B1-B2 transition in CaO and possibility of CaSiO₃-perovskite decomposition under high pressure

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X-ray powder diffraction measurements of CaO at high pressure and temperature have been performed using a lever-spring type diamond anvil cell equipped with an external ring heater. The B1 structure transformed into B2 at about 61.2~63.2GPa at room temperature during the compression, and the back transformation from the B2 to B1 structure was found at 59.8GPa during the depression. The equation of states of both the B1 and B2 structures are obtained by Birch-Murnaghan equation. Because B2 structure of CaO is unstable at ambient conditions, the bulk modulus of the B2 structure at high temperature was firstly determined from the P-V-T curve. The B1-B2 transition pressure slightly lowers from 58.8GPa at 295K to 53.1GPa at 685K, resulting in dP/dT<0. A back transformation from the B2 to B1 structure by depression shows a large hysteresis. The B1-B2 transition highly depends on pressure rather than temperature. Only from the volumes of the CaSiO₃ components, CaSiO₃ perovskite possibly decomposes to SiO₂ (CaCl₂ type) and CaO (B2) in the pressure and temperature range of the lower mantle.

Introduction

It has been known that (Mg,Fe)O magnesiowüstite (Mw), (Mg,Fe)SiO₃ perovskite (MgSiO₃ (Pv)) and CaSiO₃ perovskite (CaSiO₃ (Pv)) are the major minerals in the lower mantle. Phase stabilities of MgSiO₃ (Pv) and CaSiO₃ (Pv) have been significant research themes. In order to understand the phase stabilities under the condition of upper and lower mantle, numerous high-pressure experiments using various types of diamond anvil cells (DAC) or multianvil cells have been carried out. Recently Hirose et al., (2001) reinvestigated the phase boundaries of MgSiO₃ polymorphs and showed a series of transformation of majolite-akimotoite-perovskite.

CaSiO₃ wollastonite decomposes to CaO and SiO₂ under low pressure and then formed as CaSiO₃ (Pv) under further compression (Liu and Ringwood, 1975). Tamai and Yagi (1989) studied the high-pressure and high-temperature phase relation in CaSiO₃ and CaMgSi₂O₆. Under extremely high-pressure region such as in the deep lower mantle, phase changes or decompositions of CaSiO₃ (Pv) have been attracted attention. The structure transition of CaSiO₃ (Pv) has been investigated using DAC by Yagi et al., (1989) up to 120GPa, Tarrida and Richet (1989) up to 96GPa and Mao et al., (1989) up to 134GPa. The stability of CaSiO₃ (Pv) has been reinvestigated using a DAC with

a laser-heating system by Wang et al., (1996) and Shim and Duffy (2000). In the experimental pressure and temperature range of these studies CaSiO₃ (Pv) is thought to be stable all through the lower mantle region.

The mutual relation between $^{VIII}A^{2+}$ and $^{VI}B^{4+}$ ionic radii defines the structure type of $^{VIII}A^{2+VI}B^{4+}O_3$ perovskite under ambient conditions. A possibility of the structure transition of perovskites was proposed in consideration of thermal expansion and isothermal compression of ionic radii under high-pressure and high-temperature condition (Yamanaka et al., 2002). Figure 1 summarizes this proposition.

CaO, one of the components of CaSiO₃, shows a phase transition from B1 structure ($Fm\bar{3}m$, Z=4, NaCl-type) to B2 structure ($Pm\bar{3}m$, Z=1, CsCl-type) at 60-70GPa. The transition reduces the unit cell volume by 11%. The total volume of B1 and SiO₂ (stishovite) is much larger than the volume of CaSiO₃ (Pv) but that of B2 and SiO₂ (CaCl₂ type) is very similar to that of CaSiO₃ (Pv). Note that SiO₂(stishovite) transformed to CaCl₂ type structure at 58GPa (Andrault et al., 1998). Many structure transition mechanisms between B1 and B2 have been proposed, such as Buerger mechanism caused by <111> shear stress (Buerger, 1951) and stacking slip mechanism. Equation of state (EOS) of CaO was reported by shock experiments up to 175GPa (Jeanloz et al., 1979) and reinvestigated by Richet et al., (1988). The precise measurements of P-V-T data of
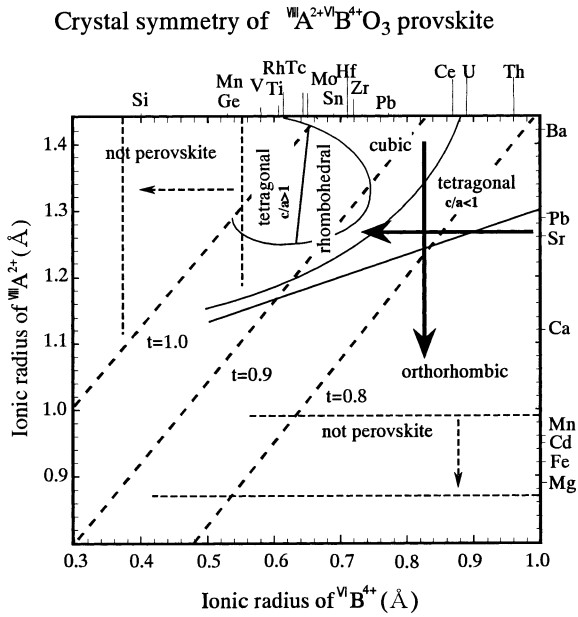
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Crystal symmetry of $^{VIII}A^{2+VI}B^{4+}O_3$ provskite

