Non-monotonic compositional dependence of isothermal bulk modulus of the (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$ spinel solid solutions...
Non-monotonic compositional dependence of isothermal bulk modulus of the \((Mg_{1-x}Mn_x)Cr_2O_4\) spinel solid solutions, and its origin and implication

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Abstract

The compressibility of the spinel solid solutions, \((Mg_{1-x}Mn_x)Cr_2O_4\) with \(x = 0.00 (0), 0.20 (0), 0.44 (2), 0.61 (2), 0.77 (2)\) and 1.00 (0), has been investigated by using a diamond-anvil cell coupled with synchrotron X-ray radiation up to ~10 GPa (ambient \(T\)). The second-order Birch–Murnaghan equation of state was used to fit the \(P–V\) data, yielding the following values for the isothermal bulk moduli \((K_T)\): 198.2 (36), 187.8 (87), 176.1 (32), 168.7 (52), 192.9 (61) and 199.2 (61) GPa, for the spinel solid solutions with \(x = 0.00 (0), 0.20 (0), 0.44 (2), 0.61 (2), 0.77 (2)\) and 1.00 (0), respectively (\(K'_T\) fixed as 4). The \(K_T\) value of the Mg\(_2\)Cr\(_2\)O\(_4\) spinel is in good agreement with existing experimental determinations and theoretical calculations. The correlation between the \(K_T\) and \(x\) is not monotonic, with the \(K_T\) values similar at both ends of the binary Mg\(_2\)Cr\(_2\)O\(_4\)–Mn\(_2\)Cr\(_2\)O\(_4\), but decreasing towards the middle. This non-monotonic correlation can be described by two equations, \(K_T = -49.2 (11)x + 198.0 (4) (x \leq -0.6)\) and \(K_T = 92 (41)x + 115 (30) (x \geq -0.6)\), and can be explained by the evolution of the average bond lengths of the tetrahedra and octahedra of the spinel solid solutions. Additionally, the relationship between the thermal expansion coefficient and composition is correspondingly reinterpreted, the continuous deformation of the oxygen array is demonstrated, and the evolution of the component polyhedra is discussed for this series of spinel solid solutions. Our results suggest that the correlation between the \(K_T\) and composition of a solid solution series may be complicated, and great care should be paid while estimating the \(K_T\) of some intermediate compositions from the \(K_T\) of the end-members.

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Keywords: Bulk modulus; Non-monotonic correlation; Spinel solid solutions \((Mg_{1-x}Mn_x)Cr_2O_4\); Synchrotron X-ray radiation

1. Introduction

Isothermal bulk modulus \((K_T)\) is an important parameter in studies of the deep interior of the Earth (e.g., Duffy and Wang, 1998). It has been intensively investigated by different techniques such as high-\(P\) compression experiment (e.g., Mao et al., 1969; Hazen, 1993; Fei and Mao, 1993; Shieh et al., 2006), ultrasonic interferometry (e.g., Liebermann et al., 1977; Li et al., 1998), Brillouin scattering (e.g., Weidner et al., 1984; Jackson et al., 2000), empirical calculation (e.g., Anderson and Nafe, 1965; Hazen and Yang, 1999), advanced theoretical simulation (Oganov et al., 2000; Deng et al., 2010), and many more. In the last century, much
knowledge about the $K_T$ of minerals has been obtained and enormously expanded our understanding about the geochemical and geophysical process of the deep Earth (e.g., Ricollet et al., 2009; Liu et al., 2012).

With some notable exceptions (e.g., Mao et al., 1969; Hazen, 1993; Higo et al., 2006; Liu et al., 2011; Nestola et al., 2011a; He et al., 2012; Yamanaka et al., 2013; Huang and Chen, 2014; Du et al., 2015), numerous experimental investigations have been devoted to determining the $K_T$ of pure end-members of minerals. Most geologically important minerals like olivine (Ol), pyroxene, garnet (Grt), spinel (“spinel” sensu lato; Sp), plagioclase, amphibole and mica, however, are extremely complicated solid solutions, in terms of mineral chemistry and crystal structure. Consequently, the $K_T$ values of a series of solid solutions may vary significantly (He et al., 2012). And more importantly, they may have a compositional dependence, as recently demonstrated by Du et al. (2015) for the pyrope-grossular Grt solid solutions ((Mg$_{1-x}$Ca$_x$)$_3$Al$_2$Si$_2$O$_7$–Grt$_{ts}$). On the other hand, large amounts of direct experimental determinations on the $K_T$ values of different compositions for one series of solid solutions are usually unavailable, and the potentially complicated compositional effect is often unquantified. As a result, the $K_T$ values for the minerals with compositions practically relevant to the Earth have to be approximated from the measurements on the end-members by assuming a generally linear compositional dependence (e.g., Powell and Holland, 1985; Ita and Stixrude, 1992; Stixrude and Lithgow-Bertelloni, 2005). Alternatively, they may be simply assumed as compositionally independent (e.g., Cammarano et al., 2005a, 2005b). This is hardly satisfactory. When the mineral solid solutions vary their compositions, the lengths and characteristics of their chemical bonds, and the relative sizes and roles of their component polyhedra may vary significantly and in complicated ways, so that their $K_T$ values can not be easily predicted, as demonstrated here for the Sp solid solution series (Sp$_{ts}$) along the MgCr$_2$O$_4$–Sp and MnCr$_2$O$_4$–Sp join in this study.

