American Mineralogist, Volume 67, pages 788–793, 1982

$MgSiO_3$ (ilmenite-type): single crystal X-ray diffraction study

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Abstract

A structure refinement of $MgSiO_3$ with the ilmenite-type structure has been carried out with single crystal X-ray diffraction techniques. Magnesium and silicon atoms are completely ordered in the structure. The magnesium silicates with higher transition pressures have smaller MgO_6 and larger SiO_6 octahedra than those with lower transition pressures, resulting in more compact arrangements of oxygen atoms in the higher-pressure phases. Cation–oxygen distances of ilmenite-type structures systematically change depending on the ionic radii of cations, and this relation is followed for Mg–O and Si–O distances of ilmenite-type $MgSiO_3$. The degree of distortion of cation octahedra in the ilmenite-type structures is independent of the kinds of cations but the shifts of cations from the centers of octahedra systematically change as a function of ionic radius.

Introduction

A "hexagonal" modification of $MgSiO_3$ was first synthesized by Kawai *et al.* (1974) at ultra-high-pressure. Detailed investigations by Ito and Matsui (1974) revealed that it is trigonal (space group $R\bar{3}$) with the ilmenite-type structure.

In a series of high-pressure phase transformations in $MgSiO_3$, it has been established that the ilmenite-type structure is stabilized in the pressure range approximately from 210 to 250 kbar at 1100° C (Ito and Yamada, 1981), suggesting that the ilmenite structure with octahedrally coordinated Si is one of the important constituents of the deep mantle. It has also been observed that the solid solution of Fe for Mg in the ilmenite-type phase is limited to only 10 mole percent (Ito and Yamada, 1981), whereas that of 2Al for Mg plus Si is more extensive, resulting in the pyrope composition of $3MgSiO_3 \cdot Al_2O_3$ (Liu, 1977). In this context, the details of the structure of ilmenite-type $MgSiO_3$ are basic to an understanding of the stability of silicate ilmenite and to mantle mineralogy.

There are only a few structure determinations for high-pressure compounds in which Si atoms are octahedrally coordinated; *e.g.*, SiO_2 stishovite (Baur and Khan, 1971, and Sinclair and Ringwood, 1978) and perovskite-type $MgSiO_3$ (Ito and Matsui, 1978, and Yagi *et al.*, 1978); all of these studies except that of Sinclair and Ringwood (1978) were performed by powder X-ray diffraction. Structure analysis of ilmenite-type $MgSiO_3$ is thus basic to an understanding of the SiO_6 octahedral configuration. In the case of ilmenite-type structures, however, single crystal analysis is indispensable because many crystallographically non-equivalent reflections with the same Bragg angles are superposed in the powder diffraction pattern. In the present study the crystal structure of ilmenite-type $MgSiO_3$ was therefore refined by single-crystal X-ray diffraction techniques.

Experimental

The specimen used in this work was synthesized at approximately 220 kbar pressure and 1550° C with the run time of 20 minutes, using a uniaxial split-sphere-type high-pressure apparatus (Kawai *et al.*, 1973) with synthetic clinoenstatite as starting material. The single crystal specimen which was used in the crystal structure analysis is platy in shape parallel to (001), approximately 40 μm in thickness and 90 μm in diameter. It is transparent

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and colorless, and shows uniaxial positive optical properties.

X-ray photographs indicate that only reflections with $-h + k + l = 3n\pm1$ are absent, as consistent with the space group $R3$ or $R\bar{3}$. Cell dimensions are $a = 4.7284(4)$ and $c = 13.5591(16)$Å (Ito and Matsui, 1977).

