Revision 2

Chromium solubility in perovskite at high pressure:

The structure of $(Mg_{1-x}Cr_x)(Si_{1-x}Cr_x)O_3$ (with $x = 0.07$) synthesized at 23 GPa and 1600 °C

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ABSTRACT

The crystal structure and chemical composition of a crystal of $(Mg_{1-x}Cr_x)(Si_{1-x}Cr_x)O_3$ perovskite (with $x = 0.07$) synthesized in the model system $Mg_3Cr_2Si_3O_{12}$–$Mg_4Si_4O_{12}$ at 23 GPa and 1600 °C have been investigated. The compound was found to be orthorhombic, space group *Pbnm*, with lattice parameters $a = 4.8213(5)$, $b = 4.9368(6)$, $c = 6.9132(8)$ Å, $V = 164.55(3)$ Å^3. The structure was refined to $R = 0.046$ using 473 independent reflections. Chromium was found to substitute for both Mg at the dodecahedral X site (with a mean bond distance of 2.187 Å) and Si at the octahedral Y site (mean: 1.814 Å), according to the reaction $Mg^{2+} + Si^{4+} = 2Cr^{3+}$. Such substitutions cause a shortening of the <X-O> and a lengthening of the <Y-O> distances with respect to the values typically observed for pure $MgSiO_3$ perovskite. Although no high Cr-contents are considered in the pyrolite model, Cr-bearing perovskite may be an important host for chromium in the lower mantle. The successful synthesis of perovskite with high-Cr contents and its structural characterization are of key importance because the study of its thermodynamic constants combined with the data on phase relations in the lower-mantle systems can provide new constraints on thermobarometry of perovskite-bearing assemblages.

KEYWORDS: perovskite, chromium, lower mantle, crystal structure, microprobe analysis, synthesis

INTRODUCTION

Although it is well accepted that $(Mg,Fe)SiO_3$ perovskite is one of the major phases in the Earth's lower mantle, there is still a debate about the trace-elements incorporation in its structure. As pointed out by Andrault (2003), three mechanisms can be invoked for the incorporation of a trivalent cation in $(Mg,Fe)SiO_3$ perovskite: (*i*) incorporation of X^{3+} cations in the octahedral Y site with formation of oxygen vacancies; (*ii*) coupled-substitution of X^{3+} cations at both X and Y sites; and (*iii*) coupled-substitution of X^{3+} cations and Fe^{3+}, after oxidation of some Fe^{2+} into Fe^{3+}. Obviously, all these mechanisms can vary with pressure, temperature, X^{3+} cations content, and/or oxygen fugacity (fO_2). Among the X^{3+} elements, chromium is considered to be very minor in the primitive mantle (~0.3-0.4 wt% Cr_2O_3; Ringwood 1979; Allègre et al. 1995; O'Neill and Palme 1998) and the largest amount of Cr reported so far in synthetic $MgSiO_3$ perovskite does not exceed 0.006-0.008 atoms per formula unit (Irifune 1994; Eeckhout et al. 2007). Thus, as Cr is present in the lower mantle, it is important to investigate the crystal chemistry of high-pressure Cr-bearing phases under such conditions. Moreover, there is also considerable discussion about the valence state of chromium in lower mantle (Cr^{2+} vs. Cr^{3+}) related to its role played to influence properties such as electrical conductivity (Dobson and Brodholt 2000), ionic diffusion (Mackwell et al. 2005), and lower mantle oxygen fugacity (McCammon et al. 2004).

To verify the possible incorporation of large amounts of Cr into perovskite and the response of the crystal structure, we present a structural study by means of single-crystal X-ray diffraction of an $MgSiO_3$-perovskite synthesized at high pressures exhibiting the highest Cr content ever reported.