Chromium spinels have the general chemical formula MCr$_2$O$_4$ and the space group $Fd\bar{3}m$ (No. 227; $Z = 8$). In their structure, the oxygen ions form a cubic close packing array (equipoint 32e), the M cations occupy one eighth of the tetrahedral (equipoint 8a) sites and the Cr$^{3+}$ cations occupy half of the octahedral (equipoint 16d) sites. Due to the large excess octahedral crystal field stabilization energy of Cr$^{3+}$ (–160 kJ/mol; O’Neill and Navrotsky, 1984), significant disordering (cations M and Cr$^{3+}$ switching their sites) is not expected. This gives us an opportunity to closely examine the influence of the compositional variation of the tetrahedral sites on the bond lengths of different chemical bonds, the volumetric systematics of different component polyhedra, and the $K_T$ values of the MCr$_2$O$_4$–Sp. The result may deepen our understanding of the controlling factors of the $K_T$ of other mineral solid solutions.

MgCr$_2$O$_4$–Sp plays a very important role in the partial melting process of the upper mantle (Liu and O’Neill, 2004). With the substitution of Mg by Mn on the tetrahedral sites, a large range of solid solutions may form, as implied by some field work conducted a long time ago (Graham, 1978; Paraskevopoulos and Economou, 1981). Recently we synthesized a full series of Sp solid solutions along the join MgCr$_2$O$_4$–MnCr$_2$O$_4$, abbreviated as (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$–Sp$_{ts}$ hereafter, and directly confirmed those field observations (Wang et al., 2012). Considering the large size difference (–12%) between the Mg$^{2+}$ (0.585 Å) and Mn$^{2+}$ (0.655 Å) on a tetrahedral site (O’Neill and Navrotsky, 1983), this is important. Additionally, we investigated the volume-composition relationship, and determined the effect of the Mg–Mn substitution on the thermal expansivities (Wang et al., 2012).

In this study, we conducted a large number of high-$P$ experiments to investigate the compressibility of the (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$–Sp$_{ts}$, and found a non-monotonic compositional effect on the $K_T$. On the basis of the new result, we reexamined the compositional effect on the thermal expansion coefficients reported by Wang et al. (2012), and discovered a non-monotonic compositional effect as well. Furthermore, we explored the origin of this non-monotonic compositional effect by resorting to the variations of the constituent chemical bonds, the distortion evolution of the oxygen array and the mixing behaviors of the component polyhedra in the (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$–Sp$_{ts}$, and discussed some of its implications to other mineral solid solutions pertinent to the geosciences.

2. Experiments

The (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$–Sp$_{ts}$, with $x = 0.00$ (0), 0.20 (0), 0.44 (2), 0.61 (2), 0.77 (2) and 1.00 (0), were synthesized in an open air at 1200 °C for 48 h by using a conventional muffle furnace (Wang et al., 2012). Their compositional and powder X-ray diffraction (XRD) data suggested that they were essentially 2–3 spinels, with nearly all Mg$^{2+}$ cations and Mn cations (appearing as Mn$^{2+}$) on the tetrahedral sites and nearly all Cr cations (appearing as Cr$^{3+}$) on the octahedral sites. This observation was fully compatible with previous studies (Raccah et al., 1966; O’Neill and Dollase, 1994; Gilewicz-Wolter et al., 2005; Stefan and Irvine, 2011). Arguably, a trace amount of Cr$^{4+}$ or Cr vacancy might be present according to O’Neill and Dollase (1994) or Moriwake et al. (2002), respectively, but its amount is too small to be meaningful to the physical properties of the Sp$_{ts}$.

To investigate the compression behavior, we have carried out high-$P$ powder X-ray diffraction experiments (ambient $T$) at the beamline X17C, National Synchrotron Light Source, Brookhaven National Laboratory. We compressed the (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$–Sp$_{ts}$ up to ~10 GPa with a symmetrical diamond-anvil cell (DAC). Since the experimental techniques have been well established and routinely used by our group (e.g., Liu et al., 2009, 2011; Chang et al., 2013; Xiong et al., 2015), they are only briefly described here. We used T301 stainless steel plates as the gaskets, a 1:4 ethanol-methanol mixture as the pressure media, and the ruby fluorescence method as the $P$ scale (Mao et al., 1978). The incident synchrotron X-ray beam was monochromatized to a wavelength of either 0.4066 or 0.4112 Å, and its beam size was collimated...
to a size of about ~25 × 20 μm². The X-ray diffraction data were collected for 600–1200 s using an online CCD detector, and later processed to generate the conventional one-dimension X-ray profile using the Fit2D program (Hammersley, 1996). With a full profile refinement of the collected X-ray data, the positions of the diffraction peaks such as 111, 220, 311, 222, 400, 331, 422, 511, 440 and 531 were determined, and the unit-cell parameters of the (Mg₁₋ₓMnₓ)Cr₂O₄−Sp at different P were subsequently refined from them.

3. Results and discussions

Our high-P experiments for the MgCr₂O₄−Sp were conducted up to ~10.3 GPa. According to Wang et al. (2002), Yong et al. (2012) and Nestola et al. (2014), no phase transition should be expected for this Sp in the investigated P range, which was confirmed by the present DAC experiments. Furthermore, the high-P experiments for other (Mg₁₋ₓMnₓ)Cr₂O₄−Sp with x = 0.20 (0), 0.44 (2), 0.61 (2), 0.77 (2) and 1.00 (0) were carried out up to ~5.46, 10.33, 5.84, 7.56 and 9.12 GPa, respectively. No phase transition was observed in these compression experiments as well. Table 1 summarises the unit-cell parameters at different pressures derived from our X-ray diffraction patterns. In total, 42 sets of unit-cell parameters have been obtained for the (Mg₁₋ₓMnₓ)Cr₂O₄−Sp in this study.

