

Single Crystal X-ray Diffraction Study of MgSiO₃ Perovskite from 77 to 400 K

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Abstract. Single crystal X-ray diffraction study of MgSiO₃ perovskite has been completed from 77 to 400 K. The thermal expansion coefficient between 298 and 381 K is $2.2(8) \times 10^{-5} \text{ K}^{-1}$. Above 400 K, the single crystal becomes so multiply twinned that the cell parameters can no longer be determined.

From 77 to 298 K, MgSiO₃ perovskite has an average thermal expansion coefficient of $1.45(9) \times 10^{-5} \text{ K}^{-1}$, which is consistent with theoretical models and perovskite systematics. The thermal expansion is anisotropic; the *a* axis shows the most expansion in this temperature range ($\alpha_a = 8.4(9) \times 10^{-6} \text{ K}^{-1}$) followed by *c* ($\alpha_c = 5.9(5) \times 10^{-6} \text{ K}^{-1}$) and then by *b*, which shows no significant change in this temperature range. In addition, the distortion (i.e., the tilting of the [SiO₆] octahedra) decreases with increasing temperature. We conclude that the behavior of MgSiO₃ perovskite with temperature mirrors its behavior under compression.

Introduction

The 670-km seismic discontinuity marks the separation between the Earth's upper and lower mantle. It is widely accepted that the bulk properties of the lower mantle can be accounted for with an assemblage of (Mg,Fe)SiO₃ perovskite and magnesiowüstite, with the possible addition of stishovite. Silicate perovskite is believed to be the most abundant mineral in the lower mantle, it is therefore critical to determine the physical properties of this phase so that constraints can be placed on geophysical models of the earth. One such property is the thermal expansion coefficient, which is crucial to placing constraints on compositional models for the lower mantle.

Knittle et al. (1986) studied polycrystalline samples of (Mg_{0.9}Fe_{0.1})SiO₃ perovskite from room temperature to 840 K using a high-temperature Guinier X-ray diffraction camera. At 840 K, silicate perovskite reverts to orthopyroxene. They found that the *b/a* and *c/a* lattice parameter ratios remained constant within the resolution of their experiments up to 840 K, thus concluding that (Mg_{0.9}Fe_{0.1})SiO₃ does not undergo significant change from its zero-pressure, room-temperature orthorhombic structure at high temperature. They also reported that the average thermal expansion coefficient of silicate perovskite between 450 and 840 K is $4 \times 10^{-5} \text{ K}^{-1}$. This value, unusually high for silicates, supports layered models of the thermal and convective state of the mantle.

We undertook a study of the thermal expansion of MgSiO₃ perovskite for the following reasons. First, Ito and Weidner (1986) successfully synthesized single crystals of MgSiO₃ perovskite of high enough quality to use in experimental studies. With a high-temperature, single-crystal X-ray diffraction study, we could improve the precision of volumes measured at high temperatures, thus obtaining better constraints on the thermal expansion coefficient of silicate perovskite. Second, we wished to determine whether the distortion of MgSiO₃ perovskite changed with temperature. The experimental errors in the previous work done on powder samples were too large to detect any such subtle structural changes.

We report here the results of two single crystal X-ray diffraction studies done at various temperatures on MgSiO₃ perovskite. First, we describe the results obtained from a high-temperature study of silicate perovskite. Unfortunately, we were unable to increase the temperature beyond 400 K because the crystal deteriorated. Second, we report the results from a more successful study of MgSiO₃ perovskite at low temperatures, between 77 and 298 K. These results are compared with those obtained from theoretical models of MgSiO₃ perovskite, from calculations based on perovskite vibrational spectra, and with expansion systematics of other orthorhombic perovskites of varying compositions and degrees of distortion from cubic symmetry.