Figure 1. Various structure types of $^{VIII}A^{2+VI}B^{4+}O_3$ perovskites at ambient condition as the conbination of ionic radii of A and B cations. The ionic radii are taken from Shannon and Prewitt (1976). The observed torece factors shown by the dashed lines are based on $r_{oxy}=1.40$ of six-folded oxygen atoms. Arrows indicate the structure change or deformation trends at elevated pressures.

Figure 2. Volume compressions of $CaSiO_3$ (Pv), SiO_2 (stishovite) + CaO (B1) and SiO_2 $(CaCl_2)$+CaO (B2). Those of $CaSiO_3$ (Pv), CaO (B1) and SiO_2 $(CaCl_2)$ are taken from Shim et al., (2000), Richet et al., (1988) and Andrault et al., (1998), respectively.

CaO and SiO_2 together with that of $CaSiO_3$ are necessary to elucidate the possibility of $CaSiO_3$ (Pv) decomposition. Fig. 2 presents the compression curves of all three phases on the basis of the reported EOS data:

$CaSiO_3$ Ko=236GPa   Ko'=3.9   Vo= 45.58Å^3
                                      (Shim et al., 2000)
CaO (B1)   Ko=111GPa   Ko'=4.2   Vo=111.326Å^3
                                      (Richet et al., 1988)
$SiO_2(CaCl_2)$ Ko=291GPa   Ko'=4.29   Vo=46.615Å^3
                                      (Andrault et al., 1998).

Guided by the previously reported elastic and thermal properties of CaO by high temperature experiments (Okajima, 1978; Garvin et al., 1988; Oda et al., 1992), we aims to discuss the possibility of $CaSiO_3$ (Pv) decomposition from the view point of the volume change of each component of $CaSiO_3$.

X-ray diffraction study of CaO under high pressure and temperature is a significant subject not only for the mantle science but also for the high-pressure material science. Our experimental results of the EOS data of B1 and B2 give a light on an effective candidate of the pressure scale. High melting temperature of CaO of 2843K has a big advantage as a pressure marker in high pressure and temperature studies in comparison with Au of 1335K, which is often used as an internal pressure marker.
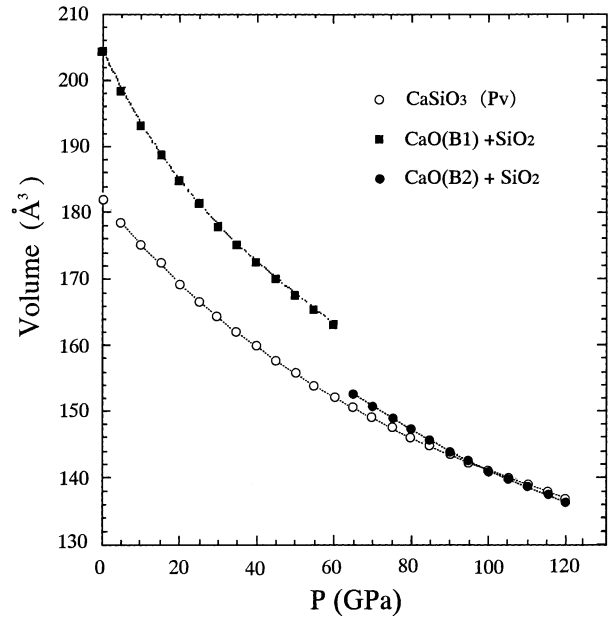
Experiment

A powder sample of CaO was prepared by decomposition of a reagent-grade $CaCO_3$ powder. Since CaO is a highly hygroscopic substance, it was kept in an evacuated desiccator before mounting it in DAC. High pressure was generated by a lever-spring type DAC, which was originally designed by Mao and Bell (1978). The load pressure of the conventional DAC was controlled by the spring compression. Our new system combined the previously devised oil-pressure controller (Yamanaka et al., 1992) and a cylinder compresser instead of the spring. An inner ring-heater of Pt-Rh(40) covered with a ZrO_2-CaO cement thermal-insulator was installed in the high-pressure generator and also an outer heater of Ni-Cr wire electric resistance heater was applied in order to supply a preheat to the sample room (Fig. 3). Temperature was regulated by a PID regulation system and measured by an almel-cromel thermocouple of which the head contacts on the diamond surface.