3.1. Kₚ of the MgCr₂O₄−Sp

Table 1

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</table>

* Data at ambient P and T are from Wang et al. (2012).

a P in the high-P experiments was determined by averaging the values measured before and after collection of synchrotron data. Fully hydrostatic pressure was potentially not maintained in the experiments, so that a P error of 0.05 GPa was assumed for samples of x = 0.00, 0.22, 0.41 and 0.61 wherever the measured P error was less than 0.05 GPa, and a P error of 0.1 GPa was assumed for samples of x = 0.22, 0.77 and 1.00 wherever the measured P error was less than 0.1 GPa.

b Number in the parentheses represents one standard deviation in the rightmost digit.

c The assumption of Kₚ = 4 for the MgCr₂O₄−Sp is sound. The Kₚ value was experimentally determined as either 7.2 (3) (Yong et al., 2012) or 5.8 (4) (Nestola et al., 2014), with the former generally influenced by the non-hydrostatic condition in...
the DAC experiments whereas the latter inadequately accurately determined by the limited volume reduction in the high-P experiments (~4.33%, similar to what we achieved in this study). In contrast, early theoretical simulations with variant methods constrained the \( K'_T \) value as 3.94 (Catti et al., 1999) or 4.066 (Ottonello et al., 2007). Furthermore, recent first-principles calculations with the CASTEP code using density functional theory and planewave pseudopotential technique, carried out up to 19 GPa by Zhang et al. (2016), generated similar \( K'_T \) values, 4.41 (6) (the exchange–correlation interaction treated with the generalized gradient approximation; GGA) and 4.5 (1) (the exchange–correlation interaction treated with the local density approximation; LDA). It is thus clear that the \( K'_T \) values for the MgCr\(_2\)O\(_4\)–Sp must be close to 4.

Using our \( P-V \) data for the MgCr\(_2\)O\(_4\)–Sp (Table 1) and with the assumption of \( K'_T = 4 \), we have obtained the following BM-EoS parameters: \( V_0 = 579.33 \ (4) \ A^3 \) and \( K'_T = 198.2 \ (36) \) GPa. If we assumed \( K'_T = 4.45 \), a value averaged from the results reported by Zhang et al. (2016), we would have obtained essentially identical values for the BM-EoS parameters: \( V_0 = 579.33 \ (4) \ A^3 \) and \( K'_T = 196.5 \ (35) \) GPa. As shown in Table 2, the \( K'_T \) value determined in this study is in good agreement with Yong et al. (2012; 207 (2) GPa) and Nestola et al. (2014; 189.6 (7) GPa); compared on the basis of \( K'_T = 4 \), it is ~4.3% lower than that from Yong et al. (2012) but ~4.5% higher than that from Nestola et al. (2014). This result is well reflected in the comparison of the \( P-V \) trends from these different studies, as shown in Fig. 1.

The \( K'_T \) value determined here, 198.2 (36) GPa, is very much compatible with the results from all available theoretical investigations. Previously, Catti et al. (1999) and Ottonello et al. (2007) constrained its values as 197.3 and 192.56 GPa, respectively (Table 2). Recently, Zhang et al. (2016) predicted that its value should be between 181.4 (48) GPa (GGA; low boundary) and 216.1 (11) GPa (LDA; high boundary).

### 3.2. Non-monotonic correlation between \( K'_T \) and \( x \) of the \((\text{Mg}_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4\)–Sp

The \( P-V \) data obtained for all other \((\text{Mg}_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4\)–Sp\(_{\text{SS}}\) are compared to those for the MgCr\(_2\)O\(_4\)–Sp in Fig. 2, and are similarly processed with equation (1), with the derived EoS parameters listed in Table 2.

The variation of the \( K'_T \) values with the compositions of the \((\text{Mg}_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4\)–Sp\(_{\text{SS}}\) is illustrated in Fig. 3. As the
substitution of Mn for Mg progresses, the $K_T$ value first decreases and late increases, with a minimum value of $\approx 168.7$ (52) approximately at $x = 0.61$. This non-monotonic correlation can be arithmetically described by the following two equations (determined with a weighted linear-squares method):

$$K_T = -49.2(11)x + 198.0(4) \quad (x \leq 0.61),$$  

(2) and

$$K_T = 92(41)x + 115(30) \quad (x \geq 0.61).$$  

(3)

Evidently in Fig. 3, our $K_T$ values for the intermediate compositions between the two end-members MgCr$_2$O$_4$–Sp and MnCr$_2$O$_4$–Sp are significantly different to those estimated with the assumption of an almost linear compositional dependence (Stixrude and Lithgow-Bertelloni, 2005).

The assumption of a constant $K'_T$ value of 4 for the (Mg$_{1-x}$Mn$_x$)$_2$O$_4$–Sp$_{ss}$ may be arguable and might affect our major findings here (equations (2) and (3)). It should be recognized that this assumption could not be critically evaluated by our experimental data due to the limited volume reductions achieved in this study. Existential investigations on other series of Sp$_{ss}$ with identical experimental techniques, however, have suggested nearly constant $K'_T$ values. Just to mention a few examples, the $K'_T$ values of the MgCr$_2$O$_4$–Sp and FeCr$_2$O$_4$–Sp are almost identical (5.8 (4) and 6.1 (5), respectively; Nestola et al., 2014), those of the MgAl$_2$O$_4$–Sp with different degrees of cation order are generally the same (5.6 (3) and 5.4 (3); Nestola et al., 2007), and those of the (Mg$_{1-x}$Fe$_x$)$_2$SiO$_4$–Sp$_{ss}$ (ringwoodites) are essentially constant (4.4 (2) for the investigated composition range $x \leq 0.5$; Higo et al., 2006). In contrast, the $K'_T$ values for one certain Sp$_{ss}$ determined in different experimental investigations can be very different, for example 7.2 (3) by Yong et al. (2012) and 5.8 (4) by Nestola et al. (2014) for the MgCr$_2$O$_4$–Sp, which was mostly caused by different experimental techniques (pressure media, pressure scales, pressure ranges, etc.) and different sample qualities.