EXPERIMENTAL

Synthesis

Experiments at $P = 23$ GPa and $T = 1600$ °C were performed 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. Pyrophyllite gaskets were placed between the anvils to make the compression easier. 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. Approximate sample volumes after experiments were 1.0 mm^3. As the starting materials, mixtures of MgO, SiO_2 and Cr_2O_3 in stoichiometric proportions were prepared for the composition knorringite (Knr) – majorite (Maj) $Knr_{70}Maj_{30}$ (mol %). Temperature was controlled by a $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple. Pressure was calibrated at room temperature using semiconductor-metal transitions of Bi, ZnS

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72 and GaAs (Irifune et al. 2004). The effect of temperature on pressure was further corrected

73 using the α-β and β-γ phase transitions of olivine (Katsura and Ito 1989; Yamada et al. 2004).

74 MgSiO$_3$ perovskite (Pv) prevailed in run products being accompanied by MgCr$_2$O$_4$ with

75 calcium titanate structure (Ct) and stishovite (St) (Fig. 1).

Data collection and crystal-structure refinement

77 A small crystal (30 × 32 × 40 μm), hand-picked under a reflected light microscope from

78 the run product 2413-70 (Fig. 1), was preliminarily examined with a Bruker-Enraf MACH3

79 single-crystal diffractometer using graphite-monochromatized Mo$K\alpha$ radiation. The data

80 collection was then done with an Oxford Diffraction Xcalibur 3 diffractometer (X-ray Mo$K\alpha$

81 radiation, λ = 0.71073 Å) fitted with a Sapphire 2 CCD detector (see Table 1 for details).

82 Intensity integration and standard Lorentz-polarization corrections were done with the

83 *CrysAlis* RED (Oxford Diffraction 2006) software package. The program ABSPACK of the

84 *CrysAlis* RED package (Oxford Diffraction 2006) was used for the absorption correction. The

85 R_{int} (Laue group *mmm*) decreased from 0.081 to 0.048 after the absorption correction.

86 Reflection conditions ($h0l$: $h + l = 2n$; $0kl$: $k = 2n$; $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$) are

87 consistent with the space group *Pbnm* (*Pnma* as standard), reported for orthorhombic

88 perovskites. The full-matrix least-squares program SHELXL-97 (Sheldrick 2008), working on

89 F^2, was used for the refinement of the structure, which was carried out starting from the

90 atomic coordinates reported by Kojitani et al. (2007) for Al-bearing MgSiO$_3$ perovskite. Site-

91 scattering values were refined using scattering curves for neutral species (Ibers and Hamilton

92 1974) as follows: Mg vs. Cr for the X site, Si vs. Cr for the Y site, and O vs.   for the anion

93 sites. The O sites were found fully occupied, and the occupancy factors were then fixed to

94 1.00. The refined mean electron numbers at the X and Y cation sites were found to be

95 12.83(1) and 14.69(1), respectively, thus indicating the same amount of Cr substituting for

96 both Mg (at the X site) and Si (at the Y site). Therefore, in order to reduce the number of free

97 variables, only one parameter was refined to constrain ^{X}Cr = ^{Y}Cr. Successive cycles were run

98 introducing anisotropic temperature factors for all the atoms leading to $R1$ = 0.036 for 191

99 observed reflections [$F_o > 4\sigma(F_o)$] and $R1$ = 0.046 for all 473 independent reflections.

100 Fractional atomic coordinates and atomic displacement parameters are shown in Table 2.

101 Table 3[1] lists the observed and calculated structure factors. Bond distances are reported in

102 Table 4 together with those of other synthetic MgSiO$_3$ perovskites.

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

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Chemical composition

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104   A preliminary chemical analysis using energy dispersive spectrometry, performed on the

105   same crystal fragment used for the structural study as well as on other fragments from the

106   same run product, did not indicate the presence of elements ($Z > 9$) other than Cr, Mg and Si.