Experimental

Two single crystals of MgSiO₃ perovskite were selected from a batch of crystals synthesized at 22 GPa and 1000° C (Ito and Weidner 1986) that were generously provided by Dr. E. Ito of Okayama University, Japan. No splitting of reflections was observed in precession photographs taken of these two crystals. Individual peaks scans completed on the four-circle diffractometer, however, showed well-defined peaks which were broad in both crystals, possibly caused by an extremely small mosaic size. Lattice parameters were measured using a Picker four-circle diffractometer with unfiltered MoK α radiation ($\lambda = 0.7107 \text{ \AA}$). They were determined at room temperature from 12 to 16 reflections between $23^\circ \leq 2\theta \leq 33^\circ$ using the procedure of King and Finger (1979) in which the crystal is centered in eight equivalent diffractometer positions. The cell parameters compare favorably with those of other workers (Table 1). It should be noted, however, that differences will arise in lattice constants determined from single crystal studies depending on

Table 1. Comparison of cell parameters and volume of MgSiO₃ perovskite crystals in this study with those of previous studies

<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Vol. (Å ³)	Reference
4.7786 (9)	4.9293 (9)	6.9003 (8)	162.54 (5)	This study: Crystal 1
4.7747 (14)	4.9319 (9)	6.8987 (9)	162.45 (6)	This study: Crystal 2
4.7787 (4)	4.9313 (4)	6.9083 (8)	162.80 (2)	Horiuchi et al. (1987) ^a
4.774 (1)	4.928 (2)	6.893 (2)	162.1 (1)	Kudoh et al. (1987) ^a
4.7754 (3)	4.9292 (4)	6.8969 (5)	162.35 (2)	Ito and Matsui (1978) ^b
4.783 (7)	4.953 (8)	6.886 (7)	162.1 (4)	Knittle et al. (1986) ^b
4.780 (1)	4.933 (1)	6.902 (1)	162.75 (5)	Yagi et al. (1978) ^b
4.790 (4)	4.943 (4)	6.897 (6)	163.2 (2)	Liu (1976) ^b

^a Single-crystal results; ^b Powder results

the centering technique used as well as what class of reflections (i.e. low or high angle) are used.

Intensity data were collected on both crystals as a final check of their overall quality. The intensities of 1105 reflections including symmetrically-equivalent reflections were collected in a hemisphere of reciprocal space for Crystal 1 within the range, $0^\circ < 2\theta \leq 60^\circ$, using the ω -scan technique. For Crystal 2, a total of 605 reflections were measured in a quadrant of reciprocal space between $0^\circ < 2\theta \leq 60^\circ$. Corrections were made for Lorentz and polarization effects. The structure refinements were initiated with the atomic coordinates reported by Horiuchi et al. (1986) using the least-squares program RFINE (Finger and Prince 1975). Neutral atomic scattering factor curves for Mg, Si and O were taken from the International Tables for X-ray Crystallography (1974). The refinement of Crystal 1 converged to *R* and *wR* values of 0.078 and 0.058, respectively, and that of Crystal 2 to *R* and *wR* values of 0.061 and 0.046, respectively. Tables listing *F*_{obs} and *F*_{calc} are available upon request from the authors. The refined positional parameters show excellent agreement with those of Horiuchi et al. (1986) (Table 2).

Crystal 1, $60 \times 40 \times 30 \mu\text{m}$, was mounted in a silica-glass capillary with a $40 \times 30 \times 30 \mu\text{m}$ CaF₂ crystal that was used as an internal temperature calibrant (Hazen and Finger 1981). This mount was inserted into a radiative heater for single-crystal x-ray diffraction, designed by Y. Ohashi (Hazen and Finger 1982). The temperature was controlled by a sensing thermocouple near the crystal position that was used as input to a controller designed by Finger et al. (1973). The automatic control system eliminates the 'chimney effect' resulting from various orientations of the furnace (pointing up and down) brought about by moving the crystal into diffracting positions. The cell volume of CaF₂ was determined from the {220} class of reflections. Upon increasing the temperature to 381(7)K, the sharp diffraction peaks of perovskite present at room temperature became broad and diffuse, indicating the formation of numerous domains. Indeed, Yeganeh-Haeri et al. (1987) found in their Brillouin spectroscopic experiments that the green light from the argon ion laser easily damaged the single crystals of MgSiO₃ perovskite and that light levels as low

Table 2. Refined positional parameters and isotropic temperature factors (Å²) for the two crystals in this study compared with the results of Horiuchi et al. (1987)

