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High Pressure Transformations in Zinc Silicates

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Phase transformations in Zn_2SiO_4 and $ZnSiO_3$ have been investigated at high pressure up to 170 kbar and temperature to 1500°C. Crystal structures of high pressure polymorphs have been studied by means of single crystal and powder X-ray diffraction analyses. Chemical compositions have been determined by electron microprobe and wet chemical analyses.

Five polymorphs have been identified in Zn_2SiO_4, designated as I–V in the order of increasing pressure. Coordination numbers of metal ions in the crystal structures of Zn_2SiO_4 II–IV are four, the same as those in Zn_2SiO_4 I with the phenacite structure. The crystal structure of Zn_2SiO_4 II is composed of an approximately body-centered tetragonal arrangement of oxygen ions. Zn_2SiO_4 III and IV are suggested to be nonstoichiometric. Zn_2SiO_4 V, appearing above 130 kbar, is identified to be of the modified spinel structure. Zn^{2+} ions enter the octahedrally coordinated sites in it, accompanied by a large density increase. No olivine-like structures could be found among five polymorphs in Zn_2SiO_4. The solubility limit of Zn_2SiO_4 in Mg_2SiO_4 with the olivine structure is determined to be close to 75% at 90 kbar.

Only a clinopyroxene form of $ZnSiO_3$ is found to be stable over a relatively wide region in the pressure-temperature diagram. However, it has anomalous unit cell parameters when compared with more conventional pyroxenes.

The extreme instability of the olivine structure in Zn_2SiO_4, and unusual cell parameters in $ZnSiO_3$ pyroxene are discussed in terms of crystal structures. Stability of the modified spinel structure is also inferred in some detail. It is suggested from the study of phase transformations in Zn_2GeO_4 and $ZnGeO_3$ that simple analogy in the mode of the high-pressure transformation between silicates and the corresponding germanates should be reexamined carefully.

Introduction

High pressure phase transformations in silicates and germanates have extensively been studied for these ten years by many earth scientists in order to throw light upon the phase transformation in the earth's mantle. Various types of transformations have been reported so far. One of the important transformations among them is the olivine-spinel transformation at high pressure, which has thoroughly been investigated for magnesium and transition metal orthosilicates M_2SiO_4 ($M = Mg$, Fe, Co, and Ni) and their solid solutions (*1–11*). The most interesting topic was the recent discovery of the modified spinel structure in some silicates and germanates (Mg_2SiO_4, Co_2SiO_4, and Mn_2GeO_4) and the detailed crystal structure analysis and phase diagram studies made (*10–12*). Phase transformations for metasilicates of these divalent cations have also been studied in some detail.

Under these circumstances, the Zn^{2+} ion is one of the divalent cations whose silicates have not been studied in detail at high pressure. Ringwood and Major (*13*) reported two unidentified polymorphs of Zn_2SiO_4 above 100 kbar and a pyroxene-like compound of $ZnSiO_3$. Hayashi et al. (*14*) also reported two types of pyroxenes $ZnSiO_3$ at high pressure and published a tentative phase diagram up to 40 kbar. However, these studies are still of a preliminary nature.

It is to be noted here that Zn_2SiO_4 and Zn_2GeO_4 crystallizes in the phenacite structure (*15*) at atmospheric pressure, in which both Zn and Si atoms are in the tetrahedral coordination. Both $ZnSiO_3$ and $ZnGeO_3$ (*16*) are not stable at atmospheric pressure. It is quite striking that both Zn_2SiO_4 and Zn_2GeO_4 take the same structure type as phenacite Be_2SiO_4, although the ionic radius of Zn^{2+} is far greater than that of Be^{2+} and even that of Mg^{2+}, which occupies the octahedrally coordinated sites in the olivine and pyroxene structures. Such a strong preference of Zn^{2+} ions for tetrahedral sites was also observed in the fact that ZnO crystallizes in the wurtzite structure instead of the rock salt structure and more than 90 kbar is necessary to obtain ZnO with the rock salt structure (*17*).

In the case of zinc germanates, Zn_2GeO_4 with the spinel structure and $ZnGeO_3$ with the ilmenite structure were reported to be high pressure polymorphs by Ringwood and Major (*13*) and Rooymans (*18*). In this case, Zn^{2+} ions occupy the six coordinated sites at high pressure. Therefore, it is quite interesting to know whether any densely packed structures such as olivine, spinel or ilmenite can be realized in the zinc silicate system.

