
173 shorter than 2.4 Å, with an additional bond at 3.0 Å (Fig. 3a). This feature, together with the
174 cation ordering occurring at the octahedral sites, represents the main difference with respect to
175 the undistorted *Cmcm* calcium-titanate structure where the medium-sized A cations (A = Fe²⁺,
176 Mg, Co, Zn) coordinate eight oxygen atoms at distances shorter than 2.7-2.8 Å (Fig. 3b). If

177 we consider also the long bond at 3.0 Å with O1, the average Mg-O distance is 2.304 Å. Such
178 a value is slightly greater than that observed for the pure Mg site in the orthorhombic calcium
179 ferrite-type MgAl_2O_4 (2.259 Å; Kojitani et al. 2007), and that obtained by the sum of the ionic
180 radii (2.270 Å; Shannon 1976), whereas it is closer to that observed in the tetragonal structure
181 of synthetic MgSiO_3 garnet (2.284 Å; Angel et al. 1989).

182 The bond valence sums calculated using the parameters given by Brese and O’Keeffe
183 (1991) are 1.80(2), 2.70(2) and 2.91(3) for the Mg, M1 and M2 sites, respectively, thus
184 corroborating either the trivalent state for Cr and the proposed cation distribution at the
185 structural sites.

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IMPLICATIONS

188 Since magnesiochromite-rich spinel is commonly reported as inclusions in diamonds,
189 the successful synthesis of the new post spinel phase $\text{Mg}[(\text{Cr},\text{Mg})(\text{Si},\text{Mg})]\text{O}_4$ with a
190 symmetry different from either the cubic $Fd\bar{3}m$ typical of spinel or the $Cmcm$ typical of
191 calcium-titanate post-spinel is of key importance, because it could represent an important
192 ultrahigh-pressure marker for diamond formation using for example the elastic geobarometry
193 as showed by Angel et al. (2014). Our results are directly applicable to the phase associations
194 of podiform chromitites in the Luobusa ophiolite (Southern Tibet) containing diamond and
195 other former ultrahigh-pressure minerals, such as precursor stishovite for blade-shaped coesite
196 (Yang et al. 2007) and ringwoodite as a precursor of altered Mg–Fe silicate with an octahedral
197 shape (Robinson et al. 2004). Yamamoto et al. (2009) suggested a UHP precursor with a
198 calcium ferrite structure originally formed at a pressure of >12.5 GPa and then decomposed to
199 low-pressure chromite containing silicate exsolutions. Ishii et al. (2015) suggested a lower
200 pressure origin of these chromitites because of the absence of the assemblage $\text{Mg}_2\text{Cr}_2\text{O}_5 +$
201 Cr_2O_3 ($\text{Fe}_2\text{Cr}_2\text{O}_5 + \text{Cr}_2\text{O}_3$) in them. The new Cr-rich phase synthesized at 16 GPa and 1600°C,
202 containing significant amounts of the Mg_2SiO_4 component never reported before in a post-
203 spinel phase may be an intermediate product in deep recycling of silicate-bearing UHP
204 chromitites (Arai 2013). Exsolution silicate lamellae in chromite might be formed by inverse
205 transformation from the new post spinel phase $\text{Mg}[(\text{Cr},\text{Mg})(\text{Si},\text{Mg})]\text{O}_4$ to chromite during
206 mantle upwelling. Moreover, its structural characterization is crucial for thermodynamic
207 calculations of phase equilibria in the mantle systems, which can provide new constraints on
208 thermobarometry of wadsleyite/ringwoodite-bearing assemblages. Further experimental
209 studies are required to evaluate the compositional range and P - T stability of this phase.

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FIGURE CAPTIONS

317 FIGURE 1. SEM-BSE image of idiomorphic crystals of the new Cr-rich phase studied here (Ct)
318 associated with $\text{Mg}_2\text{Cr}_2\text{O}_5$ (mLd) and eskolaite (Esk) in the run 2629-40 ($P = 16$
319 GPa, $T = 1600$ °C). CamScan electronic microscope MV2300.

320 FIGURE 2. The crystal structure of $\text{Mg}(\text{Cr},\text{Mg})(\text{Si},\text{Mg})\text{O}_4$ projected down [100]. M1 (Cr,Mg)
321 and M2 (Si,Mg) cations are depicted as dark gray and white polyhedra,
322 respectively, whereas the eightfold-coordinated Mg cations as black spheres. The
323 unit-cell is outlined. The vertical axis is the b -axis.