107   The chemical composition was then determined using wavelength dispersive analysis (WDS)

108   by means of a Jeol JXA-8600 electron microprobe. We used 40 s as counting time. The

109   matrix correction was performed with the Bence and Albee (1968) program as modified by

110   Albee and Ray (1970). The standards employed were forsterite (Mg, Si) and synthetic Cr_2O_3

111   (Cr). The crystal used for the X-ray study was found to be homogeneous within the analytical

112   uncertainty. The average chemical composition (five analyses on different spots) is (wt %),

113   SiO_2 53.17(24); Cr_2O_3 10.35(14); MgO 35.66(16); total 99.18(23); corresponding, on the

114   basis of 3 oxygen atoms, to $[Mg_{0.93(5)}Cr_{0.07(3)}][Si_{0.93(3)}Cr_{0.07(3)}]O_3$.

115

116   **RESULTS AND DISCUSSION**

117   The unit-cell parameters are strongly influenced by the entry of Cr into the structure. We

118   observed an increase of all the values with the most affected being the a parameter. It

119   increases by 0.9% with respect to pure $MgSiO_3$ whereas the increase of the b and c

120   parameters is close to 0.1–0.2%. This feature is quite surprising as Kojitani et al. (2007)

121   observed a contraction, although small, of the a parameter with increasing the Al content in

122   perovskite-type $MgSiO_3$ by means of X-ray powder diffraction data. Al-bearing

123   stoichiometric perovskites should indeed behave in a similar way since Al substitutes for both

124   Mg and Si, that is it replaces a larger cation in the dodecahedral X site and a smaller cation in

125   the octahedral Y site. It should be pointed out, however, that O'Neill and Jeanloz (1994) and

126   Irifune et al. (1996) had described a linear increase of the a parameter with increase of the Al

127   content in stoichiometric perovskites according to the linear equations: a (Å) = 0.016(8)X_{Al} +

128   4.779(1) and a (Å) = 0.019(7)X_{Al} + 4.777(1), respectively. In general, it seems that Cr has a

129   larger effect on the perovskite structure than does Al. The Cr–for–Si substitution inducing the

130   enlargement of the Y site seems stronger than the Cr–for–Mg substitution inducing the

131   shrinkage of the X site, thus implying an overall increase of the unit-cell volume. Such a

132   feature can also be pointed out by the analysis of the degree of polyhedral tilting (Φ),

133   calculated as $\Phi = 1 - \cos^2\theta_m\cos\theta_z$ (Thomas 1996), as a function of the minor substituent for Si

134   in the perovskite structure. In Figure 2 the ratio of the two polyhedral volumes (V_X/V_Y) is

135   plotted against the degree of polyhedral tilting Φ. For an untilted perovskite ($\Phi = 0$), $V_X/V_Y =$

136   5. On the basis of the analysis of the geometry of several synthetic perovskites, Thomas

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137 (1996) predicted the tendency given as dotted line in Figure 2. Interestingly, pure $MgSiO_3$

138 (Dobson and Jacobsen 2004), Al-bearing perovskites (Kojitani et al. 2007) and the Cr-bearing

139 crystal studied here, plot exactly on the trend. Although irreducible representations and

140 symmetry-adapted modes would provide a clear and unambiguous way to separate the effects

141 of distortion and tilting of octahedra in perovskites (Wang and Angel 2011), the data for the

142 Cr-bearing perovskite are markedly different with respect to those calculated for pure $MgSiO_3$

143 thus indicating that the polyhedral tilting seems the dominant mechanism to accommodate

144 different sized X and/or Y cations.