This paper mainly concerns the phase transformations in Zn_2SiO_4 and $ZnSiO_3$ at high pressure and temperature. For comparison with the zinc silicate systems, high pressure polymorphs of Zn_2GeO_4 and $ZnGeO_3$ were reexamined. Detailed crystal structure analysis of several polymorphs of Zn_2SiO_4 and $ZnSiO_3$, newly found in the course of the study, will be reported elsewhere.

Experimental Procedure

Starting materials for high pressure experiments were prepared by blending, pelletizing and sintering the oxides of guaranteed quality. The prepared specimen of Zn_2SiO_4 has unit cell dimensions of the hexagonal lattice, $a = 13.934$ (1) Å, $c = 9.307$ (1) Å, $V = 1564.5$ (3) Å^3, which are in good agreement with the values of willemite (ASTM card No. 8-492). Starting materials for $ZnSiO_3$ runs were composed of Zn_2SiO_4 (willemite) + SiO_2. The chemical composition of starting materials was examined by conventional chemical analysis to be stoichiometric. In some auxiliary runs for Zn_2SiO_4, starting materials containing excess ZnO or SiO_2 were used in order to study the effect of nonstoichiometry. For the high pressure experiments in Zn_2GeO_4 and $ZnGeO_3$, a mixture of ZnO and GeO_2 in the required proportion was used as starting materials.

High pressure and high temperature experiments were carried out using a tetrahedral anvil type high-pressure apparatus up to 100 kbar and 1500°C. Anvils with edge lengths of 9, 15, and 20 mm were used. The pressure was calibrated at room temperature based on the NBS pressure scale (*19*) (Bi I–II, 26 kbar; Ba I–II, 55 kbar; Bi III–V, 77 kbar and Sn I–II, 100 kbar). A tubular graphite furnace, which served as a sample container, was placed in a pyrophyllite tetrahedron. Temperature was measured with a Pt/Pt-13%Rh thermocouple without any correction for the pressure effect on thermoelectromotive force. The experimental method used in the phase equilibrium study was a conventional quenching method. The specimen was held at a certain temperature-pressure condition for a time interval sufficient for equilibrium (20 min. at 1200°C and 60 min. at 800°C) and then quenched to room temperature by turning off the heating power. The pressure was then released slowly.

In the runs for pressures exceeding 110 kbar, a Bridgman anvil type high pressure apparatus with internal heating system originally designed by Ringwood and Major (*20*) and an ultrahigh pressure apparatus (*21*) equipped at MAPI high-pressure center were used.

Identification of the phases present in the recovered specimen was made by powder X-ray analysis and microscopic observation. The crystal symmetry and the space group were determined on a single crystal obtained from high temperature runs (>1400°C), using Weissenberg camera with Ni filtered CuKα radiation. An accurate determination of unit cell parameters was made by a least-squares refinement of the powder data which were collected by X-ray diffractometer with scanning speed of 0.5° (2θ) per min. 2θ angles were calibrated with pure silicon standard. CuKα_1 radiation was used throughout. Zn to Si ratio in the high pressure phases was determined for several runs by electron microprobe analyzer. The internal standards are ZnO (zincite), SiO_2 (quartz), and Zn_2SiO_4 (willemite).

Experimental Results

(a) Zn_2SiO_4

Experimental results on the phase equilibrium study up to 100 kbar are summarized in Fig. 1 for Zn_2SiO_4. In the figure, the ratio of the phases present in the run products, which was roughly estimated from X-ray powder data, is shown in proportion to

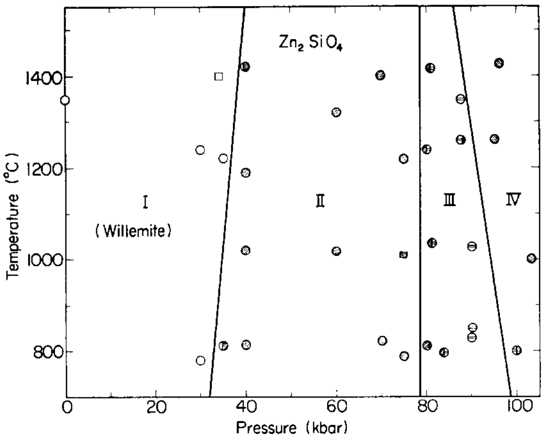

FIG. 1. Phase diagram for Zn_2SiO_4. Starting materials are Zn_2SiO_4 I (Willemite), except for reverse reaction runs indicated by squares.

the area in the circles. Reverse reactions are also indicated by the rectangular marks. Five polymorphs of Zn_2SiO_4 were found in the present experiments up to 170 kbar. Each phase is hereafter designated as Zn_2SiO_4 I–V, in the order of phases with increasing pressure. Crystal data for Zn_2SiO_4 polymorphs are summarized in Table I.