Nevertheless, available theoretical investigation conducted with identical techniques simultaneously on both the MgCr$_2$O$_4$–Sp and the MnCr$_2$O$_4$–Sp indeed suggested some small fluctuation in the $K'_T$ values, from 3.94 for the MgCr$_2$O$_4$–Sp to 3.67 for the MnCr$_2$O$_4$–Sp (Catti et al., 1999; Quantum-mechanical calculations conducted with the periodic unrestricted Hartree-Fock approach). According to Liu et al. (2016), this level of fluctuation may lead to an uncertainty of $<5$ GPa in the $K_T$, and is therefore unimportant. Consequently, it has to be concluded that the non-monotonic correlation between the $K_T$ values and the compositions of the (Mg$_{1-x}$Mn$_x$)$_2$O$_4$–Sp$_{ss}$ with the $K'_T$ values decreasing by $\approx 30$ GPa from the two end-members (198.2 (36) GPa for the MgCr$_2$O$_4$–Sp and 199.2 (61) GPa for the MnCr$_2$O$_4$–Sp) towards the intermediate compositions (168.7 (52) GPa for the (Mg$_{1-x}$Mn$_x$)$_2$O$_4$–Sp with $x = 0.61$ (2) for example), must be real.

3.3. Origin of the non-monotonic correlation between $K_T$ and $x$ of the (Mg$_{1-x}$Mn$_x$)$_2$O$_4$–Sp$_{ss}$

The isothermal bulk moduli of a group of pure compounds (or end-members for complex solid solutions) with the same crystal structure are strongly dependent on their volumes (Anderson and Nafe, 1965). As proposed by Anderson and

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**Table 2**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Volume (angs$^3$)</th>
</tr>
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<td>MgCr$_2$O$_4$–Sp</td>
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</tr>
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<td>MnCr$_2$O$_4$–Sp</td>
<td>58.0</td>
</tr>
<tr>
<td>Cr$_2$O$_3$–Sp</td>
<td>61.0</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$–Sp</td>
<td>56.0</td>
</tr>
<tr>
<td>FeCr$_2$O$_4$–Sp</td>
<td>54.0</td>
</tr>
</tbody>
</table>

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**Fig. 2.** $V$–$P$ relations for the (Mg$_{1-x}$Mn$_x$)$_2$O$_4$–Sp$_{ss}$ observed in this study (ambient $T$). Curves are drawn according to the regressed BM-EoS parameters, as listed in Table 2 (with $K'_T$ set at 4). For most data, their error bars are equal to or smaller than the symbols.

**Fig. 3.** Correlations between the $K_T$ and $x$ of the (Mg$_{1-x}$Mn$_x$)$_2$O$_4$–Sp$_{ss}$ (ambient $P$ and $T$). Data at $x = 0$ and 1 are slightly shifted horizontally to display them more clearly. The broken line was drawn according to equations (5) and (6) in Stixrude and Lithgow-Bertelloni (2005), with the data for the two end-members from this study.
Anderson (1970), a relationship of $K_TV_0 = \text{constant}$ holds for the end-members of the Sp group, which implies a monotonic correlation between the $K_T$ and $V_0$. For a series of solid solutions such as the $(\text{Mg}_1-x\text{Mn}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$ along a binary system, the intermediate structures should be more or less strained, so that they do not necessarily follow the same pattern as the end-members do, which is clearly demonstrated here by the non-monotonic correlation between the $K_T$ and $x$ of the $(\text{Mg}_1-x\text{Mn}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$ (Fig. 3). Recently, similar phenomenon was observed for the $(\text{Mg}_1-x\text{Ca}_x)\text{Al}_2\text{Si}_3\text{O}_12-\text{Grt}_{ss}$, which show a “W”-shaped compositional dependence of their $K_T$ and thermal expansion coefficient ($\alpha_0$) at ambient $P-T$ conditions (Du et al., 2015). Note that in both cases the compositional parameter $x$ exerts a monotonic effect on the $V_0$ (Wang et al., 2012; Du et al., 2015).

For the $(\text{Mg}_1-x\text{Mn}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$, their $V_0-x$ data at ambient $P$ and $T$ showed some deviation from the Vegard’s law (i.e., ideal mixing; Wang et al., 2012). Here we have further explored their excess mixing volumes ($V_{0-excess}$) in Fig. 4. With the two end-members attaining zero $V_{0-excess}$ by definition (hence zero microstrain), the $(\text{Mg}_1-x\text{Mn}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$ have a third nearly-zero $V_{0-excess}$ point locating approximately at $x = 0.5$. Additionally, two local $V_{0-excess}$ maximum points appear at about $x = 0.25$ and $x = 0.75$, which could have been better constrained with more data. Similar $V_{0-excess-x}$ relationship was also observed for the $\text{Co(Al}_1-x\text{Ga}_x)\text{O}_4-\text{Sp}_{ss}$, with three zero $V_{0-excess}$ points but one $V_{0-excess}$ maximum point and one $V_{0-excess}$ minimum point (Lilova et al., 2010). It follows that the binary Sp$_{ss}$, with cation substitution either on the tetrahedral sites or on the octahedral sites, may have a rather complicated mixing behavior.

Both the $\text{MgCr}_2\text{O}_4-\text{Sp}$ and the $\text{MnCr}_2\text{O}_4-\text{Sp}$ are $2-3$ normal spinel, and the Mg and Mn cations replace each other on the tetrahedral sites of the $(\text{Mg}_1-x\text{Mn}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$. The size difference between the $\text{Mg}^{2+}$ and $\text{Mn}^{2+}$ in their fourfold coordination is large, ~12% (O’Neill and Navrotsky, 1983), so that a regular positive mixing behavior may be expected. This would have been broadly confirmed by our observation if we ignored the intermediate part of the $V_{0-excess-x}$ curve (Fig. 4). Since the Sp$_{ss}$ at about $x = 0.5$ has a nearly-zero $V_{0-excess}$, its structure should be generally microstrain-free, which presumably implies an even and ordered Mg–Mn distribution on the tetrahedral sites. It follows that this Sp$_{ss}$ at about $x = 0.5$ may behave like a “ghost” end-member for the $(\text{Mg}_1-x\text{Mn}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$.