145 The assignment of Cr to both the X and Y sites according to the reaction $Mg^{2+} + Si^{4+} =$

146 $2Cr^{3+}$ is required both to account for the electron density at those sites and to justify the

147 decrease and the increase of the X–O and Y–O distances, respectively, relative to pure

148 $MgSiO_3$ (Table 4). The geometry of the X-polyhedron in the crystal studied here shows

149 specific characteristics never previously reported for the $MgSiO_3$-perovskite structure. The

150 mean <X–O> value of 2.187 Å is by far the shortest among those observed in $MgSiO_3$

151 perovskites. In particular, the decrease of the X–O distances is not isotropic; the shortest X–

152 $O1^{ii}$ distance (i.e., 1.933 Å) decreases the most while there is a slight lengthening of the X–

153 $O2^{iii,iv}$ distances at 2.064 Å. Moreover, the four long X–O2 distances become almost equal,

154 and do not show the usual difference ($\Delta = $ X–$O2^{vi,vii}$ – X–$O2^{i,v}$) observed between them (e.g.,

155 $\Delta = 0.143$ in pure $MgSiO_3$; Dobson and Jacobsen 2004). Similar, but reversed geometrical

156 changes are caused by the entry of Cr in the Y site. The Cr–for–Si substitution induces a

157 general increase of the mean octahedral distance, which pass from 1.793 Å in pure $MgSiO_3$

158 (Dobson and Jacobsen 2004) to 1.814 Å in the present crystal. Such a value exceeds those

159 observed for ^{VI}Si in synthetic $Na_2MgSi_5O_{12}$ garnet (1.793 Å; Bindi et al. 2011) and that in

160 stishovite (1.757 Å; Hill et al. 1983), whereas it is similar to those found in pyroxenes

161 synthesized in the $Na(Mg_{0.5}Si_{0.5})Si_2O_6$–$NaAlSi_2O_6$ system (l.807–1.813 Å; Yang et al. 2009).

162 This is not surprising as the octahedral site of these pyroxenes are occupied by minor amounts

163 of Mg (or Al) substituting for silicon. The Cr–for–Si substitution also induces a distortion of

164 the octahedral site quantifiable with an increase of the octahedral angle variance σ^2 (Robinson

165 et al. 1971) from 1.56 in pure $MgSiO_3$ (Dobson and Jacobsen 2004) to 7.48 in the studied

166 crystal. A similar value ($\sigma^2 = 7.63$) can be calculated for $(Mg_{1-x}Al_x)(Si_{1-x}Al_x)O_3$ with $x =$

167 0.050 (Kojitani et al. 2007). Taking into account that Cr^{3+} is not expected to be Jahn-Teller

168 active, it appears that the substitution of a trivalent cation for Si in the perovskite structure

169 increases the distortion of the octahedra.

170 Since Mg-rich perovskite is the most abundant phase in the pyrolitic lower mantle and its

171 structure seems rather flexible to various crystal-chemical environments, this mineral may

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accommodate Cr and other minor elements of the pyrolitic composition. Cr-bearing perovskites were described in the lower mantle associations in diamonds from São Luiz, Brazil (Harte et al. 1999). Most of them are Mg-rich, with Cr_2O_3 up to 0.5 wt % and Al_2O_3 up to 2.7 wt %. The highest Cr_2O_3 content registered in these perovskites is 1.19 wt % (10.0 wt % Al_2O_3), which is ~3 times higher than the estimated bulk Cr concentration in the mantle. In this relation, there is no doubt that the perovskite phase would be capable of storing all of the Cr content expected for the pyrolitic-type composition (i.e., 0.4 wt% of Cr_2O_3). It is important to note that, as for Fe^{3+}, the entry of Cr^{3+} in perovskite is not related to the usual consideration of oxygen fugacity (Lauterbach et al. 2000). On the usual basis of $Al–Fe^{3+}$ (Cr^{3+}) substitution relationships in silicate structures, the high content of Cr^{3+} and Fe^{3+} in some natural perovskites may be linked to the high Al content (McCammon 1997), which increases with pressure.