	Reference:	Horiuchi et al. (1986)	This study Crystal #1	This study Crystal #2
Mg	<i>x</i>	0.9859 (1) ^a	0.9856 (10)	0.9857 (9)
	<i>y</i>	0.0560 (1)	0.0564 (6)	0.0556 (6)
	<i>z</i>	1/4	1/4	1/4
	<i>B</i>	0.46	0.75 (7)	0.63 (7)
Si	<i>x</i>	0	0	0
	<i>y</i>	1/2	1/2	1/2
	<i>z</i>	0	0	0
	<i>B</i>	0.25	0.49 (4)	0.39 (4)
O1	<i>x</i>	0.1028 (2)	0.1015 (17)	0.1037 (13)
	<i>y</i>	0.4660 (2)	0.4673 (13)	0.4655 (14)
	<i>z</i>	1/4	1/4	1/4
	<i>B</i>	0.32	0.45 (12)	0.45 (13)
O2	<i>x</i>	0.6961 (1)	0.6962 (10)	0.6974 (8)
	<i>y</i>	0.2986 (2)	0.2983 (8)	0.2989 (8)
	<i>z</i>	0.0531 (1)	0.0524 (9)	0.0538 (7)
	<i>B</i>	0.34	0.47 (8)	0.31 (8)

^a Original coordinates were transformed to equivalent positions

as 20 mW were sufficient mW were sufficient to induce twinning. Fortunately, both the 220 and 004 peaks were sufficiently strong so that we were able to center these reflections reproducibly. We obtained averaged, centered 2θ values for the 004 and 220 reflections of 23.769(5)° and 23.890(6)°, respectively, at 381(7) K, compared with values of 23.779(2)° and 23.914(3)°, respectively, at 298 K. Estimates of the volumes at 298 and 381 K, based on the 004 and 220 reflections and the assumption that the angle between 220 and 200 (and 020) does not change with temperature, are 162.3 Å³ and 162.7 Å³, respectively. Thus the mean volumetric thermal expansion coefficient between 298 and 381 K is approximately $2.2 \times 10^{-5} \text{ K}^{-1}$.

A single-crystal X-ray diffraction study from 77 K to 298 K was then undertaken with an AC-1-101A Cryo-Tip refrigerator system designed by Air Products and Chemicals. Refrigeration was obtained in a heat exchanger using a Joule-Thomson cycle which is the simplest means of achieving cooling because no moving parts are required in the system. The temperature of the cold tip was varied by matching the flow rate of the refrigerant (in this case, high-pressure nitrogen gas from a cylinder) to the heat load. Temperature was stable to within ± 5 K. Crystal 2 of MgSiO₃ perovskite, $40 \times 40 \times 20 \mu\text{m}$, was mounted directly on the cold tip and enclosed in a beryllium vacuum shroud. Lattice parameters were determined at 77, 123, 166, 203, 238 and 298 K from 10 reflections between $23^\circ \leq 2\theta \leq 29^\circ$ centered at $\pm 2\theta$ (Table 3). Eight-position centering was not possible due to restrictions imposed by the low-temperature apparatus; consequently, the room temperature lattice parameters of Crystal 2 (Table 3) vary slightly from those reported in Table 1. It was critical to employ the same set of reflections and same centering procedure at all temperatures in order to study the crystal's response to decreasing temperature. We also checked whether we obtained the same results upon increasing temperature as we did when decreasing temperature. The lattice parameters at room temperature determined after the temperature was cycled