The Sp structure is completely determined by its two independent cation-anion distances, termed as $d_{T-O}$ (averaged bond length of the tetrahedron) and $d_{M-O}$ (averaged bond length of the octahedron) in this study (Hill et al., 1979; O’Neill and Navrotsky, 1983). According to Lenaz et al. (2004) who investigated the $(\text{Mg}_1-x\text{Fe}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$ with single-crystal X-ray diffraction method, it is appropriate to assume that the $d_{T-O}$ varies linearly with the $x$ for the $(\text{Mg}_1-x\text{Mn}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$, $d_{T-O} = 1.965 + 0.07x$ Å; the radius for the $\text{Mg}^{2+}$, $\text{Mn}^{2+}$ and $\text{O}^{2-}$ is 0.585, 0.655 and 1.38 Å, respectively (O’Neill and Navrotsky, 1983; Shannon, 1976). The response of the $d_{M-O}$ to this Mg–Mn substitution can then be calculated with the following equations (Hazen and Yang, 1999),

$$d_{M-O} = 1.997 + 0.0005x$$

$$d_{M-O-excess} = 1.997 + 0.0005(x - 0.5)$$

![Fig. 4. Relationship between the $V_{0-excess}$ and $x$ of the $(\text{Mg}_1-x\text{Mn}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$ (ambient $P$ and $T$). Data at $x = 0$ and 1 are slightly shifted horizontally to display them more clearly. The broken line was drawn for the case of an ideal mixing whereas the dash line was eye-fitted according to our calculated results.](image)

![Fig. 5. Correlations between the $d_{M-O}$ and $x$ (a), and between the $d_{M-O-excess}$ and $x$ (b) of the $(\text{Mg}_1-x\text{Mn}_x)\text{Cr}_2\text{O}_4-\text{Sp}_{ss}$ (ambient $P$ and $T$). Data at $x = 0$ and 1 are slightly shifted horizontally to display them more clearly. The broken lines represent the case of an ideal mixing whereas the dash lines were eye-fitted according to our calculated results.](image)
\[ d_{M-O} = \sqrt{\frac{A + 8d_{T-O}^2}{33}}, \]

where

\[ A = \left( \frac{11\sqrt{3}a - 40d_{T-O}}{8} \right)^2. \]

The result is shown in Fig. 5. As the substitution of Mg by Mn progresses, the \(d_{M-O}\) firstly increases gradually up to about \(x = 0.25\), secondly remains generally constant for the \(x\) interval of \(-0.25-0.5\), then increases quickly up to about \(x = 0.75\), and finally decreases gradually towards \(x = 1\). In contrast, the \(d_{M-O}\) of the \((Mg_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4-Sp_m\) remains nearly constant (Lenaz et al., 2004), presumably mainly because the size difference of the Mg\(^{2+}\) and Fe\(^{2+}\) cations is much smaller (0.585 versus 0.615 Å, or ~5.1% only; O’Neill and Navrotsky, 1983).

This complicated variation pattern of the \(d_{M-O}\) combined with the assumed linear relationship between the \(d_{T-O}\) and \(x\), can at least qualitatively explain the non-monotonic correlation between the \(K_T\) and \(x\) of the \((Mg_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4-Sp_m\) (Fig. 3). For the composition interval from \(x = 0\) to about \(x = 0.75\), both the \(d_{M-O}\) and \(d_{T-O}\) generally increase, and the M-O and T-O bonds become weaker and hence more compressible, leading to smaller \(K_T\) values for the \((Mg_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4-Sp_m\) with \(x = 0.20(2), 0.44(2)\) and 0.61 (2) (Table 2). For the composition interval from about \(x = 0.75\) to \(x = 1\), however, the \(d_{M-O}\) generally decreases whereas the \(d_{T-O}\) continuously increases, suggesting stronger M-O bonds but weaker T-O bonds. Since the number of the M-O bonds is three times that of the T-O bonds in the Sp structure, the role of the M-O bonds dominates the composition range from about \(x = 0.75\) to \(x = 1\), and results in increasing \(K_T\) values for the \((Mg_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4-Sp_m\) with \(x = 0.77 (2)\) and 1.00 (0) (Table 2). To quantitatively finish all the details, more measurements on the \((Mg_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4-Sp_m\) with different compositions are deemed necessary.

Following the same reasoning, the combined effect of the linear correlation between the \(d_{T-O}\) and \(x\) and the constant \(d_{M-O}\) suggested by Lenaz et al. (2004) for the \((Mg_{1-x}\text{Fe}_x)\text{Cr}_2\text{O}_4-Sp_m\) may result in a nearly linear relationship between the \(K_T\) and \(x\), with a slope which may be too small for any high-\(P\) experimental investigations. Indeed, Nestola et al. (2014) investigated the MgCr\(_2\)O\(_4\)–Sp and FeCr\(_2\)O\(_4\)–Sp with identical experimental techniques, and reached similar \(K_T\) values (182.5 (14) GPa with \(K_T^0 = 5.8\) (4) and 184.8 (17) GPa with \(K_T^0 = 6.1\) (5), respectively). The intermediate compositions of the \((Mg_{1-x}\text{Fe}_x)\text{Cr}_2\text{O}_4-Sp_m\) should have similar \(K_T\) as well.