(b) Zn_2SiO_4 II

The atmospheric pressure phase of Zn_2SiO_4 I with the phenacite structure was found to transform to a tetragonal polymorph of Zn_2SiO_4 II beyond about 30 kbar. The equilibrium phase boundary determined was $P(\text{kbar}) = 25 + 0.009\,T(°\text{C})$. Microscopic observation revealed that the samples were composed of granular crystals with significant birefringence. Electron microprobe analysis gave the same Zn:Si ratio for Zn_2SiO_4 II as that for Zn_2SiO_4 I, indicating the crystal is stoichiometric. The crystal symmetry was determined to be tetragonal by Weissenberg photographs taken for a single crystal of 100μ size. Only reflections with $h + k + l = 2n$ for general hkl and $2h + l = 4n$ for hhl were observed. This indicates the possible space group alternatives $I\bar{4}2d$ or $I4_1md$. Powder X-ray diffraction lines were

TABLE I

CRYSTAL DATA FOR Zn_2SiO_4 POLYMORPHS

Phase	Crystal symmetry and space group	Unit cell parameters	Z	Volume per unit formula
I (Willemite)	Hexagonal $R\bar{3}$	$a = 13.934(1)$ Å $c = 9.307(1)$ Å $V = 1564.5(3)$ Å^3	18	86.92 Å^3
II	Tetragonal $I\bar{4}2d$	$a = 7.0069(3)$ Å $c = 6.4637(4)$ Å $V = 317.35(5)$ Å^3	4	79.34 Å^3
III	Monoclinic[a] ($P2_1/n$)	$a = 5.069(1)$ Å $b = 10.292(3)$ Å $c = 6.677(2)$ Å $\beta \simeq 90°$ $V = 348.1(1)$ Å^3	Atomic ratio of Zn:Si = 1.7	
IV	Orthorhombic $Pcab$	$a = 9.678(2)$ Å $b = 10.920(2)$ Å $c = 6.120(1)$ Å $V = 646.8(3)$ Å^3	Atomic ratio of Zn:Si = 1.9	
V (Modified spinel)	Orthorhombic $Imma$	$a = 5.740(1)$ Å $b = 11.504(1)$ Å $c = 8.395(2)$ Å $V = 554.4(2)$ Å^3	8	69.30 Å^3
"Virtual olivine"	Orthorhombic ($Pbnm$)	$a = 4.79$ Å $b = 10.3$ Å $c = 6.02$ Å $V = 297$ Å^3	4	74.3 Å^3

[a] Pseudo-orthorhombic cell was assumed.

TABLE II

POWDER DIFFRACTION DATA FOR Zn_2SiO_4 II

Zn_2SiO_4 II
(Tetragonal)

hkl	d_{obsd}	d_{calcd}	I
1 0 1	4.754	4.751	10
2 0 0	3.504	3.503	20
2 1 1	2.820	2.820	100
1 1 2	2.707	2.707	100
2 2 0	2.476	2.477	5
2 0 2	2.375	2.375	5
3 1 0	2.216	2.216	15
3 0 1	2.197	2.197	10
1 0 3	2.060	2.059	5
3 2 1	1.8610	1.8611	50
3 1 2	1.8270	1.8275	15
2 1 3	1.7752	1.7754	20
4 0 0	1.7511	1.7517	5
4 1 1	1.6439	1.6436	5
0 0 4	1.6163	1.6159	10
3 0 3	1.5831	1.5837	1
4 2 0	1.5671	1.5668	1
4 0 2	1.5400	1.5400	15
3 3 2	1.4700	1.4706	1
2 0 4	1.4671	1.4674	10
3 2 3	1.4429	1.4431	30
4 2 2	1.4099	1.4098	5
5 1 0	1.3741	1.3742	3
5 0 1 4 3 1	1.3696	1.3696	10
1 4 3	1.3344	1 3343	2
3 1 4	1.3056	1.3056	1
5 2 1	1.2756	1.2756	2
1 0 5	1.2716	1.2713	1