The DAC lever body was cooled by water circulating through an inner pipe of the high-pressure system. The DAC was mounted on an XY stage with a rotation mechanism around the Z-axis for setting the sample on the X-ray beam. The detailed specification will be reported in elsewhere.
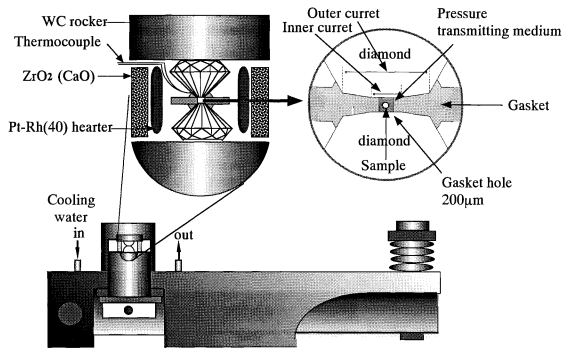
Figure 3. Lever-spring type DAC designed by Mao and Bell (1973)
   equipped with an external ring heater of Pt-Rh(40).

The powder sample, together with an Au pressure-marker or a few ruby chips, was loaded into the Re gasket hole of 200 mm in diameter, which was initially 250 mm thick and preindented to 60 mm thick. A pair of diamond crystals of 0.29 carats with a culet plane of 350 mm (outer) and 200 mm (inner) and a table plane of 3mm in diameter was used as the anvils. A mixture of methanol : ethanol : H_2O = 16 : 3 : 1 was used for pressure medium to keep a hydrostatic condition at room temperature, but it solidifies over 15GPa. Silicon grease was also used as pressure medium in the present high-temperature studies. The pressure at high temperature was determined by the Au internal pressure marker through the Anderson scale (Anderson et al., 1989). The pressure was determined by the ruby fluorescence method at room temperature.

In situ X-ray powder diffraction measurements of CaO was performed at pressures up to 75GPa at room temperature, 473, 573 and 673K using a Mo rotating anode X-ray source (RIGAKU RU-200). The MoKα incident beam was monochromated with a pyrolytic graphite plate and collimated by a long collimator with the single-hole of 200mm in diameter. Each powder diffraction pattern was observed for about two hours by X-ray diffraction after keeping the sample at the desired temperature for one hour in order to attain the equilibrium state. The diffraction measurements were performed at an interval of 2-3GPa with both increasing and decreasing pressure to observe the hysterisis of the transition. The diffraction patterns were recorded by a two-dimensional imaging plate (IP) detector (RIGAKU R-AXIS IV[++]) having a large dynamic range and high quantum efficiency. The Debye-Scherrer rings observed by IP were converted to one-dimensional diffraction patterns by the computer program of PIP (Fujihisa and Aoki, 1998).   Diffraction measurement was also performed by the synchrotron radiation at BL18C of Photon Factory, KEK in Tsukuba.   The incident beam

was collimated to 80mm in diameter and monochromated to the wavelength of 0.6876 Å.

The lattice constants of the two polymorphs of B1 and B2 structures are determined by a profile fitting method for several diffraction peaks. To overcome the inconvenience of observations due to the overlapping of four diffraction patterns (samples with B1 and B2 structures, Au pressure scale and Re gasket), the profile fitting was performed by the program RIETAN (Izumi, 1993).

Experimental results

(1) Compression of CaO at elevated temperature
The lattice constant of B1 structure was determined from 111, 200 and 220 peak profiles and that of B2 structure from 100 and 110 peaks. The lattice constants under high pressures at room temperature are presented in Table 1. It was found that the B1 structure transforms to B2 at about 61.2-63.2GPa during the compression. The transition pressure is more precise than the previous data at 60-65.8GPa (Richet et al., 1988) and 60-70GPa (Jeanloz et al., 1979). Because of the kinetics of the transition and/or the deviatory stress in the gasket hole, two phases of B1 and B2 coexist until 73GPa. The diffraction patterns obtained at 63.2, 65.9, 68.2 and 73.3GPa are shown in Figure 4.

Table 1. Unit cell parameters of CaO under high pressure at 300k

P(GPa)	a(Å)	V/V_0*	Phase
		Compression	
0.0001	4.806(2)	1.0000	B1
4.5	4.754(3)	0.9682	B1
10.1	4.696(1)	0.9327	B1
14.5	4.650(3)	0.9058	B1
19.3	4.607(3)	0.8808	B1
25.5	4.562(3)	0.8554	B1
31.8	4.520(1)	0.8319	B1
36.9	4.493(3)	0.8172	B1
42.7	4.450(3)	0.7939	B1
48.0	4.426(4)	0.7813	B1
52.2	4.404(2)	0.7693	B1
56.2	4.380(1)	0.7572	B1
59.2	4.368(1)	0.7501	B1
61.2	4.359(2)	0.7461	B1
63.2	2.632(2)	0.6570	B1+B2
65.9	2.631(2)	0.6563	B1+B2
68.2	2.626(3)	0.6527	B1+B2
70.5	2.623(4)	0.6500	B1+B2
73.3	2.616(2)	0.6451	B2
		Decompression	
62.3	2.638(2)	0.6618	B2
59.8	2.648(2)	0.6694	B2+B1
56.0	2.658(4)	0.6769	B2+B1
51.5	2.666(1)	0.6831	B2+B1