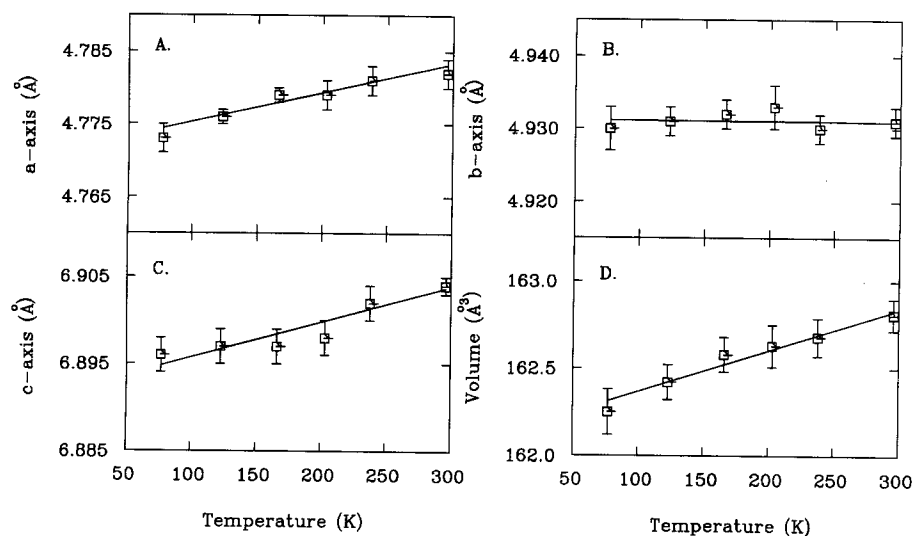


Fig. 1 A–D. Variation of the cell parameters, a (A), b (B), and c (C), and volume (D) of MgSiO_3 perovskite between 77 and 298 K. The linear thermal expansivity of a is $81.4(9) \times 10^{-6} \text{ K}^{-1}$ ($a(\text{Å}) = 4.7713(8) + 4.0(4) \times 10^{-5} T(\text{K})$), c is $5.9(5) \times 10^{-6} \text{ K}^{-1}$ ($c(\text{Å}) = 6.8917(8) + 4.1(4) \times 10^{-5} T(\text{K})$), and b shows no significant expansion in this temperature range. The mean volumetric thermal expansion coefficient between 77 and 298 K is $1.45(9) \times 10^{-5} \text{ K}^{-1}$ ($V(\text{Å}^3) = 162.13(3) + 2.4(1) \times 10^{-3} T(\text{K})$).

Table 3. Cell parameters and volume of MgSiO_3 perovskite (Crystal 2) between 77 and 298 K

Temp. (K)	a (Å)	b (Å)	c (Å)	Vol. (Å ³)
298	4.782 (2)	4.931 (2)	6.904 (1)	162.81 (9)
238	4.781 (2)	4.930 (2)	6.902 (2)	162.68 (11)
203	4.779 (2)	4.933 (3)	6.898 (2)	162.63 (12)
166	4.779 (1)	4.932 (2)	6.897 (2)	162.58 (10)
123	4.776 (1)	4.931 (2)	6.897 (2)	162.42 (10)
77	4.773 (2)	4.930 (3)	6.896 (2)	162.26 (13)

were within one standard deviation of those determined before the temperature was cycled.

Results and Discussion

Linear Thermal Expansivities and Unit Cell Distortions

The variation of the lattice parameters of MgSiO_3 perovskite between 77 and 298 K is shown in Figure 1a, b and c. There is significant anisotropy in the expansion of the three axes. The linear thermal expansivities of the a and c axes are $8.4(9) \times 10^{-6} \text{ K}^{-1}$ and $5.9(5) \times 10^{-6} \text{ K}^{-1}$, respectively. The b axis shows no significant change in this temperature range. Thus the linear expansivities of the cell axes increase in the order b, c, a . In a high-pressure, single-crystal X-ray diffraction study of MgSiO_3 perovskite, Ross et al. (in prep.) found that the a axis is most compressible, followed closely by c and then by b . Ross et al. (in prep.) also observed that both axial ratios show a significant increase between 0 and 10.6 GPa. In another high-pressure, single-crystal X-ray diffraction study, Kudoh et al. (1988) observed an increase in b/a but no significant change in c/a . In this low-temperature study, both c/a and b/a show a small, but significant, increase upon decreasing temperature (Fig. 2). These combined low-temperature and high-pressure results suggest that MgSiO_3 exhibits the 'inverse relationship' of temperature and pressure whereby the structural changes upon cooling from high temperature are similar to those upon compression (Hazen 1977).

The high-pressure studies of Kudoh et al. (1987) and Ross et al. (in prep.) conclude that MgSiO_3 perovskite be-