Mo$K\alpha$ radiation monochromatized by pyrolytic graphite was used for intensity measurements. The intensities of 1984 reflections including crystallographically equivalent reflections within the range $0 < 2\theta < 100°$ were obtained by employing the 2θ–θ scan technique on a four-circle diffractometer (RIGAKU AFC-3). All the observed reflections were processed to yield 619 unique reflections, of which 253 had high standard deviations ($|F_o| < 3\sigma_{hkl}\ (F_o)$) or zero intensity, where $\sigma_{hkl}\ (F_o)$ is the standard deviation of each reflection obtained from counting statistics. Conventional polarization and Lorentz corrections were carried out in the process of the data collection. No absorption corrections were applied because of the small value of $\mu r(<0.1)$.

The refinement of the structure

The refinement of the structure was initiated with the idealized atomic coordinates of ilmenite, $FeTiO_3$ (Shirane *et al.*, 1959b). The space group of ilmenite, $R\bar{3}$, was assumed, and it was subsequently confirmed to be correct by the present structure analysis. The scattering factor curves of Mg, Si and O used for calculations are those of neutral atoms (*International Tables for X-ray Crystallography, Vol. IV* (1974)). The 366 reflections with $|F_o| > 3\sigma_{hkl}\ (F_o)$ were used in the structure refinement with weights $1/\sigma^2_{hkl}\ (F_o)$.

There are two schemes to index reflections which are mutually related by the relation $(h'/k'/l') = (\bar{1}\bar{1}0/010/00\bar{1})\ (h/k/l)$.

The Mg and Si atoms correspond to Fe and Ti atoms of the ilmenite structure, respectively, in one of two indexing schemes. In this case idealized atomic coordinates result in (0 0 1/3) for Mg, (0 0 1/6) for Si and (1/3 0 1/4) for oxygen atoms. In another indexing scheme, Mg and Si correspond to Ti and Fe for ilmenite structure, however, this is inconvenient to compare $MgSiO_3$ ilmenite with other compounds of ilmenite-type structure. Therefore, refinements were carried out for each of the two schemes of indexing, using former Mg and Si arrangement.

The value of the weighted R-value approximately 0.45 for the initial atomic parameters for both cases, was reduced to 0.038 (R for unit weight; 0.049) for one of the two indexing schemes after approximately ten cycles of refinement of atomic coordinates and anisotropic temperature factors. The refinement did not converge for the second indexing scheme. In order to determine the degree of cation order, refinement of the site occupancies (starting from 0.5Mg + 0.5Si for both cation sites) was carried out and a difference-Fourier synthesis was computed. The results of both procedures indicate that the Mg and Si atoms are completely ordered within experimental error.

The final atomic coordinates and anisotropic temperature factors are given in Tables 1 and 2, respectively, and interatomic distances and angles are shown in Table 3. Observed and calculated structure factors are listed in Table 4[1]. All computations for the least-squares refinement of the structure, interatomic distances and angles, and drawing of the crystal structure were carried out by using RFINE 2 (Finger, 1969), UMBADTEA (Finger, 1968, University of Minnesota Program for Computing Bond Angles and Distances, and Thermal Ellipsoids with Error Analysis) and ORTEP-II (Johnson, 1971), respectively, at the Crystallographic Research Center, Institute of Protein Research, Osaka University (ACOS-700 computer).

Description and discussion of the structure

The structure is obtained by substituting Mg for Fe and Si for Ti in the ilmenite structure. The Mg and Si atoms are completely ordered. Figure 1 shows a perspective view of the structure. The arrangement of oxygen atoms is based on a distorted hexagonal closest packing having a wide range of O–O distances (2.331 to 3.076Å). In particular, the

Table 1. Refined atomic coordinates for ilmenite–type $MgSiO_3$

	x	y	z	$B_{eq}/\text{Å}^2$
Mg	0	0	0.35970(12)	0.59
Si	0	0	0.15768(10)	0.42
Oxy	0.3214(5)	0.0361(4)	0.24077(11)	0.48

B_{eq}: *Equivalent isotropic temperature factors computed according to the relation* $B_{eq} = \frac{4}{3}\sum_{i}\sum_{j} \beta_{ij}(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Estimated standard errors refer to the last digit.