$a = 7.0069(7)$ Å
$c = 6.4637(7)$ Å
$V = 317.35(9)$ Å^3

TABLE III

POWDER DIFFRACTION DATA FOR Zn_2SiO_4 III

Zn_2SiO_4 III[a]
(Monoclinic)
(Pseudo-orthorhombic)

hkl	d_{obsd}	d_{calcd}	I
0 2 0	5.151	5.146	40
1 1 0	4.555	4.547	10
0 2 1	4.075	4.076	30
1 0 1	4.040	4.037	30
1 1 1	3.757	3.758	10
1 2 0	3.616	3.611	100
0 0 2	3.340	3.338	40
1 3 0	2.844	2.841	30
0 2 2	2.800	2.801	30
1 1 2	2.691	2.691	30
1 3 1	2.616	2.614	10
0 4 0	2.573	2.573	90
2 0 0	2.536	2.535	80
2 1 0 1 2 2	2.456	2.461 2.451	60
1 4 0	2.295	2.294	10
1 3 2	2.165	2.164	10
0 4 2	2.038	2.038	10
2 0 2	2.020	2.019	10
2 1 2	1.9815	1.9809	10
1 4 2	1.8911	1.8908	10
2 4 0	1.8067	1.8056	10
0 6 0	1.7152	1.7153	10
0 0 4	1.6684	1.6692	10
0 6 2	1.5251	1.5257	10
3 3 0	1.5149	1.5158	10
3 1 2	1.4918	1.4917	10

$a = 5.069(1)$ Å
$b = 10.292(3)$ Å
$c = 6.677(2)$ Å
$V = 348.3(3)$ Å^3

[a] Prepared at 90 kbar and 1030°C.

completely indexed using the single crystal data. No extra peaks could be found. Unit cell dimensions determined by the least-squares method are summarized in Table II, together with the observed and calculated *d* values. The unit cell of Zn_2SiO_4 II contains four molecular units. This gives a density increase of 9.6% for the Zn_2SiO_4 I-II transformation.

Detailed structure analysis for Zn_2SiO_4 II crystal is now being carried out, using intensity data obtained from Weissenberg photographs. Preliminary results suggest that the crystal structure consists of a distorted body-centered framework of oxygen in which both Zn and Si atoms occupy tetrahedrally coordinated sites. This structure is believed to be a new silicate structure. A more comprehensive report will be published elsewhere (*22*).[1]

(c) Zn_2SiO_4 III

Zn_2SiO_4 II became unstable above about 80 kbar and a new high pressure phase Zn_2SiO_4 III appeared. The equilibrium phase boundary between these two phases is substantially temperature independent.

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[1] The space group of Zn_2SiO_4 II was found to be $I\bar{4}2d$ in the course of structure determination (*22*).

The crystals of Zn_2SiO_4 III have a rectangular prismatic shape with weak birefringence and shows a nearly straight extinction under microscopic observation.

The crystal was thought to have a monoclinic symmetry, very close to orthorhombic symmetry, with the absence rule of $h0l$, $h + l$ odd, and $0kl$, k odd. A probable space group to which the crystal belongs is $P2_1/n$. Reflections from the odd c layers were generally weak. The diffraction spots of Zn_2SiO_4 III were very diffuse, in contrast to the sharp spots obtained for Zn_2SiO_4 II. Powder diffraction lines, in spite of rather broad profile, were well indexed on the basis of a pseudo-orthorhombic lattice. Unit cell dimensions together with both the observed and calculated d values are tabulated in Table III.

Chemical composition of Zn_2SiO_4 III was determined by the electron microprobe analysis to be 68.5 wt% ZnO and 29 wt% SiO_2 (cf. 73.0 wt% ZnO and 27.0 wt% SiO_2 for the stoichiometric Zn_2SiO_4). This indicates the crystal is apparently nonstoichiometric and Zn:Si atomic ratio is estimated to be 1.7. During the course of electron microprobe analysis, only Zn_2SiO_4 III did not show significant fluorescence, while the other Zn_2SiO_4 phases I, II and IV showed distinct fluorescence, purplish blue in colour. This is consistent with the reduced Zn:Si ratio in the crystal. Excess ZnO, which was expected to be exsolved from stoichiometric starting materials of Zn_2SiO_4, could not be detected by powder X-ray analysis. However, careful observation of run products under the microscope revealed that very fine transparent grains with high refractive index precipitated around the host crystals. These precipitates might be considered to be ZnO.