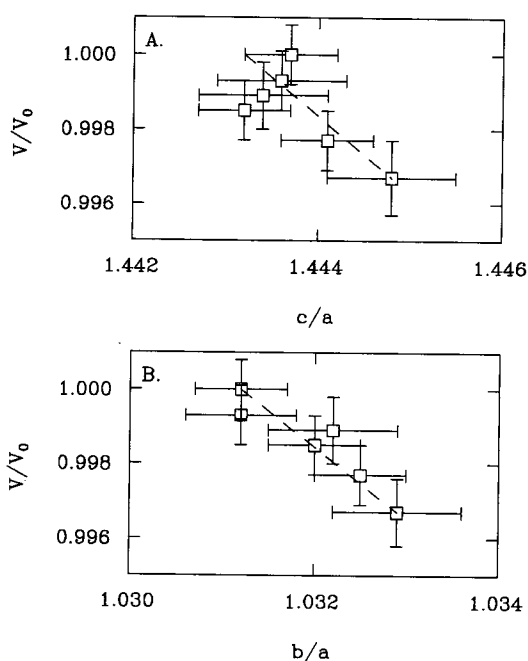


Fig. 2 A, B. Variation of MgSiO_3 perovskite's c/a (A) and b/a (B) as a function of V/V_0 , where V_0 is the volume at 298 K. Both ratios show a decrease with increasing temperature (i.e. increasing V/V_0 values)

comes more distorted with increasing pressure. Kudoh et al. (1987) state that the unit cell compression is controlled mainly by the tilting of relatively rigid SiO_6 octahedra. Ross et al. (in prep.) show that the Si–O–Si angle decreases with pressure, the O(2)–O(2)–O(2) angle related to tilting in the ab plane decreases with pressure, and the O(2)–O(2)–O(2) angle related to tilting the bc plane increases with pressure; all of these effects are consistent with an increased distortion in the structure (Sasaki et al. 1983). O'Keeffe et al. (1979) demonstrated that considerable structural information about orthorhombic perovskites could be extracted from their lattice parameters. Provided that the octahedra remain regular, all the structural parameters can be related to one parameter, ϕ , the angle through which the octahedra are rotated about their $\bar{3}$ axes. For the ideal cubic perovskite, ϕ is equal to zero. We have plotted the cosine of this

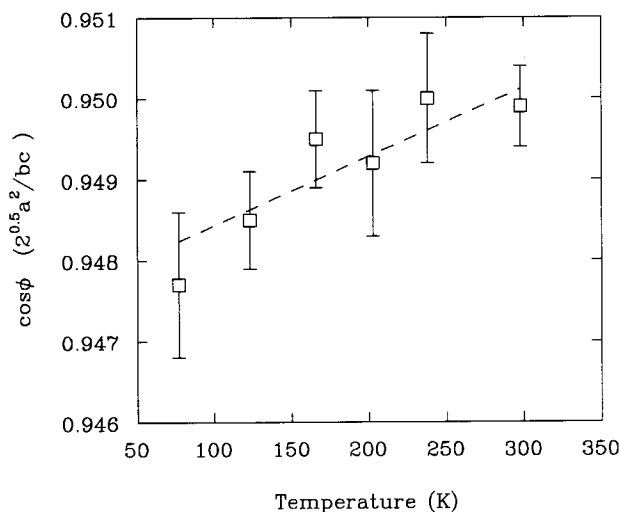


Fig. 3. Variation of the cosine of the distortion angle, ϕ , between 77 and 298 K. The octahedral tilting decreases with increasing temperature

distortion angle between 77 and 298 K (Fig. 3). With increasing temperature, $\cos\phi$ shows a significant increase, indicating MgSiO_3 perovskite is becoming less distorted with increasing temperature. These findings support the conclusion that temperature and pressure have inverse effects on MgSiO_3 perovskite; distortion increases with pressure, and decreases with temperature.

Volume Thermal Expansivity

The variation of MgSiO_3 perovskite volume as a function of temperature is shown in Figure 1d. The mean volumetric thermal expansion coefficient from 77 to 298 K is $1.45(9) \times 10^{-5} \text{ K}^{-1}$. These volume expansion data are consistent with powder X-ray diffraction results of Knittle et al. (1986), as illustrated in Figure 4. The combined data, however, reveal a curvature in the temperature-volume data that is significantly greater than for most other perovskites (see below). The thermal expansion coefficient observed by Knittle et al. above 500 K is $4 \times 10^{-5} \text{ K}^{-1}$, more than twice our low-temperature value. Since we were unable to obtain volumetric data at temperatures above 400 K, we cannot confirm whether MgSiO_3 has such a large increase in thermal expansion coefficient at higher temperatures.