* V_0 = 111.002Å^3

B1→B2 transition at 300K

B1→B2 transition at 60GPa
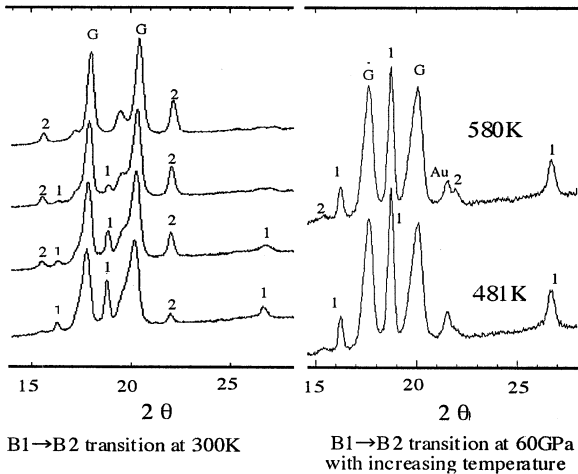with increasing temperature

Figure 4. X-ray powder diffraction patterns showing B1-B2 transition obtained at 63.2, 65.9, 68.2 and 73.3GPa at 300K and those at a fixed pressure of 60GPa at elevated temperatures. Peaks symbolized of 1 and 2 assign to CaO (B1) and CaO (B2) structure, respectively. The peaks pointed by G and Au are from gasket and pressure marker of Au, respectively.

A reverse transformation from B2 to B1 phase was confirmed at 59.8GPa during the depression. The hysteresis of the structure transition was observed but its range is not so large as the data derived by a molecular dynamics calculation (Matsui, 1998).

The diffraction measurements at high pressures have been performed at three different temperatures of 481(2)K, 591(4)K and 646(3)K with elevating pressure.

Table 2. Unit cell parameters of CaO (B1) structure at various temperatures and pressures

T(K)	CaO (B1) a (Å)	Volume(Å³)	P(GPa)	Au[1] 63.21(1)
485(2)[2]	4.6459(3)	100.28(1)	14.9	61.44(1)
490(3)	4.5804(4)	96.10(2)	22.1	58.51(1)
489(2)	4.4994(7)	91.09(2)	37.1	56.99(2)
491(8)	4.4354(6)	87.26(2)	46.8	56.33(2)
495(5)	4.4114(7)	85.85(2)	51.5	55.48(2)
488(5)	4.3772(4)	83.87(2)	57.8	54.83(2)
481(2)	4.3559(6)	82.65(2)	63.1	54.83(2)
583(3)	4.6293(3)	99.21(1)	17.1	61.31(1)
583(2)	4.5838(5)	96.31(2)	23.2	58.23(1)
581(3)	4.4955(8)	90.85(3)	39.3	57.07(2)
585(5)	4.4354(6)	87.25(2)	46.7	56.31(2)
583(5)	4.4110(7)	85.82(2)	52.1	55.42(2)
591(4)	4.3770(5)	83.86(2)	58.8	55.42(2)
639(4)	4.6288(4)	99.18(1)	17.5	61.21(1)
644(5)	4.5858(5)	96.44(2)	24.1	58.33(1)
644(5)	4.4993(9)	91.08(3)	39.1	57.15(2)
646(3)	4.4351(7)	87.24(2)	46.5	

1) Au is a pressure indicator.
2) The numbers in parentheses denote errors of the last dismals.

The unit cell parameters of B1 and B2 structures with increasing pressure at high temperatures are presented in Table 2 and Table 3, respectively.

(2) EOS of CaO

The volume compression curves of B1 and B2 structures at room temperature are expressed as a function of V/Vo, (Fig. 5). The following isothermal Birch-Murnagham equation of state was applied to the constant high-temperature P-V-T data.

$$P = Ko\{(\frac{V_T}{V_{To}})^{-\frac{7}{3}} - (\frac{V_T}{V_{To}})^{-\frac{5}{3}}\}[1+\frac{3}{4}(Ko'-4)$$

$$\{(\frac{V_T}{V_{To}})^{-\frac{2}{3}} - 1\}] \qquad (1)$$

The present results of bulk modulus Ko, first-order pressure derivative of Ko' and Vo of B1 structure at room temperature are very similar to those calculated data by the molecular dynamics (MD) (Matsui ,1998), the local density approximation (LDA) (Mehl et al., 1988; Karki and Crain, 1998) and the compression experiment (Richet et al., 1988), as shown below:

Ko(GPa)	Ko'	Vo (Å³)	experiment	ref.
124	3.57	111.00	static comp.	present data
129	4.47	104.75	LDA	Mehl et al., 1988
117	4.41	111.24	LDA	Karki et al., 1998
113	3.49	-	MD	Matsui, 1998
111	4.2	111.33	static comp.	Richet et al., 1988

However, no data of those values at high temperatures have been so far given. The present experimental data of KTo and KTo' of B1 and B2 structures at several temperatures are presented in Table 4.