Even if starting materials with excess ZnO or SiO_2 were used, no appreciable change in the lattice parameters or in Zn:Si ratio could be detected. Therefore, the reduced Zn:Si ratio in the Zn_2SiO_4 III polymorph seems to be essential.

(d) Zn_2SiO_4 IV

Zn_2SiO_4 III transformed to Zn_2SiO_4 IV at around 90 kbar. The phase boundary curve has a negative slope and is expressed by $P(\text{kbar}) = 109 - 0.015\ T(°\text{C})$. The Zn_2SiO_4 IV polymorph, consisting of a rectangular prismatic crystal with straight extinction, was found to have orthorhombic symmetry from the single crystal data. The systematically absent reflections of the type $0kl$, l odd, $h0l$, h odd, and $hk0$, k odd, show the space group is $Pcab$. All the reflections from the crystal fell on the powder lines, indicating almost single-phase material. Unit cell dimensions determined by the least squares method using powder data are summarized in Table IV, together with the observed and calculated d values. The agreement between them is very good.

TABLE IV

POWDER DIFFRACTION DATA FOR Zn_2SiO_4 IV

	Zn_2SiO_4 IV[a] (Orthorhombic)			Ringwood & Major's *A* Phase[b]		
$h\,k\,l$	d_{obsd}	d_{calcd}	I	d_{obsd}	d_{calcd}	I
0 2 0	5.473	5.460	10	5.46	5.45	1
1 2 1	3.743	3.755	20	3.75	3.75	1
2 2 0	3.621	3.622	50	3.60	3.61	6
2 1 1	3.588	3.585	20			
2 2 1	3.116	3.117	30	3.11	3.11	4
0 0 2	3.059	3.060	10			
1 3 1	2.979	2.977	50	2.972	2.970	5
1 1 2	2.819	2.819	100	2.815	2.815	10
3 2 0	2.776	2.778	90	2.766	2.768	10
0 4 0	2.731	2.730	20			
1 4 0	2.628	2.628	70	2.621	2.621	6
1 2 2	2.574	2.573	30	2.568	2.569	3
3 2 1	2.530	2.529	10			
4 0 0	2.417	2.420	10			
2 4 0	2.379	2.378	10			
0 3 2	2.342	2.342	10			
1 3 2	2.277	2.277	10			
4 0 1	2.248	2.250	30	2.244	2.243	5
4 1 1	2.204	2.204	10			
3 1 2	2.176	2.176	10			
2 3 2	2.108	2.108	10			
3 4 0	2.085	2.084	10			
1 1 3	1.9640	1.9637	20			
1 2 3	1.8764	1.8748	10			
5 1 1	1.8202	1.8198	10			
0 5 2	1.7781	1.7777	10			
3 1 3	1.7033	1.7031	10			
4 3 2	1.6831	1.6829	10			
5 3 1	1.6468	1.6461	10			
3 2 3	1.6439	1.6442	10			
4 5 1 5 2 2	1.5669	1.5672 1.5670	10			
0 6 2	1.5637	1.5642	10			
0 0 4	1.5296	1.5301	10			
0 1 4	1.5149	1.5152	10			
	$a = 9.678(2)$ Å $b = 10.920(2)$ Å $c = 6.120(1)$ Å $V = 646.8(3)$ Å^3			$a = 9.644(6)$ Å $b = 10.893(8)$ Å $c = 6.113(5)$ Å $V = 642(1)$ Å^3		

[a] Prepared at 96 kbar and 1425°C. Zn:Si ratio in the crystal is 1.9.

[b] Prepared at 110 kbar and 900°C. After Ringwood and Major (*13*).

(This phase is confirmed, as shown in Table IV, to be identical with Ringwood and Major's *A* phase (*13*) which was synthesized at 110 ~ 130 kbar and around 900°C).

Electron microprobe analysis showed that the chemical composition of the Zn_2SiO_4 IV polymorph is 72 wt% ZnO and 28 wt% SiO_2. This again indicates Zn_2SiO_4 IV is apparently nonstoichiometric, although the deviation from 2.0 is smaller than that in Zn_2SiO_4 III. Zn:Si atomic ratio was estimated to be 1.9 in Zn_2SiO_4 IV. Excess ZnO exsolved from Zn_2SiO_4 IV lattice could be detected by powder X-ray analysis only when ZnO had the rock salt structure.