### 3.4. Thermal expansivities of the \((Mg_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4-Sp_m\): a reinterpretation

The thermal expansivity of the \((Mg_{1-x}\text{Mn}_x)\text{Cr}_2\text{O}_4-Sp_m\) was experimentally investigated by Wang et al. (2012) at room \(P\) and up to 1000 °C, and a linear correlation between the \(\alpha_0\) and \(x\) at ambient \(P\) and \(T\) was suggested (Fig. 6). In light of the non-monotonic correlation between the \(K_T\) and \(x\) observed in this study, this linear relationship needs a new interpretation. Due to the relatively small volume variations observed in Wang et al. (2012; up to ~2.40% only), the thermal expansion coefficients should have been less well constrained than the \(K_T\). Note that the volume variations accomplished in this study were much larger, ~5.11% (Table 1).

In general, a compound easy to be compressed at high \(P\) should be ready to expand at high \(T\), which roots in the toughness of the constituent chemical bonds. Consequently, the correlation between the \(\alpha_0\) and \(x\) is expected to be approximately opposite to that of the \(K_T\) and \(x\) for one certain series of solid solutions. A careful rescrutinizing of the experimental result of Wang et al. (2012) indeed suggests a possible kink for the \(\alpha_0-x\) curve, somehow about \(x = 0.44\) rather than at \(x = 0.61\) for the \(K_T\) case, with a small kink for the approximately first half of the compositional range but a small decrease for the second half (Fig. 6). A different kink position at about \(x = 0.44\) may partially reflect the relatively low accuracy of the \(\alpha_0\), and partially indicate the necessity of more experimental measurements. Alternatively, the difference of the kink positions may simply be real. The thermal expansivity probes the anharmonicity of the interatomic potential whereas the compressibility probes the entire potential in the region where repulsion begins to dominate, so that the \(K_T-x\) curve and the \(\alpha_0-x\) curve for a series of solid solutions need not be exactly opposite to each other (Navrotsky, 1994).

For instance, the order of the \(K_T\) and \(\alpha_0\) of the isochemical minerals kyanite, andalusite and sillimanite are kyanite > sillimanite > andalusite and andalusite > kyanite > sillimanite, respectively, indicating not exactly opposite roles of \(T\) and \(P\) on mineral structures (Hu et al., 2011).

Similarly, He et al. (2011, 2012) observed a generally opposite relationship between the \(\alpha_0-x\) curve and the \(K_T-x\) curve and the \(\alpha_0-x\) curve and the \(K_T-x\) curve. Note that the volume variations accomplished in this study were much larger, ~5.11% (Table 1).
The primary feature of the Sp structure is a cubic close packing array of the oxygens. The positions of the oxygens are determined by the oxygen parameter $u$, which reflects the adjustment of the Sp structure to different cation substitutions on the tetrahedral and octahedral sites (Hill et al., 1979). The $u$ parameter can be calculated with the following equation:

$$ u = \frac{R^2/4 - 2/3 + (11R^2/48 - 1/18)^{1/2}}{2R^2 - 2}, \quad (6) $$

where $R$ is the ratio of $d_{MO}/d_{TO}$; it attains the value of 0.25 for an ideal cubic close packing oxygen array. For the (Mg$_{1-x}$Mn)$_2$O$_4$ solid solutions, the calculated $u$ gradually increases from $-0.2611$ to $0.2642$ as the substitution of Mg by Mn proceeds (Fig. 7a), suggesting that the oxygens move farther away from the nearest tetrahedral Mg$^{2+}$ (or Mn$^{2+}$) along the [111] direction and their close packing arrangement is more distorted. In detail, however, this distortion is not strictly proportional to the magnitude of the Mg–Mn substitution, but shows some retardance to the compositional change, as indicated by the generally negative $u_{-excess}$ values in Fig. 7b. The $u_{-excess}$ curve is evidently divided into two parts by the (Mg$_{1-x}$Mn)$_2$O$_4$–Spss with approximately $x = 0.5$, or the “ghost” end-member, which shows a nearly zero $u_{-excess}$ value and has a relatively relaxed structure. The negativity of the $u_{-excess}$ curve for the (Mg$_{1-x}$Mn)$_2$O$_4$–Spss with $x > 0.5$ is small, implying a small capability accommodating the structural deformation caused by the Mg–Mn substitution. In comparison, the negativity of the $u_{-excess}$ curve for the (Mg$_{1-x}$Mn)$_2$O$_4$–Spss with $x < 0.5$ is much larger, suggesting that large structural deformation caused by the Mg–Mn substitution can be readily absorbed. This contrast is understandable because a larger cation (Mn$^{2+}$) is more difficult to replace a smaller cation (Mg$^{2+}$) on sites dominated by the smaller cation ($x < 0.5$) than a smaller cation (Mg$^{2+}$) to replace a larger cation (Mn$^{2+}$) on sites dominated by the larger cation ($x > 0.5$).

The polyhedra in the Sp structure extensively share their edges in three dimensions, but have very different physical properties ($K_T$ for example; Hazen and Yang, 1999; Zhang et al., 2016), so that they may have extensive but nonuniform responses to the compositional variation along a binary Spss. Following Gracia et al. (2002), Zhang et al. (2016) fully decomposed the entire unit cell of the MgCr$_2$O$_4$–Sp into five types of polyhedra without introducing any volumetric overlapping, MgO$_4$, (O$_{4h}$), (O$_{4v}$), CrO$_6$ and O$_6$ with multiplicities 8, 8, 48, 16 and 16, respectively. They further calculated the volumes of these component polyhedra using the following equations (Yamanaka and Takéuchi, 1983):