Predictions of thermal expansion coefficients in this temperature range obtained from quasi-harmonic theoretical models are presented in Table 4. The models, with predicted thermal expansion coefficients at room temperature between 1.1 and $2.3 \times 10^{-5} \text{ K}^{-1}$, are in reasonable agreement with our experimental data. Cohen et al. (1989), however, point out that there is significant error in their earlier calculations of MgSiO_3 perovskite's thermal expansivity (Cohen 1987) because of the occurrence of a number of unphysical imaginary frequencies in the PIB model. Calculations were done by Hemley et al. (1989) to remove the effect of these unstable modes on thermodynamic properties of MgSiO_3 perovskite. The corrected instantaneous thermal expansion coefficients at 298 and 1000 K are given in Table 4. The SSMEG models (Hemley et al. 1987) show the best agreement with our study, and this agreement should improve when one corrects for the overestimation of the bulk modulus and its effect on α (Hemley, personal comm.).

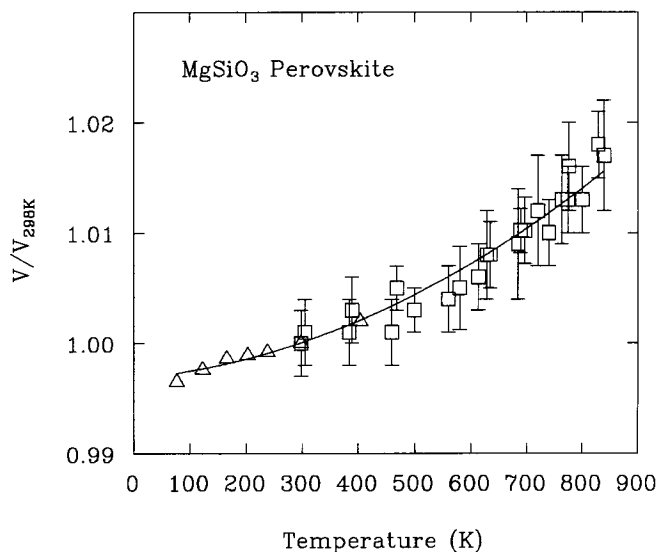


Fig. 4. Comparison of the thermal expansion results from the single-crystal X-ray diffraction experiments of this study (triangles) with those from the powder X-ray diffraction experiments of Knittle et al. (1986) (squares). The height of the triangles represent one standard deviation from the mean. The smooth curve is a second order, weighted regression of all the data ($V/V_0 = 0.9968(4) + 4.5(2.8) \times 10^{-6} T + 2.1(3) \times 10^{-8} T^2$)

Table 4. Thermal expansion coefficients of MgSiO_3 perovskite predicted from theoretical models

Model	α (K^{-1})	T (K)	Ref.
SSMEG	1.3×10^{-5}	298	a
	2.1×10^{-5}	1000	a
MEG	1.8×10^{-5}	300	b
	2.9×10^{-5}	800	b
PIB	1.1×10^{-5}	298–400	c
	1.3×10^{-5}	1000	c
PIB (corr)	2.3×10^{-5}	298	d
	3.3×10^{-5}	1000	d
Kieffer-type	1.4×10^{-5}	298	e
	2.0×10^{-5}	1000	e

References: ^a Hemley et al. (1987); ^b Wolf and Bukowski (1987); ^c Cohen (1987); ^d Hemley et al. (1989); ^e Navrotsky (personal comm.)

Navrotsky (1988) used Kieffer's (1979) vibrational modelling approach to calculate the entropy of MgSiO_3 perovskite. This approach can be extended to calculate the entropy as a function of pressure if one can approximate how the vibrational density of states (in this case modelled by a single continuum) changes with pressure. Since $(dS/dP)_T = -(dV/dT)_P$, such a calculation constrains the thermal expansivity. Using observed pressure shifts in the mid-infrared spectra (Williams et al. 1987), Navrotsky (1989) calculated $\alpha = 1.4 \times 10^{-5} \text{ K}^{-1}$ at 298 K and $\alpha = 2.0 \times 10^{-5} \text{ K}^{-1}$ at 1000 K.