Provided that the unit cell contains eight formula units of Zn_2SiO_4, the volume per formula unit is estimated to be 80.8 Å^3, which is significantly larger than that of Zn_2SiO_4 II. This inconsistency may be removed when the reduced Zn:Si ratio is taken into consideration. It may safely be concluded that the volume of Zn_2SiO_4 IV does not vary much from that of Zn_2SiO_4 II, suggesting that Zn ions as well as Si ions still occupy the tetrahedral sites in the crystal structure of Zn_2SiO_4 IV, and so in Zn_2SiO_4 III. This estimation is in harmony with the refractive indices (1.75 ~ 1.77) of Zn_2SiO_4 IV determined by Ringwood and Major (*13*).

TABLE V

POWDER DIFFRACTION DATA FOR Zn_2SiO_4 V

	Zn_2SiO_4 V[a] Modified Spinel (Orthorhombic)			Ringwood & Major's *B* phase[b]		
h k l	d_{obsd}	d_{calcd}	*I*	d_{obsd}	d_{calcd}	*I*
0 1 1	6.773	6.782	40	6.78	6.77	4
1 0 1	4.739	4.738	50	4.74	4.74	7
0 3 1	3.489	3.488	20	3.48	3.48	1
1 1 2	3.251	3.250	10	3.24	3.25	<1
0 4 0	2.872	2.876	10	2.870	2.870	<1
0 1 3	2.719	2.719	60	2.712	2.713	5
2 1 1	2.643	2.643	50	2.641	2.642	5
1 3 2	2.540	2.539	10			
1 0 3	2.516	2.515	40	2.507	2.511	2
1 4 1	2.460	2.459	100	2.454	2.455	10
0 4 2	2.371	2.373	40	2.366	2.368	3
0 3 3	2.259	2.261	10	2.256	2.256	<1
0 5 1 2 3 1	2.218	2.219 2.216	30	2.215	2.215 2.214	3
0 0 4	2.099	2.099	40	2.094	2.094	3
2 4 0	2.032	2.032	70	2.029	2.030	8
2 3 3	1.7758	1.7758	20			
2 5 1	1.7552	1.7555	10			
3 0 3	1.5793	1.5795	10			
3 4 1	1.5654	1.5651	10			
2 4 4	1.4598	1.4597	50	1.458	1.457	7
0 8 0	1.4383	1.4380	20			
4 0 0	1.4349	1.4351	20	1.435	1.435	3
	$a = 5.740(1)$ Å $b = 11.504(1)$ Å $c = 8.395(2)$ Å $V = 554.4(2)$ Å^3			$a = 5.740(1)$ Å $b = 11.481(4)$ Å $c = 8.376(2)$ Å $V = 552.0(4)$ Å^3		

[a] Prepared at 170 kbar and 1000°C.

[b] Prepared at 150 kbar and 900°C after Ringwood and Major (*13*).

It is to be noted here that the crystal of Zn_2SiO_4 IV also showed diffuse diffraction spots and their intensities decrease very rapidly on going to higher 2θ angles. This phenomenon is quite similar to the case of Zn_2SiO_4 III, and is probably related to the reduced atomic ratio Zn:Si.

(e) Zn_2SiO_4 V

In the run using Bridgman anvil type high-pressure apparatus, another new phase was discovered above about 130 kbar and 900°C. This phase, Zn_2SiO_4 V, showed the same powder X-ray diffraction pattern as that of Ringwood and Major's *B* phase (*13*). We have found a remarkable resemblance between the X-ray diffraction patterns of Zn_2SiO_4 V and Co_2SiO_4 II (β phase) with the modified spinel structure (*10*, *13*) and can successfully assign the indices on the basis of the modified spinel structure. The least-squares refinement of the powder data resulted in an excellent agreement between the observed and calculated *d* values, as shown in Table V. The unit cell dimensions of the orthorhombic lattice are determined to be $a = 5.740$ (1) Å, $b = 11.504(1)$ Å, $c = 8.395(2)$ Å and $V = 554.4$ (2) Å^3. These cell parameters are very similar to those of Co_2SiO_4 II, which is consistent with the similar ionic radii of Zn^{2+} and Co^{2+} (*23*).