For the volume compression of B1 at high temperatures, the volume at T(K) at ambient pressure is expressed as

$$V_T = V_{To} \exp\{\int_{To}^{T} \alpha_o (T)dT\} \qquad (2)$$

where V_{To} is the volume at ambient pressure and 300K, and $\alpha_o(T)$ indicates the bulk thermal expansion coefficient at ambient pressure. α_o of B1 structure was reported by Okajima (1978).

$$\alpha_o(T) = a + bT - cT^{-2}$$
$$=3.73(7) \times 10^{-5} + 4.87(7) \times 10^{-9}T - 0.765(7)T^{-2} \qquad (3)$$

The replacement of $\alpha_o(T)$ in equation (2) by equation (3) gives

$V_T = V_{To}\exp[aT+1/2bT^2-cT^{-1}-(aTo +1/2bTo^2-cTo^{-1})]$.

Then

$$\ln(\frac{V_T}{V_{To}}) = aT + 1/2bT^2 - cT^{-1} - (aTo + 1/2bTo^2 - cTo^{-1})$$

Table 3. Unit cell parameters of CaO (B2) structure at various temperatures and pressures

| T(K)	a(Å)	Vol(Å³)	P(GPa)	Vol(Å³)
	CaO (B2)			Au[1]
483(3)[2]	2.6346(8)	18.287(9)	65.4	54.57(3)
485(3)	2.6316(5)	18.225(6)	67.1	54.38(3)
487(2)	2.6246(5)	18.080(6)	70.3	54.04(2)
485(2)	2.6273(5)	18.135(6)	68.7	54.20(2)
485(5)	2.6284(4)	18.158(5)	68.0	54.28(2)
485(5)	2.6430(4)	18.463(5)	62.4	54.92(2)
485(6)	2.6525(5)	18.662(6)	58.8	55.37(3)
584(4)	2.634(2)	18.27(2)	64.1	54.78(2)
580(5)	2.6348(8)	18.291(9)	65.8	54.58(3)
587(7)	2.6321(5)	18.234(6)	67.6	54.38(3)
585(3)	2.6249(5)	18.085(6)	70.6	54.05(3)
592(3)	2.6277(5)	18.144(6)	68.9	54.23(2)
583(5)	2.6313(4)	18.219(5)	67.2	54.42(2)
583(5)	2.6451(4)	18.506(5)	62.1	55.01(2)
583(5)	2.6540(5)	18.694(6)	58.2	55.50(3)
581(5)	2.6588(9)	18.79(1)	53.7	56.09(2)
684(6)	2.6264(5)	18.118(6)	69.9	54.17(2)
692(5)	2.6248(5)	18.083(6)	70.1	54.15(3)
683(5)	2.6350(4)	18.295(5)	66.5	54.55(2)
685(8)	2.6474(4)	18.554(5)	62.0	55.09(2)
685(6)	2.6576(5)	18.770(6)	57.2	55.69(3)
685(6)	2.6622(9)	18.87(1)	53.1	56.23(3)

1) Au is a pressure indicator.
2) The numbers in parentheses denote errors of the last dismals.

In the present experiment, the thermal expansion coefficients of B1 at high pressure were determined to the volumes at high temperatures. The a, b and c constants at ambient pressure reported by Okajima (1978) were used for α_o(T). The parameters, α(300K) and α(500K) obtained by a least-squares fitting to the
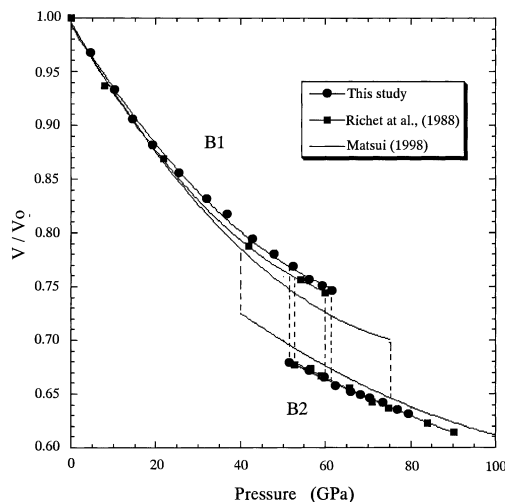
Figure 5. Compression curves of B1 and B2 structures at 300K.