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[1] To obtain a copy of this table, order Document AM-82-206 from the Mineralogical Society of America, Business Office, 2000 Florida Avenue, NW, Washington, DC 20009. Please remit $1.00 in advance for the microfiche.

Table 2. Ilmenite–type $MgSiO_3$; anisotropic temperature factors (×10^4)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg	100(6)	β_{11}	5.9(8)	$(1/2)\beta_{11}$	0	0
Si	63(5)	β_{11}	5.7(6)	$(1/2)\beta_{11}$	0	0
Oxy	68(10)	60(10)	8.0(8)	34(8)	-1(2)	1(2)

Coefficients in the expression $exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+2\beta_{12}hk+2\beta_{13}h\ell+2\beta_{23}k\ell)]$.

Estimated standard errors refer to the last digit.

edge shared O–O distance between two SiO_6 octahedra is the shortest, and it is shorter even than the O–O distance of the shared face between MgO_6 and SiO_6 octahedra. The mean value of Si–O distances, 1.799Å, is about 0.1 to 0.15Å larger than those of SiO_4 tetrahedra of β– and γ–Mg_2SiO_4.

It is of interest to compare the volumes of polyhedra in the structures of high-pressure magnesium silicates. The MgO_6 octahedra are more compressed and SiO_4 tetrahedra more expanded in higher pressure phases than lower pressure ones so as to minimize the variation of O–O distances in the structures. This has been discussed for the structures of polymorphs of Co_2SiO_4 (Morimoto *et al.*, 1974) and Mg_2SiO_4 (Horiuchi and Sawamoto, 1981). The volume change of SiO_6 octahedra, which are observed in the structures of SiP_2O_7 (AIII modification, Bissert and Liebau, 1970), SiO_2 (stishovite, Baur and Khan, 1971, and Sinclair and Ringwood, 1978), $MgSiO_3$ (ilmenite-type; present work: perovskite-type; Ito and Matsui, 1978, and Yagi *et al.*, 1978) shows the same tendency as that of SiO_4 tetrahedra in Co_2SiO_4 and Mg_2SiO_4. That is, SiO_6 octahedra are expanded in higher pressure phases relative to lower pressure ones. The mean values of cation–oxygen and oxygen–oxygen distances of MgO_6, SiO_4 and SiO_6 in the structures of the above compounds and in the Mg_2SiO_4 polymorphs are listed in Table 5, and the octahedral volumes of MgO_6 and SiO_6 are plotted in Figure 2 against the phase transition pressures for a temperature of approximately 1000° C. The results of refinements of stishovite by Baur and Khan (1971) and Sinclair and Ringwood (1978) are identical. The interatomic distances and octahedral volumes for γ–Mg_2SiO_4 were approximately estimated from those of γ – $(Mg_{0.5}Fe_{0.5})_2SiO_4$ (Sawamoto *et al.*, 1981) and γ–Fe_2SiO_4 (Yagi *et al.*, 1974) by the relation $x_M = 2x_{MF} - x_F$, where x_M signifies the value of a parameter such as interatomic distance, volume of the polyhedron *etc.* for γ–Mg_2SiO_4, and x_{MF} and x_F, those for γ–$(Mg_{0.5}Fe_{0.5})_2SiO_4$ and γ = Fe_2SiO_4, respectively. The octahedral volumes of MgO_6 are remarkably smaller in the phases with higher transition pressures. On the other hand, those of SiO_6 increase with increasing pressure of phase transition. It is noteworthy that the volumes change