The density increase during the transformation is estimated to be about 14% from Zn_2SiO_4 II–IV to Zn_2SiO_4 V and 26% from Zn_2SiO_4 I (willemite) to Zn_2SiO_4 V. The latter value showed a reasonable agreement with the density change estimated by Ringwood and Major, using the observation of refractive indices (*13*). Since the relative intensity of each diffraction line of Zn_2SiO_4 V is quite similar to that of Co_2SiO_4 II, with the modified spinel structure (*10*, *13*), the ionic configuration is supposed to be the same in cobalt and zinc isomorphs, i.e., coordination numbers of metal ions are six for Zn or Co and four for Si. This coordination change (4 → 6) in Zn ions with the transformation explains the large volume decrease from Zn_2SiO_4 IV to V.

TABLE VI

CELL CONSTANTS AND UNIT CELL VOLUMES FOR $(Mg,Zn)_2SiO_4$ SOLID SOLUTION WITH THE OLIVINE STRUCTURE SYNTHESIZED AT 70 kbar AND 1200°C

Specimen	Molar % of Zn_2SiO_4	a (Å)	b (Å)	c (Å)	V ($Å^3$)
Mg8[a]	0	4.7553(6)	10.1977(14)	5.9820(7)	290.09(11)
Zn2	26	4.765(1)	10.231(3)	5.986(2)	291.8(3)
Zn4	50	4.775(1)	10.250(3)	5.994(2)	293.3(3)
Zn5	63	4.778(2)	10.264(4)	6.000(2)	294.3(3)
Zn6[b]	75	4.782(2)	10.273(3)	6.006(2)	295.0(3)

[a] After Matsui and Syono (1968) (*25*).

[b] Trace of extra phase (s) other than the olivine structure. Synthesized at 90 kbar and 1200°C.

(f) $(Mg,Zn)_2SiO_4$ Solid Solution System

Among five polymorphs of Zn_2SiO_4, no olivine-like structure could be found. In order to make the situation clear, $(Mg,Zn)_2SiO_4$ solid solutions were investigated at high pressure up to 90 kbar. The solid solution system $(Mg,Zn)_2SiO_4$ was prepared by mixing Mg_2SiO_4 with the olivine structure, and Zn_2SiO_4 with the phenacite structure, in the required proportions and fired at 70 kbar and 1200°C for 40 minutes. Homogeneity of the specimen was examined by powder X-ray analysis and by microscopic observation. The composition was determined by conventional chemical analysis. Specimens with the olivine structure were synthesized up to 63 mol% Zn_2SiO_4 at 70 kbar and 1200°C. For the specimen with 75% Zn_2SiO_4 at 90 kbar and 1200°C, the product revealed that a small amount of extra phase (probably Zn_2SiO_4 IV solid solution) is present, even though the product was mostly composed of the olivine solid solution. Therefore, we conclude that the solubility limit of Zn_2SiO_4 in the Mg_2SiO_4 olivine is very close to 75% at 90 kbar. This solubility limit at high pressure is much greater than that at atmospheric pressure which amounts to only 24% (*24*). However, it is very striking that the Zn_2SiO_4 olivine could not be stabilized even at high pressure.

Unit cell dimensions of $(Mg,Zn)_2SiO_4$ system were determined by the least-squares method, using powder data. Results are summarized in Table VI and Fig. 2. As is seen from the figure, the unit cell

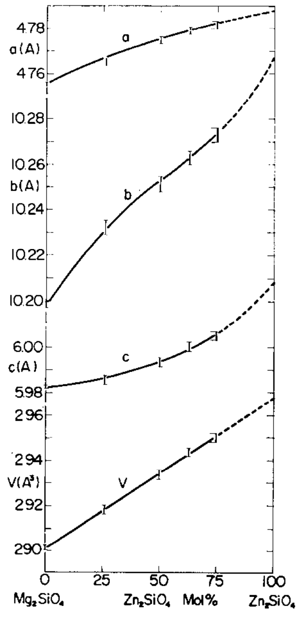

FIG. 2. Composition dependence of unit cell parameters and cell volume for $(Mg,Zn)_2SiO_4$ system with the olivine structure.