$$ V_{\text{MgO}_4} = 64V \cdot |u_{18}|^3/3, \quad (7) $$

$$ V_{\text{(O}_{4h})} = 64V \cdot |u_{38}|^3/3, \quad (8) $$

$$ V_{\text{(O}_{4v})} = 8V \cdot |u_{18}| \cdot |u_{38}|/3, \quad (9) $$

$$ V_{\text{CrO}_6} = 128V \cdot u \cdot |u_{38}|^2/3, \quad (10) $$

and

$$ V_{O_b} = 128V \cdot |u_{18}| \cdot |u_{12}|/3, \quad (11) $$

where
Similarly, we have carried out the calculations for the (Mg1−xMnx)Cr2O4−Spss. The results show that the volume percentages for the five types of polyhedra MgO4, (O4)1, (O4)2, CrO6 and O6 in the MgCr2O4−Sp structure are −5.4, 3.2, 24.8, 28.9 and 37.8%, respectively. As the Mg−Mn substitution proceeds and accomplishes, the volume changes of these five types of polyhedra in the unit cells of the (Mg1−xMnx)Cr2O4−Spss are not uniform indeed: the volume of the (Mg,Mn)O4 increases by ~7.1% (from 31.05 to 34.60 Å³), that of the (O4)1 decreases by ~8.0% (from 18.27 to 17.43 Å³), that of the (O4)2 remains almost constant (reduced by ~0.5%; from 143.70 to 148.32 Å³), that of the CrO6 decreases by ~4.3% (from 167.48 to 166.32 Å³), and that of the O6 increases by ~3.3% (from 218.74 to 234.39 Å³). On the other hand, the total volume of the tetrahedra MgO4, (O4)1 and (O4)2 increases by 3.75% (from 193.11 to 200.36 Å³), so does the total volume of the octahedra CrO6 and O6 by 3.75% from 386.23 to 400.71 Å³. A constant volume ratio of 1:2, as embedded in equations (7)−(11), is therefore maintained between these tetrahedra and these octahedra whatever the deformation extent of the oxygen array is (Fig. 7).

$$u_{ij} = u - i/j.$$  

(12)

The volumes of the individual polyhedra ($V_{\text{poly}}$) must have different responses to the compositional change as well. The ($V_{\text{poly}}$)$-x$ relationships are shown in Fig. 8a−e, and the $V_{\text{poly-excess}}$-$x$ relationships are shown in Fig. 8a*−e*.

Although volumetrically unimportant, the (Mg,Mn)O4 tetrahedron shows the largest volume variation, ~11.1% (from 3.894 (4) to 4.325 (4) Å³), as x increases from zero to one (Fig. 8a). This is totally expected since the compositional variation of the (Mg1−xMnx)Cr2O4−Spss takes place on the (Mg,Mn)O4 tetrahedra. In addition, a negative $V_{\text{poly-excess}}$-$x$ relationship is demonstrated by our results (Fig. 8a*), as dictated by the assumed ideal mixing behavior.

In contrast, the other two types of tetrahedra, (O4)1 and (O4)2, show completely different behaviors; their $V_{\text{poly}}$-$x$ relationships and $V_{\text{poly-excess}}$-$x$ relationships are rather complicated (Fig. 8b and c, and Fig. 8b* and c*, respectively). Although their volumes either linearly decrease (by ~4.6% from 2.283 (3) to 2.179 (3) Å³ for the (O4)1) or increase (by ~3.2% from 2.994 (0) to 3.090 (0) Å³ for the (O4)2), both types of tetrahedra show generally positive mixing behaviors. In detail, their $V_{\text{poly-excess}}$-$x$ curves are divided into two parts approximately by the “ghost” end-member, the (Mg1−xMnx)Cr2O4−Spss with x = 0.5. Interestingly, the first local maximum positivity is much smaller than the second in both cases, suggesting that the (Mg1−xMnx)Cr2O4−Spss in the compositional range of 0.5 < x < 1 have much larger compliances to any local strains caused by the Mg−Mn substitution.

The CrO6 octahedron shows a peculiar volumetric variation (Fig. 8d). Its overall variation is an extremely small reduction (~0.7% from 10.468 (6) to 10.395 (6) Å³), which is mostly expected due to its relatively large bulk modulus (~230 (30) GPa; Hazen and Finger, 1979). Against this general trend, and interestingly, the volumes of the CrO6 octahedron in the (Mg1−xMnx)Cr2O4−Spss at x = 0.61 (2) and 0.77 (2) are somewhat larger than the volume of the CrO6 octahedron in the (Mg1−xMnx)Cr2O4−Spss at x = 0.44 (2). Combined with the general positive correlation between the $d_{M-O}$ and x (Fig. 5a), the overall negative relationship between the CrO6 volume and x implies continuous deformation of the CrO6 octahedron. Furthermore, the $V_{\text{poly-excess}}$-$x$ curve is much similar to the $d_{M-O-excess}$-$x$ curve (Figs. 8d* and 5a). Like in the cases of the (O4)1 and (O4)2 (Fig. 8b* and c*), the positive $V_{\text{poly-excess}}$-$x$ curve for the CrO6 octahedron is divided into two parts by the “ghost” end-member, with the second part much more prominent than the first part.

The volume of the individual O6 octahedron of the (Mg1−xMnx)Cr2O4−Spss increases significantly, by ~7.2% (from 13.671 (6) to 14.650 (7) Å³; Fig. 8e). The O6 octahedron is the second most compressible polyhedra in the MgCr2O4−Sp (only less compressible than the MgO4 tetrahedron; Zhang et al., 2016), and its volumetric variation comes as the second largest. The $V_{\text{poly-excess}}$-$x$ curve is very interesting, with the first part at x < 0.5 negligible whereas the second part at x > 0.5 distinctively positive (Fig. 8e*).