Table 4. Bulk modulus of B1 and B2 structures at high temperature and those calculated by the MD simulation

T(K)	B1 structure K_{To} (GPa)	$K_{To'}$
300	125(1)	3.57
488(8)	123(1)	3.57(fixed)
584(9)	122(1)	3.57(fixed)
643(7)	120(3)	3.57(fixed)

T(K)	B2 structure K_{To} (GPa)	$K_{To'}$
300	128(1)	4(fixed)
485(6)	126(8)	4(fixed)
584(9)	124(1)	4(fixed)
686(9)	122(2)	4(fixed)

MD simulation of B1 structure T(K)	K_{To} (GPa)	(Matsui, 1998) $K_{To'}$
300	111.7	3.56
500	108.9	3.56
700	105.9	3.56

observed data at various pressures are presented in Table 5. Those data are plotted in Figure 6, which indicates the decrease of the coefficient with increasing pressure. Volume changes with pressure and temperature are expressed by $\ln(\dfrac{V_T}{V_{To}})$ versus T(K), which is shown in Figure 7. It is elucidated that the temperature derivative of the bulk modulus of the B1 structure is $(\dfrac{\partial K_o}{\partial T})_P = -0.0114(4)$. The value is very similar to $(\dfrac{\partial K_o}{\partial T})_P = -0.0147(4)$ derived from the MD simulation (Matsui, 1998).
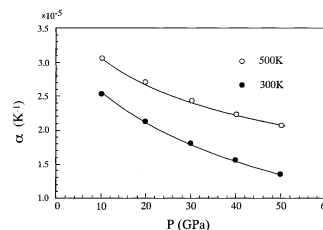
**Figure 6** Pressure dependence of the thermal expansion coefficient of α at 300K and 500K.

Vo of B2 cannot be directly measured, because B2 is not stable under the ambient conditions. Hence Ko, Ko' and Vo are variable parameters in the curve fitting based on the observed lattice constants of the B2 structure. Vo and Ko of the B2 structure were determined by the P-V-T curve fitting with the fixed Ko'=4. Firstly the lattice constant a of the B2 structure was determined from the observed data at pressures 58-70GPa at elevated temperatures, and then α_o(T) at ambient pressure was calculated because B2 does not exist at the condition. V_T was taken from the obtained α_o(T), and further Ko was determined by the calculation with EOS of eq. (1).

Table 5. Volume thermal expansion coefficients of B1 structure as a function of pressure

P (GPa)	10	20	30	40	50
α (295) x 10^{-5}(K^{-1})	2.55	2.11	1,80	1.55	1.35
α (500) x 10^{-5}(K^{-1})	3.06	2.70	2.43	2.26	2.06

Table 6. Thermodynamical parameters related to the B1-B2 transition in alkaline halides (Basset et al., 1968)

	NaCl	KCl	RbCl	CsCl
dP/dT (GPa·K^{-1})	−64±10	−0.3±0.2	3.0±0.2	5.0±0.2
ΔV (cm^3·$mole^{-1}$)	−1.00±0.05	−4.25	−6.06	−8.85
ΔS (cal·$mole^{-1}$·K^{-1})	1.5±0.3	−0.03±0.02	−0.44±0.04	−1.06±0.04
r_M/r_X	0.56	0.76	0.84	0.92
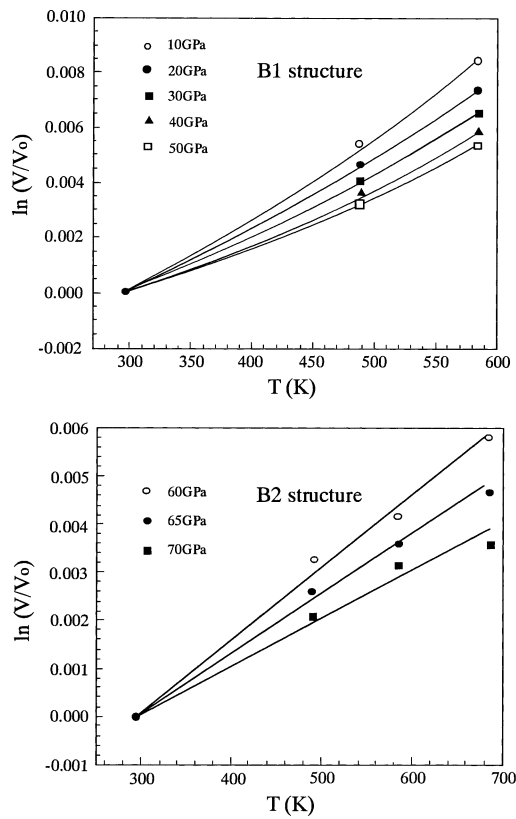
Figure 7. Volume change, ln(V/Vo), of B1 and B2 structures, with pressure and temperature.

Discussion on the B1-B2 transition

The B1-B2 phase transition was confirmed with increasing and decreasing pressure at several temperatures. In the high-pressure region, deviatory stress of the sample and kinetics of the structure

transition including nucleation and grain growth were encountered as inevitable problems. The transition pressure was assigned to the pressure where the new phase was firstly detected during the compression and decompression. It was clarified that the transition pressure slightly lowers with increasing pressure resulting in dP/dT<0. With decreasing pressure the reverse transformation from the B2 to B1 structures shows a large hysteresis. The B1-B2 transition is highly dependent on pressure.