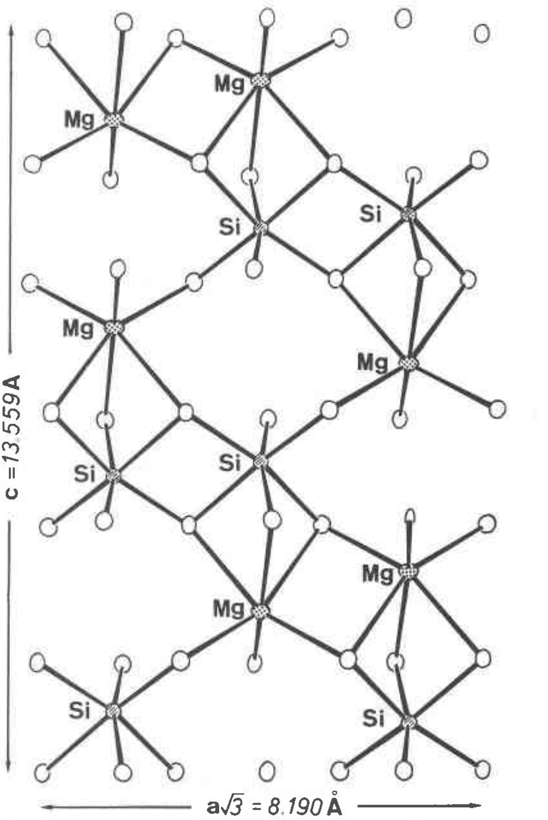

Fig. 1. A perspective view of the structure of ilmenite–type $MgSiO_3$ drawn using the program ORTEP (Johnson, 1971).

Table 3. Crystal data, and interatomic distances and angles of ilmenite–type $MgSiO_3$

cell constants	a_{hex} = 4.7284(4) Å		R$\bar{3}$, Z = 6	
	c_{hex} = 13.5591(16)		D_{calc} = 3.810 g/cm^3	
	Vol. = 262.54 Å^3		μ = 11.330 cm^{-1}	
SiO_6 octahedron			distances	O-M-O angles
Si - O	1.830(2) [3]	O - O	2.331(4) [3]e_{Si}	80.8(1)°
	1.768(2) [3]		2.497(4) [3]f_{Mg}	86.1(1)
mean	1.799		2.653(3) [3]	97.2(1)
			2.682(3) [3]	96.4(1)
		mean	2.541	
MgO_6 octahedron				
Mg - O	2.163(2) [3]	O - O	2.497(4) [3]f_{Si}	70.5(1)°
	1.990(2) [3]		2.941(3) [3]	90.1(1)
mean	2.077		3.052(3) [3]e_{Mg}	94.5(1)
			3.076(4) [3]	101.2(1)
		mean	2.892	

Estimated standard errors are given in parentheses and refer to the last decimal place.
e_M ; Edge shared between two MO_6 octahera,
f_M ; Face shared with MO_6 octahedron.
Numbers in square brackets are multiplicity factors.
Cell constants; Data by Ito & Matsui(1977).

Table 5. Comparison of the mean Si–O, Mg–O and O–O distances of the cation polyhedra of high-pressure phases of SiO_2 and magnesium silicates

	SiO_4 and MgO_6		SiO_6 and MgO_6		SiO_6 and MgO_8	
	β-$Mg_2SiO_4^{*)}$	γ-$Mg_2SiO_4^{*)}$	stishovite	ilmenite-type $MgSiO_3^{*)}$	perovskite-type $MgSiO_3$ (1)	(2)
Si-O O -O	1.651 2.693	1.670 2.725	1.775 2.508	1.799 2.541	1.79 2.53	1.79 2.53
Mg-O	2.069 2.084 2.090	2.062	-	2.077	2.21	2.20
O -O	2.925 2.942 2.954	2.910	-	2.892	2.71	2.70
Ref.	Horiuchi & Sawamoto	see text	Baur & Khan	Present work	Yagi *et al.*	Ito & Matsui

*Specimen with *-mark;single crystal, others;powder specimen*
The O-O for perovskite-type $MgSiO_3$;the average of 17 polyhedral edges.

approximately linearly versus phase transition pressures with slopes of about -5.7×10^{-3} and $+1.3 \times 10^{-3}$Å^3/kbar for MgO_6 and SiO_6 octahedra, respectively. Their slopes are shown with dotted lines in Figure 2. Furthermore, the slope for MgO_6 is in very good agreement with the curve $V/V_o = [1 + 2.85 \times 10^{-3}P(\text{kbar})]^{-0.219}$ obtained by *in situ* X-ray diffraction measurements of MgO in a diamond high-pressure cell at 25° C by Mao and Bell (1979). This curve is shown with a solid line in Figure 2.