Comparison of MgSiO_3 with Other Perovskites

Comparison of the thermal expansivity of MgSiO_3 with those of other perovskites provides an indirect means of

Table 5. Mean volumetric thermal expansion coefficients for perovskites

Formula	Symmetry	α (K^{-1})	T (K)	Ref.
KNbO ₃	Ortho.	1.6×10^{-5}	298–473	a
KNbO ₃	Tetr.	2.1×10^{-5}	493–683	a
KNbO ₃	Cubic	3.4×10^{-5}	698–783	a
ErAlO ₃	Ortho.	2.5×10^{-5}	298–2273	b
ScAlO ₃	Ortho.	2.5×10^{-5}	298–923	c
SmAlO ₃	Ortho.	1.8×10^{-5}	298–1073	b
SmAlO ₃	Rhomb.	3.7×10^{-5}	1073–1823	b
PrAlO ₃	Rhomb.	3.0×10^{-5}	298–1223	d
LaAlO ₃	Rhomb.	3.5×10^{-5}	298–923	d
NdAlO ₃	Rhomb.	2.9×10^{-5}	298–1823	b
LaGaO ₃	Rhomb.	3.3×10^{-5}	298–1173	d
PbHfO ₃	Ortho.	2.0×10^{-5}	298–431	e
PbHfO ₃	Cubic	2.7×10^{-5}	488–573	e
PbTiO ₃	Tetr.	0.8×10^{-5}	90–298	f
PbZrO ₃	Tetr.	2.7×10^{-5}	298–503	g
PbZrO ₃	Cubic	3.3×10^{-5}	≥ 503	g
Pb _{0.25} Ba _{0.75} O ₃	Tetr.	2.2×10^{-5}	373–443	g
Pb _{0.25} Ba _{0.75} O ₃	Cubic	2.3×10^{-5}	473–513	g
Pb _{0.95} Sr _{0.05} O ₃	Tetr.	2.4×10^{-5}	433–493	g
Pb _{0.95} Sr _{0.05} O ₃	Cubic	3.2×10^{-5}	513–573	g

References: ^a Shirane et al. (1954); ^b Coutures and Coutures (1984); ^c Yamanaka (personal comm.); ^d Geller (1957); ^e Shirane and Pepinsky (1953); ^f Glazer and Mabud (1978); ^g Shirane and Hoshino (1954)

evaluating the high-temperature behavior of MgSiO₃ perovskite. Thermal expansion data for perovskites of varying compositions and symmetries (Table 5) indicate that the low-temperature the thermal expansion of MgSiO₃ perovskite is consistent with other perovskites. These compounds show a range of values from 0.8 to $3.7 \times 10^{-5} K^{-1}$ with orthorhombic perovskites having average thermal expansion coefficients ranging from 1.5 to $2.5 \times 10^{-5} K^{-1}$. The data also suggest that a value of $4.0 \times 10^{-5} K^{-1}$ is higher than one would expect for an orthorhombic perovskite. There are, however, several points that must be taken into consideration. First, the errors on Knittle et al.'s (1986) volumetric data with temperature are large (Fig. 4) and hence the thermal expansion coefficient is not well constrained. A thermal expansion coefficient of $3 \times 10^{-5} K^{-1}$, for example, would still be consistent with their data and the spread of values observed in orthorhombic perovskites (Table 5). Second, we have a limited data base with which to compare MgSiO₃ perovskite and the high thermal expansion coefficient is not unreasonable when compared with values reported for all of the perovskites.

We observe no evidence for a high-temperature phase transition from orthorhombic to tetragonal symmetry, but it is interesting that the perovskites with higher symmetry tend to have greater thermal expansion coefficients (Table 5). Recent high-temperature X-ray diffraction studies on CaGeO₃ perovskite, which is also synthesized at high pressures and temperatures (Ringwood and Seabrook 1963) and has been commonly used as an analogue for MgSiO₃ perovskite, indicates it becomes less distorted with temperature (Liu et al. 1988). Moreover, at a temperature near 523 K, CaGeO₃ undergoes a reversible phase transition from an orthorhombic to tetragonal structure. At this transition the thermal expansion coefficient increases by 50 percent. Such a discontinuous change in temperature-volume

slope cannot be precluded by data in Fig. 4. Wolf and Bukowinski (1987), furthermore, have predicted on the basis of a modified-electron-gas model that MgSiO₃ perovskite will exhibit phase transitions with temperature, transforming first to a tetragonal phase and finally to a cubic phase. Clearly, further work must be done on the high-temperature behavior of MgSiO₃ perovskite, both to constrain the thermal expansion coefficient and also to look for possible phase transitions to higher symmetry structures. To avoid the thermal decomposition seen at atmospheric pressure, work at simultaneous high pressure and temperature is needed.

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