324 FIGURE 3. Coordination environment of the Mg polyhedron in the crystal structure of
325 $\text{Mg}(\text{Cr},\text{Mg})(\text{Si},\text{Mg})\text{O}_4$ (up) and in MgCr_2O_4 (down – Bindi et al. 2014). Colors as
326 in Figure 2. The long Mg-O1 bond distance in the structure of
327 $\text{Mg}(\text{Cr},\text{Mg})(\text{Si},\text{Mg})\text{O}_4$ is indicated with a dashed line.

TABLE 1. Data and experimental details for the selected crystal

Crystal data	
Formula	Mg(Cr _{0.8} Mg _{0.2})(Si _{0.6} Mg _{0.4})O ₄
Crystal size (mm)	0.035 × 0.042 × 0.048
Form	block
Colour	transparent
Crystal system	orthorhombic
Space group	<i>Cmc</i> 2 ₁ (#36)
<i>a</i> (Å)	2.8482(1)
<i>b</i> (Å)	9.4592(5)
<i>c</i> (Å)	9.6353(5)
<i>V</i> (Å ³)	259.59(2)
<i>Z</i>	4
Data collection	
Instrument	Oxford Diffraction Xcalibur 3
Radiation type	MoK α ($\lambda = 0.71073$ Å)
Temperature (K)	293(2)
Detector to sample distance (cm)	6
Number of frames	2024
Measuring time (s)	130
Maximum covered 2 θ (°)	69.60
Absorption correction	multi-scan (<i>ABSPACK</i> ; Oxford Diffraction 2006)
Collected reflections	4529
Unique reflections	345
Reflections with $F_o > 4 \sigma(F_o)$	219
R_{int}	0.0214
R_{σ}	0.0408
Range of <i>h, k, l</i>	-4 ≤ <i>h</i> ≤ 4, -15 ≤ <i>k</i> ≤ 15, -15 ≤ <i>l</i> ≤ 15
Refinement	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4 \sigma(F_o)$]	0.0182
Final R_1 (all data)	0.0188
Flack parameter	0.01(2)
Number of least squares parameters	45
Goodness of Fit	1.045
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.60
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-0.85

TABLE 2. Atoms, atom coordinates and atomic displacement parameters (\AA^2) for the selected crystal.

atom	<i>s.o.f.</i>	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{iso}^*/U_{eq}
Mg	Mg _{1,000}	0	0.3785(2)	0.2487(2)	0.0184(8)	0.0247(9)	0.0253(6)	-0.001(1)	0	0	0.0228(4)
M1	C _{10,804(4)} Mg _{0,196}	0	0.1289(1)	0.0685(2)	0.0192(5)	0.0234(4)	0.0227(5)	-0.001(1)	0	0	0.0218(3)
M2	Si _{0,495(8)} Mg _{0,505}	0	0.8547(2)	0.9274(1)	0.023(1)	0.026(1)	0.025(1)	-0.0028(7)	0	0	0.0250(6)
O1	O _{1,000}	0	0.4971(5)	-0.0405(2)	0.027(2)	0.034(2)	0.032(2)	-0.001(2)	0	0	0.0310(9)
O2	O _{1,000}	0	0.0394(3)	0.2508(4)	0.027(2)	0.031(2)	0.030(1)	-0.001(2)	0	0	0.0292(8)
O3	O _{1,000}	0	0.2313(5)	0.8893(4)	0.025(3)	0.037(3)	0.032(2)	0.001(2)	0	0	0.031(1)
O4	O _{1,000}	0	0.7659(5)	0.1087(3)	0.023(3)	0.031(2)	0.030(2)	-0.001(2)	0	0	0.028(1)

TABLE 4. Selected bond distances (Å) and geometric parameters for the studied crystal.

<i>Mg polyhedron</i>	
Mg-O2 (×2)	2.084(3)
Mg-O3 (×2)	2.223(4)
Mg-O4 (×2)	2.232(3)
Mg-O1	2.347(4)
Mg-O1	3.004(3)
^{viii} <Mg-O>	2.304
^{viii} <i>V</i> (Å ³)	20.73
^{vii} <Mg-O>	2.204
^{vii} <i>V</i> (Å ³)	14.36
 <i>M1 octahedron (Cr,Mg)</i>	
M1-O2	1.950(4)
M1-O4 (×2)	1.964(4)
M1-O3	1.980(4)
M1-O1 (×2)	2.165(3)
<M1-O>	2.031
<i>V</i> (Å ³)	10.89
σ ²	60.18
λ	1.0197
 <i>M2 octahedron (Si,Mg)</i>	
M2-O3 (×2)	1.878(4)
M2-O4	1.938(4)
M2-O2	1.975(4)
M2-O1 (×2)	1.985(3)
<M2-O>	1.940
<i>V</i> (Å ³)	9.41
σ ²	71.25
λ	1.0227

Note: Quadratic elongation (λ) and angle variance (σ²) calculated according to Robinson et al. (1971).