The mean value of O–O distances of SiO_6 octahedra of ilmenite–type $MgSiO_3$ is about 0.2Å smaller than those of SiO_4 tetrahedra of β– and γ–Mg_2SiO_4. That for the Mg-octahedron is also smaller than those of β– and γ–Mg_2SiO_4. This is also analogous to the structural relation between perovskite–type $MgSiO_3$ and β– and γ–Mg_2SiO_4. Thus, the oxygen packing is more compact in the ilmenite– and perovskite–type structures of $MgSiO_3$ than in the structures of β– and γ–Mg_2SiO_4.

Idealized and averaged cation–oxygen distances of MO_6 octahedra in the several well-established ilmenite–type structures are shown against cation radii in Figure 3. The idealized cation–oxygen dis-

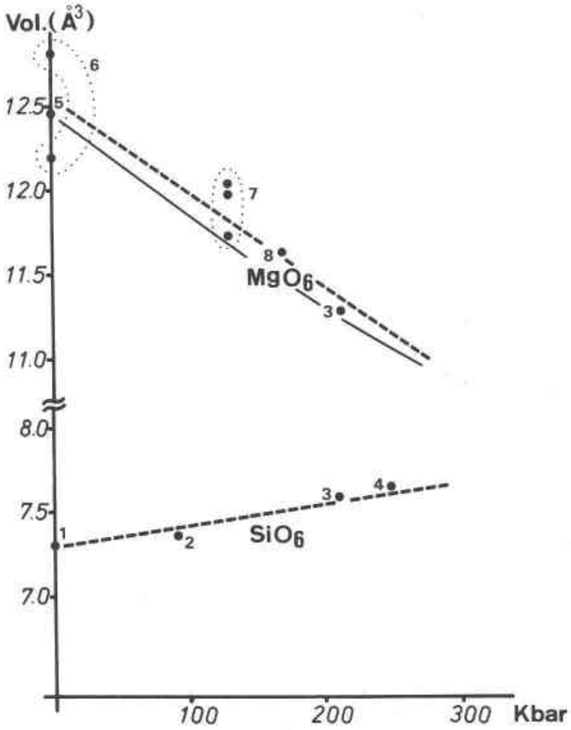

Fig. 2. Octahedral volumes of MgO_6 and SiO_6 in the structures of several magnesium silicates, MgO and SiP_2O_7 plotted against the transition pressure of each phase. 1. SiP_2O_7 (Bissert & Liebau, 1969); 2. stishovite (Baur & Khan, 1971); 3. ilmenite-type $MgSiO_3$ (present work), 4. perovskite–type $MgSiO_3$ (Ito & Matsui, 1978, and Yagi *et al.*, 1978); 5. MgO (Mao & Bell, 1979); 6. Mg_2SiO_4 (Hazen, 1976); 7. β–Mg_2SiO_4 (Horiuchi & Sawamoto, 1981); 8. γ–Mg_2SiO_4 (see text). The phase transition pressures were obtained from Ito and Yamada (1981) for both ilmenite– and perovskite-types of $MgSiO_3$, and Suito (1977) for β– and γ–Mg_2SiO_4.