Tsuchiya and Kawamura, (2001) simulated the B1-B2 transition of alkaline earth oxides by ab initio calculations and discussed the elastic stability using stiffness parameters of c_{ij} based on Born criteria ($c_{11}+2c_{12}$, c_{44} and $c_{11}-c_{12}$ in cubic system). If one of these conditions becomes negative, the B1-B2 transition is induced by the elastic instability. When the term c_{44} (the shear modulus) changes to a negative value, the B1 structure will be no more stable and transform to the B2 structure. They also disclosed that the B1-B2 phase boundary showed a negative slope resulting in dP/dT<O. Though the B1-B2 transition brings a big volume compression (VB2-4VB1)/VB1 of about 11%, the Clapeyron slope designated by dP/dT (=ΔS/ΔV) is negative, indicating that ΔS should be positive at the transition because of the negative ΔV. At this moment, however, we have no other evidence concerning ΔS.

Basset et al., (1968) reported some thermodynamical parameters of the B1-B2 transition of alkaline halides (NaCl, KCl, RbCl and CsCl), which are shown in Table 6 together with ionic radius ratios of r_M/r_X (M:Na, K, Rb, Cs; X:Cl). NaCl and KCl among these halides show negative Clapeyron slopes (Li and Jeanloz, 1987) but the other two have positive slopes. With increasing the ionic radius ratio, the value of dP/dT changes from negative to positive and becomes larger. In spite of the same configuration change of the B1-B2 transition in all these halides, their ΔS's have positive or negative values. The specific heats of these halides are supposed to have a crucial effect on ΔS. The ionic radius ratio of CaO (r_{Ca}/r_O =0.73) falls between those values of NaCl and KCl. However, it still remains why dP/dT of the B1-B2 phase boundary is negative.

EOS's of the alkaline earth oxides, MgO, CaO, SrO and BaO, have been examined by the calculation and static compression experiments. No transition has been found in MgO. BaO does not show the B1-B2 transition but the B1-BaO(II) transition. The bulk modulus (Ko) of these four oxides with B1 structure and their transition pressures to high-pressure stable phases obtained from the compression experiments are summarized in Table 7.

Table 7. Transition pressure of alkaline earth oxides at room temperature

	MgO[1]	CaO[2]	SrO[3]	BaO[4]
Ko(GPa)	160	125.4	91.3	70
Ko'	4.15	3.57	4.3	3.49
V_{B1}obs (Å^3)	74.7	111.00	140.36	169.94
V_{B1}cal(Å^3)	76.2	110.0	137.4	166.4
V_{HP}cal(Å^3)	18.99	25.23	29.62	35.26
$(V_{B1}-4V_{HP})/V_{B1}$	0.003	0.0825	0.138	0.152
r_M/r_X (VI)	0.514	0.714	0.843	0.964
r_M/r_X (VIII)	0.626	0.788	0.887	1.00
Ptran(GPa)	-	63	36	10
transition	-	B1-B2	B1-B2	B1-BaO(II)

1)Fei. (1999), 2) present data, 3) Liu and Basset (1973), 4) Weir et al. (1986) Prarameters of r_M/r_X (VI) and r_M/r_X (VIII) represent the ionic radius ratio between cation (M) and anion (X) with 6-folded and 8-folded coordination, respectively.

V_{HP} indicates the volume of high-pressure polymorph which has the B2 structure with a simple cubic (Z=1) in the case of CaO and SrO. V_{HP} in BaO is the volume of BaO (II). Noted that B1 has a structure of the face centerd cubic (Z=4).

The lattice constants (*a*) of B1 (*Fm$\bar{3}$m*, Z=4) and B2 (*Pm$\bar{3}$m*, Z=1) are defined by M-O distance (*d*) based on the radii of 6-fold and 8-fold coordinated cations, $^{VI}M^{2+}$ and $^{VIII}M^{2+}$. The former is $a_{B1}=2d(^{VI}M-^{VI}O)$ and the latter is $a_{B2}=2d(^{VIII}M-^{VIII}O)/\sqrt{3}$. Volumes of B1 and B2 ($V_{cal}B1$ and $V_{cal}B2$) calculated from the ionic radii are presented in Table 7. From the packing model of the rigid bodies, MgO hardly constructs the B2 structure consisting of 8-fold coordination because of too small ionic radius ratio ($^{VIII}r_M/^{VIII}r_O$=0.626), compared with the ideal ratio of the coordination of r_M/r_O=0.732. It is quite reasonable from $^{VI}r_M/^{VI}r_O$ and $^{VIII}r_M/^{VIII}r_O$ that the transition pressure of CaO (63GPa) is higher than that of SrO (36GPa) and BaO (10GPa). BaO transforms from B1 to BaO(II) structure at 10GPa and further to BaO(III) at 15GPa (Weir et al., 1986).