Our results on the synthesis of Al-free perovskite demonstrate that the extremely high Cr_2O_3 content results from incorporation of Cr in both the X and Y sites. The dissolution of Cr^{3+} in $MgSiO_3$ perovskite may have a considerable effect on physical properties in the lower mantle. Since the reported bulk modulus of Al-bearing $MgSiO_3$ perovskite (Zhang and Weidner 1999) differs significantly from that of pure $MgSiO_3$ perovskite, estimation of the lower mantle composition based on the elastic properties of perovskite should account for a number of major-element substitutions (including Cr) in it. The successful synthesis and structural refinement of an $MgSiO_3$ perovskite containing high amounts of Cr is important for the study of impact of this element on its thermodynamic constants and phase relations in the lower mantle.

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282

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FIGURE CAPTIONS

284

285 FIGURE 1. SEM-BSE image of idiomorphic Cr-bearing perovskite (Pv) crystals associated with
286   MgCr$_2$O$_4$ with a calcium titanate structure (Ct) and stishovite (St) in the run 2413-70
287   [P = 23 GPa, T = 1600 °C]. CamScan electronic microscope MV2300.

288 FIGURE 2. Variation of V_X/V_Y as a function of the degree of tilt Φ (see text for explanation).
289   The dotted line refers to the predicted trend reported by Thomas (1996). Numbers
290   as follows: 1 = pure MgSiO$_3$ (Dobson and Jacobsen 2004); 2 = (Mg$_{1-x}$Al$_x$)(Si$_{1-}$
291    $_x$Al$_x$)O$_3$ with x = 0.025 (Kojitani et al. 2007); 3 = (Mg$_{1-x}$Al$_x$)(Si$_{1-x}$Al$_x$)O$_3$ with x =
292   0.050 (Kojitani et al. 2007); 4 = Cr-bearing perovskite (present study).

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TABLE 1. Data and experimental details for the selected crystal

Crystal data

Formula	$(Mg_{0.928}Cr_{0.072})(Si_{0.928}Cr_{0.072})O_3$
Crystal size (mm)	$0.030 \times 0.032 \times 0.040$
Form	block
Colour	transparent
Crystal system	orthorhombic
Space group	*Pbnm* (#62 – *Pnma* as standard)
a (Å)	4.8213(5)
b (Å)	4.9368(6)
c (Å)	6.9132(8)
V (Å^3)	164.55(3)
Z	4

Data collection

Instrument	Oxford Diffraction Excalibur 3
Radiation type	Mo$K\alpha$ ($\lambda = 0.71073$)
Temperature (K)	298(3)
Detector to sample distance (cm)	5
Number of frames	2122
Measuring time (s)	135
Maximum covered 2θ (°)	75.80
Absorption correction	multi-scan (*ABSPACK*; Oxford Diffraction, 2006)
Collected reflections	3496
Unique reflections	473
Reflections with $F_o > 4\,\sigma\,(F_o)$	191
R_{int}	0.0480
R_σ	0.1185
Range of h, k, l	$-8 \le h \le 8$, $-8 \le k \le 8$, $-11 \le l \le 11$

Refinement

Refinement	Full-matrix least squares on F^2
Final $R1$ [$F_o > 4\,\sigma\,(F_o)$]	0.0364
Final $R1$ (all data)	0.0455
W$R1$[$F_o > 4\,\sigma\,(F_o)$]	0.0905
W$R1$(all data)	0.0912
GoF	0.968
Number of least squares parameters	29
$\Delta\rho_{max}$ (e Å^{-3})	0.63
$\Delta\rho_{min}$ (e Å^{-3})	-0.87

TABLE 2. Atoms, Wyckoff positions, atom coordinates and atomic displacement parameters (Å^2) for the selected crystal.

atom	Wyckoff	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$U_{iso}*/U_{eq}$
X [Mg$_{0.931(8)}$Cr$_{0.069}$]	4c	0.9879(3)	0.0726(2)	¼	0.0193(6)	0.0171(5)	0.0192(5)	0.0001(7)	0	0	0.0185(3)
Y [Si$_{0.931(8)}$Cr$_{0.069}$]	4a	0	½	0	0.0205(5)	0.0201(4)	0.0215(4)	0.0004(6)	0.0001(6)	-0.0002(3)	0.0207(2)
O1 [O]	4c	0.1025(7)	0.4478(6)	¼	0.023(1)	0.022(2)	0.028(1)	0.002(1)	0	0	0.0243(7)
O2 [O]	8d	0.6853(5)	0.3124(4)	0.0500(3)	0.025(1)	0.026(1)	0.0256(9)	-0.0001(8)	0.0003(9)	-0.0003(8)	0.0255(5)

TABLE 4. Geometric details of different perovskites.