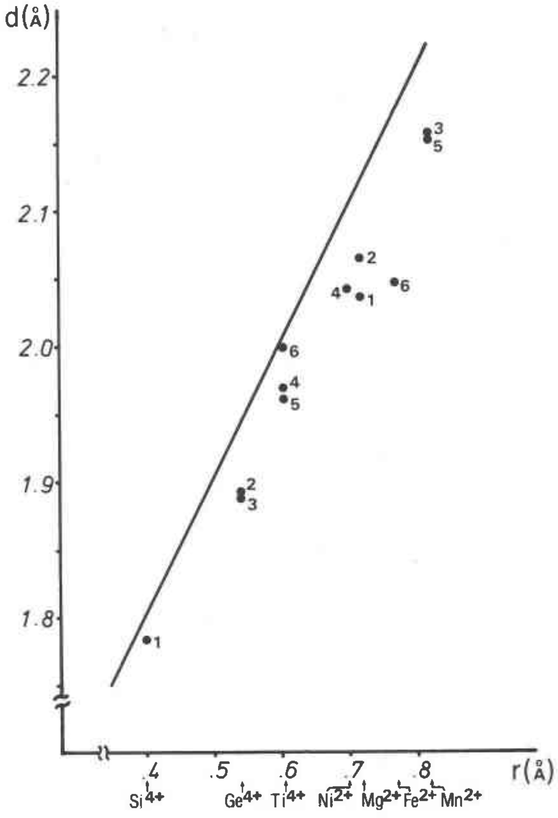

Fig. 3. Idealized and averaged cation–oxygen distances of MO_6 octahedra plotted against the M cation radius in several ilmenite–type structures. 1. $MgSiO_3$ (present work); 2. $MgGeO_3$ (Kirfel *et al.*, 1978); 3. $MnGeO_3$ (Hirano *et al.*, 1980); 4. $NiTiO_3$ (Shirane *et al.*, 1959a); 5. $MnTiO_3$; 6. $FeTiO_3$ (Shirane *et al.*, 1959b).

tance, d_i, was obtained from the relation $d_i = r_M + r_O$ which is shown by the solid line in Figure 3 (r_M is the ionic radius of the cation and r_O is the ionic radius of O^{2-}, while the averaged cation–oxygen distance, d_a, was estimated from the relation $d_a = {}^3\sqrt{(3/4)v}$ where v is the volume of the MO_6 octahedron. Radii are those of Shannon and Prewitt (1969). The plots of d_a *versus* r_M change linearly with a slope similar to that of the solid line for the relation $d_i = d_M + r_O$. The systematic difference of about 0.05Å between d_i and d_a might be attributed to (1) over-estimation of the radius of O^{2-}, 1.40Å, or (2) shortening of interatomic distances due to a covalent component of the bonding.

The mean octahedral quadratic elongation parameters (Robinson *et al.*, 1971), $\langle\lambda_{\mathrm{OCT}}\rangle_{\mathrm{OO}}$ and $\langle\lambda_{\mathrm{OCT}}\rangle_{\mathrm{MO}}$, were calculated for the above compounds with ilmenite–type structures in order to estimate the degree of distortion of the octahedra and shift of cations from the centers of octahedra. Their values were plotted against the ionic radii of cations (Fig. 4). The value $\langle\lambda_{\mathrm{OCT}}\rangle_{\mathrm{OO}}$ given by

$$\sum_{i=1}^{12} (l^{i}_{\mathrm{OO}}/l_{\overline{\mathrm{OO}}})^2/12$$

is a measure of only the degree of distortion of an octahedron, whereas, the value of $\langle\lambda_{\mathrm{OCT}}\rangle_{\mathrm{MO}}$ given by

$$\sum_{i=1}^{6} (l^{i}_{\mathrm{MO}}/l_{\overline{\mathrm{MO}}})^2/6$$

is a measure of the shift of a cation from the center of an octahedron and of the distortion of an octahedron. Values of l^{i}_{MO} and l_{OO} represent the M–O and O–O distances in the real structure, respectively, while, $l_{\overline{\mathrm{MO}}}$ $l_{\overline{\mathrm{OO}}}$ are those of M–O and O–O, respectively, for an octahedron with O_h symmetry whose volume is equal to that of the distorted octahedron. In Figure 4, solid and open circles indicate the values of $\langle\lambda_{\mathrm{OCT}}\rangle_{\mathrm{MO}}$ and $\langle\lambda_{\mathrm{OCT}}\rangle_{\mathrm{OO}}$, respectively. The values of $\langle\lambda_{\mathrm{OCT}}\rangle_{\mathrm{OO}}$ are independent of the cation radii. However, those of $\langle\lambda_{\mathrm{OCT}}\rangle_{\mathrm{MO}}$ systematically increase with the increase of cation radius. These results indicate that the degree of distortion of octahedra is almost uniform for all cations in ilmenite–type structures, while the shifts of cations from the center of octahedra are greater for larger cations.