Discussion for possibility of decomposition of CaSiO$_3$ perovskite

From high pressure and temperature experiments (Yagi et al., 1989; Tarrida and Richet, 1989; Mao et al., 1989; Wang et al., 1996; Shim and Duffy, 2000), CaSiO$_3$ (Pv) is thought to be stable all through the lower mantle region. A possibility of the decomposition of CaSiO$_3$ (Pv) to CaO and SiO$_2$ (CaCl$_2$ type) may be discussed from the respective volumes of these three phases without considering their heat capacities under the lower mantle region conditions.
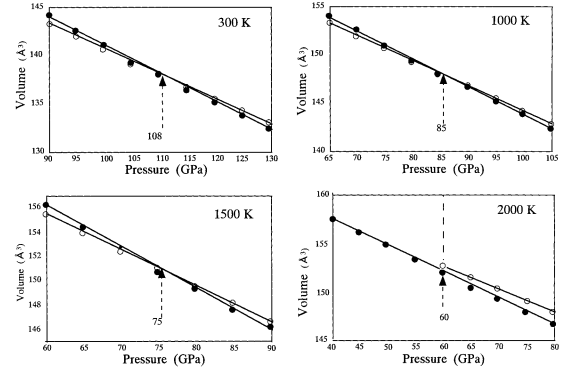

Figure 8. Compression curves of CaSiO$_3$ (Pv) indicated by open circles, SiO$_2$(stishovite)+CaO(B1) and SiO$_2$(CaCl$_2$)+CaO(B2) indicated by solid circles. Dotted line indicates the pressure at which the volume curves of CaSiO$_3$ (Pv) and total volume of CaO(B2) and SiO$_2$(CaCl$_2$ type) intersect.

The compression curves of CaSiO$_3$ (Pv), SiO$_2$ (CaCl$_2$) and CaO (B2) are needed for the discussion of the possibility of the decomposition of CaSiO$_3$ (Pv). There are no data of thermo-dynamical parameters of CaO (B2). But the volume compressions of the former two phases have been reported by the above investigators and Andrault et al., (1998). Consequently we have only to find the compressions of B2 at temperatures over 1500K and pressures 23-140 GPa.

For this purpose, KTo and αTo of B2 were obtained by the extrapolation of the present data to the lower mantle pressure and temperature regions.

All parameters needed for EOS's of B1 and B2, SiO$_2$ (CaCl$_2$) and CaSiO$_3$ (Pv) are listed in Table 8. Using the EOS parameters, the compression curves of CaSiO$_3$ (Pv) and CaO (B2) + SiO$_2$ were calculated as a function of pressure at constant temperatures of 1000 K, 1500 K and 2000 K. CaO (B1) + SiO$_2$ (CaCl$_2$) always has a volume larger than CaSiO$_3$ (Pv) in the all experimental pressure and temperature range. But the volume of CaSiO$_3$ (Pv) becomes smaller than the total volume of B2 and SiO$_2$ (CaCl$_2$) at 85GPa (1000 K), 75GPa (1500 K) and 60GPa (2000 K), as shown in Figure 8. Hence only from the viewpoint of the volume, CaSiO$_3$ (Pv) possibly decomposes to SiO$_2$ (CaCl$_2$) and CaO (B2) in the pressure and temperature range of the lower mantle, P=24-140GPa and T=1800-3000 K. However, no experimental report concerning CaSiO$_3$ (Pv) is indicating its decomposition to CaO (B2) and SiO$_2$ undr pressure. The phase stability including transition and decomposition of CaSiO$_3$ is thermo-dynamically defined not only by the respective volume of the corresponding phases but also by their entropy differences. The present study cannot provide any information of the entropy but may propose a possibility of the decomposition of CaSiO$_3$ (Pv).

Table 8. Bulk modulus , volume , thermal expansion coefficient and isobaric temperature derivative of Ko

	CaO (B1) present data	CaO (B2) present data	SiO$_2$ (stishovite) Liu et al (1999)	CaSiO$_3$ (Pv) Wang et al (1996)
Z	4	1	2	1
Space group	$Fm\bar{3}m$	$Pm\bar{3}m$	$P4/mnm$	$Pm\bar{3}m$
Ko (GPa)	125(1)	144(12)	294(2)	232(8)
Ko'	3.6(1)	4 (fixed)	5.3 (fixed)	4.8(3)
Vo (Å^3)	111.00(1)	23.8(4)	46.546(12)	45.58(4)
α (10^5 K^{-1})	(i)	6.34(3)	(ii)	3.0
$(\partial KTo/\partial T)_P$ (GPa K^{-1})	−0.0114(4)	−0.039(7)	0.041(11)	−0.033(8)

i $\alpha = 3.73(7) \times 10^{-5} + 4.87(7) \times 10^{-9}T - 0.765(7)T^{-2}$

ii $\alpha = 140(8) \times 10^{-5} + 10.9(20) \times 10^{-9}T$

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