	MgSiO$_3$*	$(Mg_{0.975}Al_{0.025})(Si_{0.975}Al_{0.025})O_3$	$(Mg_{0.95}Al_{0.05})(Si_{0.95}Al_{0.05})O_3$	$(Mg_{0.928}Cr_{0.072})(Si_{0.928}Cr_{0.072})O_3$
	(Dobson and Jacobsen 2004)	(Kojitani et al. 2007)	(Kojitani et al. 2007)	(this study)
a (Å)	4.7784(2)	4.7783(1)	4.7767(1)	4.8213(5)
b (Å)	4.9303(1)	4.9327(2)	4.9342(2)	4.9368(6)
c (Å)	6.8990(2)	6.9051(2)	6.9130(2)	6.9132(8)
V (Å^3)	162.53(1)	162.75(1)	162.93(1)	164.55(3)
Mg-polyhedron				
Mg-O1^{ii}	2.017	2.008(4)	2.060(7)	1.933(3)
Mg-O2^{iii,iv}	2.055	2.048(3)	1.982(5)	2.064(2)
Mg-O1^{ii}	2.098	2.096(4)	2.086(6)	2.069(4)
Mg-O2^{i,v}	2.282	2.283(3)	2.253(5)	2.333(3)
Mg-O2^{vi,vii}	2.425	2.428(3)	2.496(5)	2.351(2)
Average	2.205	2.203	2.201	2.187
Si-octahedron				
Si-O1^{i,xii}	1.800	1.808(1)	1.822(2)	1.816(1)
Si-O2^{x,xi}	1.795	1.803(2)	1.807(4)	1.816(2)
Si-O2^{viii,ix}	1.783	1.779(2)	1.785(4)	1.811(2)
average	1.793	1.797	1.805	1.814
O1^{xii}-Si-O2^{xi}	91.5	91.2(2)	93.3(2)	94.2(1)
O1^{xii}-Si-O2^{i}	91.3	88.2(1)	86.9(3)	85.8(1)
O2^{viii}-Si-O2^{ix}	90.6	89.5(1)	89.2(1)	89.19(4)
Si^{i}-O1-Si^{xiii}	146.8	145.5(2)	143.2(3)	144.3(2)
Si^{i}-O2-Si^{vii}	147.2	146.8(2)	145.8(2)	144.1(1)

Note: * Bond distances were calculated using lattice parameters given by Kojitani et al. (2007) for MgSiO$_3$ and with the atomic coordinates reported by Dobson and Jacobsen (2004). Symmetry codes are: *i*: *x*, *y*, *z*; *ii*: *x*+1, *y*, *z*; *iii*: -*x*+3/2, *y*-1/2, *z*; *iv*: -*x*+3/2, *y*-1/2, -*z*+1/2; *v*: *x*, *y*, -*z*+1/2; *vi*: *x*+1/2, -*y*+1/2, *z*+1/2; *vii*: *x*+1/2, -*y*+1/2, -*z*; *viii*: -*x*+1, -*y*+1, -*z*; *ix*: *x*-1, *y*, *z*; *x*: -*x*+1/2, *y*+1/2, *z*; *xi*: *x*-1/2, -*y*+1/2, -*z*; *xii*: -*x*, -*y*+1, -*z*; *xiii*: -*x*, -*y*+1, *z*+1/2.