The distances between two oxygen layers parallel to (001), which were discussed as "octahedron heights" by Kirfel *et al.* (1978), are 2.010 and 2.510Å for the heights of the Si– and Mg–octahedra, respectively. The octahedron height of the Mg–octahedra of ilmenite–type $MgSiO_3$ is fairly large in comparison with that of $MgGeO_3$ (Kiefel *et al.*, 1978), whereas, that of Si–octahedra of ilmenite–type $MgSiO_3$ is the smallest value for cation–octahedra of ilmenite–type structures reported so far, and is slightly smaller than the value estimated for SiO_6 by Kirfel *et al.*

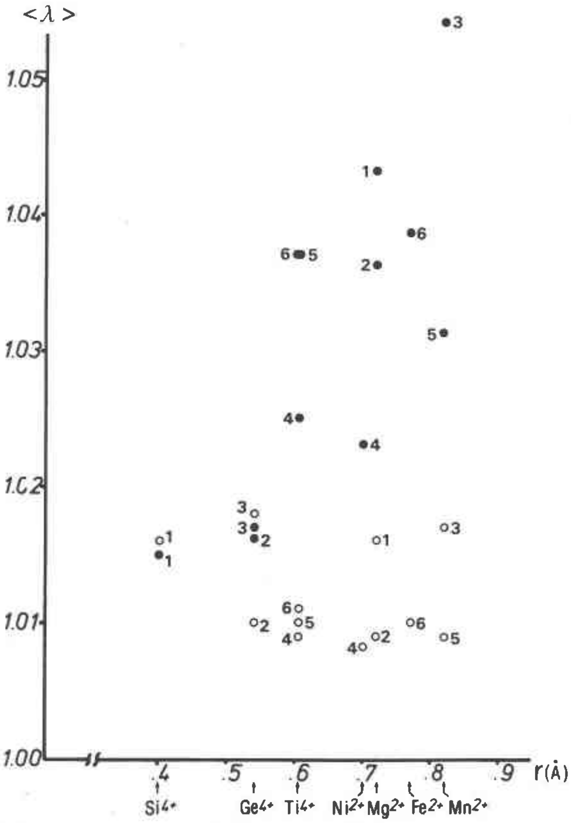

Fig. 4. The mean octahedral quadratic elongation parameters, $\langle\lambda_{\mathrm{oct}}\rangle_{\mathrm{oo}}$; open circles and $\langle\lambda_{\mathrm{oct}}\rangle_{\mathrm{MO}}$; solid circles, plotted against ionic radii in the several ilmenite–type structures as shown in Figure 3.

The difference between mean O–O distances of MgO_6 and SiO_6 octahedra is quite large in ilmenite–type $MgSiO_3$. However, that of two vacant $\square O_6$ octahedra, which are adjacent to both sides of face-shared O_3–Mg–O_3–Si–O_3 octahedra, is small and intermediate to mean O–O distances of MgO_6 and SiO_6 octahedra. Thus, the two vacant $\square O_6$ octahedra function as a buffer between expanded MgO_6 and compressed SiO_6 octahedra.

Acknowledgments

The authors would like to thank Professors Masayasu Tokonami, Fumikazu Kanamaru and Kichiro Koto for their helpful discussions regarding this work. Professor Donald R. Peacor and Dr. Robert M. Hazen contributed immensely with critical readings of the manuscript.

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Manuscript received, October 12, 1981;
accepted for publication, February 24, 1982.