In summary, a range of structural adjustments takes place when Mn substitutes for Mg in the (Mg1−xMnx)Cr2O4−Spss.
As x increases from 0 to 1, the volumes of the unit cell, the tetrahedra (the MgO₄, (O₂)₁ and (O₂)₂) and the octahedra (the CrO₆ and O₆) increase by similar amounts (i.e., 3.75%). The volume of the individual (O₄)₁ tetrahedron or CrO₆ octahedron decreases in fact (Fig. 8b and d), but is readily overcompensated by the MgO₄ and (O₂)₂ tetrahedra (Fig. 8a and c), or by the O₆ octahedron (Fig. 8e), respectively. The oxygen array continuously deforms further (Fig. 7a). The (Mg₁₋ₓMnₓ)Cr₂O₄–Sp₉₉ with x < 0.5 have smaller compliance in promoting the Mg–Mn substitution than those with x > 0.5, as indicated by the u_excess–x curve (Fig. 7b) and the V_poly–excess–x curves (Fig. 8b* – e*).

4. Implication

In order to accurately constrain the chemical composition and geophysical behavior of the interior of the Earth, precise determinations of the K_T for the constituent minerals with relevant compositions are important. With recent rapid development of some experimental techniques, especially the synchrotron-based high-P techniques, a huge body of data with increasing accuracy has been generated. Due to the large variety of the mineral species and the complex of their compositions, some extrapolation or interpolation with the assumption of a generally linear compositional dependence of the K_T is presently still employed in many cases. For such cases, our study implies that great precaution must be taken since the factors affecting the compressional behavior of mineral solid solutions have not been fully understood.

Many factors, including but not limited to the structure feature of the solid solutions (Hazen and Finger, 1979), the size mismatch of the substituting cations (O’Neill and Navrotsky, 1984), their charge difference (Fe³⁺ versus Ti⁴⁺ in Fe₁₋ₓTiₓO₄–Sp₉₉ for example; Yamanaka et al., 2013), and their electronic and magnetic contrast (Mg²⁺ versus Fe²⁺ in (Mg₁₋ₓFeₓ)₂SiO₄–Ol₉₉ for example; Dachs et al., 2007), can affect the mixing behavior of a solid solution series, affect the K_T and affect the correlation pattern of the K_T and composition.

For the crystal structures with extensive edge sharing between the component polyhedra, the size mismatch of the substituting cations is important in determining the relationship between the K_T and composition of a series of solid solutions: if the size difference is small, it has a high tendency to be linear; otherwise, it may be complicated. As demonstrated for the Sp structure, the size difference of the Mg²⁺ and Fe²⁺ in the (Mg₁₋ₓFeₓ)₂SiO₄–Sp₉₉ is relatively small (~3.5%; O’Neill and Navrotsky, 1983), the K_T has an almost linear dependence to the x (Liu et al., 2016). In comparison, the size difference of the Mg²⁺ and Mn²⁺ in the (Mg₁₋ₓMnₓ)Cr₂O₄–Sp₉₉ is somewhat large (~12%; O’Neill and Navrotsky, 1983), the K_T and x have a non-monotonic relationship.

Similar phenomena has also been observed for the Grt structure: for the (Mg₁₋ₓFeₓ)₃Al₂Si₃O₁₂–Grt₉₉ (~3.4% difference in the sizes of the Mg²⁺ and Fe²⁺; Shannon, 1976), the correlation between the K_T and x is nearly linear (Huang and Chen, 2014); for the (Mg₁₋ₓCaₓ)₂Al₂Si₃O₁₂–Grt₉₉ (~25.8% difference in the sizes of the Mg²⁺ and Fe²⁺; Shannon, 1976), the correlation between the K_T and x is “W”-shaped (Du et al., 2015). This hypothesis seems applicable to the (Mg₁₋ₓFeₓ)O periclase-wüstite solid solutions as well, as a generally linear correlation has been observed between the K_T and x (Fei, 1999; an ~3.5% difference in the cation sizes (Shannon, 1976)). For less tightly-bound crystal structures such as the pyroxene and feldspar, on the other hand, the size mismatch of the substituting cations is presumably less important in determining the correlation between the K_T and composition, which is usually monotonic with small curvature. This proposal has been supported by the experimental observations along the NaAlSi₂O₆–CaFeSi₂O₆ join and NaAlSi₂O₆–CaAl₂Si₂O₈ join which involve substituting cations with a large range of cation size differences (Angel, 2004; Nestola et al., 2008). For the least tightly-bound or open crystal structures like the olivine and apatite, further, the size mismatch of the substituting cations is usually unimportant in determining the correlation between the K_T and composition, which is commonly linear. For example, the size difference of P⁵⁺ and V⁵⁺ in the Pb₂O₃[PO₄]₁₋ₓ[VO₄]ₓ is as large as ~108.9% (Shannon, 1976), and the K_T and x relationship has been established as generally linear (He et al., 2012). For the (Mg₁₋ₓFeₓ)₂SiO₄–Ol₉₉, the cation size difference is small and the K_T and x relationship is linear (Poe et al., 2010; Nestola et al., 2011a, 2011b), matching the expectation.

Other factors like the charge difference, electronic distinction and magnetic contrast are usually associated with the substitution of different cations with different sizes, so that their effects on the correlation pattern between the K_T and composition are hard to separate and much less well constrained experimentally. O’Neill and Navrotsky (1983) had some discussions on the electronic entropy in the transition-metal Sp, and pointed out that the electronic entropy might affect the cation distribution between the tetrahedra and octahedra in a complicated way. Dachs et al. (2007) delicately constrained the electronic and magnetic contributions to the molar entropy of mixing for the (Mg₁₋ₓFeₓ)₂SiO₄–Ol₉₉, demonstrated their importance, and claimed that they might make the thermodynamic behavior of the Ol₉₉ very complicated. Apparently much more work is required before the effects of these factors on the relationship between the K_T and composition can be adequately understood.

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