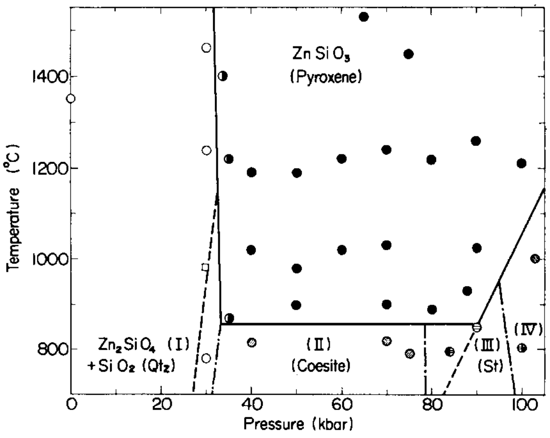

FIG. 3. Phase diagram for $ZnSiO_3$. Starting materials were mixtures of Zn_2SiO_4 I + SiO_2: circles and $ZnSiO_3$: squares.

volume is a linear function of molar composition in the $(Mg,Zn)_2SiO_4$ system within experimental error. Anomalies found in the composition dependence of cell parameters in this system are very similar to those found in $(Mg,Co)_2SiO_4$ system (*25*) except for the case of the *b* axis. An extrapolation of the composition dependence of cell parameters yields unit cell dimensions of "virtual" olivine Zn_2SiO_4 as $a = 4.79$ Å, $b = 10.31$ Å, $c = 6.02$ Å, and $V = 297$ Å^3. These hypothetical values show that the "virtual" olivine might be about 7% denser than Zn_2SiO_4 II–IV and 8.1% less dense than the modified spinel of Zn_2SiO_4 V. The latter value is again consistent with the case in Co_2SiO_4.

(g) $ZnSiO_3$

The phase diagram for $ZnSiO_3$ is shown in Fig. 3. A zinc metasilicate $ZnSiO_3$ is found to be stable for a rather wide region in the pressure-temperature diagram. The lower pressure boundary was determined to be almost temperature-independent and represented by the equation $P(\text{kbar}) = 35 - 0.002\,T(°\text{C})$. The boundary curve is located very near to the Zn_2SiO_4 I–II phase boundary. $ZnSiO_3$ is also found to be stable only at higher temperature than about 850°C. $ZnSiO_3$ seems to decompose to Zn_2SiO_4 III or IV plus SiO_2 (rutile form) in the stishovite region (*26*). This decomposition scheme is quite similar to that found in $FeSiO_3$ at high pressure (*27*), although the crystal structure of the decomposed product is the spinel Fe_2SiO_4 in the latter case. The decomposition line was tentatively assumed to coincide with the phase boundary curve of the coesite-stishovite transition.

Microscopic observation of the $ZnSiO_3$ pyroxene showed that the product is composed of long prismatic crystals mostly twinned. The crystal apparently showed a straight extinction between crossed Nicols.

Weissenberg photographs taken for single crystals of $ZnSiO_3$ revealed that the crystal structure is the clinopyroxene structure with the space group of $P2_1/c$. The powder X-ray pattern, however, showed a marked dissimilarity to those of common clinopyroxenes. The indices, given on the basis of single crystal data, explained the powder data quite satisfactorily. The unit cell parameters and both the observed and calculated *d* values are summarized in Table VII. Volume changes in the synthesis of the $ZnSiO_3$ pyroxene from Zn_2SiO_4 II plus coesite and in the disproportionation to Zn_2SiO_4 IV plus stishovite are estimated to be 2.3% and about 7.5%, respectively.

TABLE VII

POWDER DATA FOR CLINOPYROXENE $ZnSiO_3$[a]

	ZnSiO$_3$ (Monoclinic)		
h k l	d_{obsd}	d_{calcd}	*I*
1 1 0	6.467	6.466	70
0 2 0	4.555	4.555	80
2 2 0	3.235	3.233	80
2 2 1	3.098	3.098	60
3 1 0	2.901	2.900	20
1 3 0	2.884	2.883	100
1 0 2	2.638	2.638	50
1 1 2	2.534	2.534	5
2 3 1 0 0 2	2.466	2.466 2.467	15
2 2 −1	2.431	2.430	20
0 1 2	2.382	2.381	10
0 4 0	2.277	2.277	5
3 3 1	2.195	2.195	40
3 3 0	2.156	2.155	5
1 1 −2	2.129	2.128	5
2 4 0	2.041	2.040	10
2 0 −2	1.897	1.900	5
3 3 2	1.8831	1.8832	5
3 3 −1	1.8097	1.8101	5
5 1 0	1.7994	1.7995	10
2 2 −2	1.7536	1.7538	5
5 2 2	1.6987	1.6987	5
2 2 3	1.6486	1.6489	30
4 4 0	1.6166	1.6164	10
6 0 2	1.5858	1.5883	10
6 0 0	1.5297	1.5297	20
0 6 0	1.5181	1.5183	25
6 1 0	1.5076	1.5086	15

$a = 9.8728(17)$ Å
$b = 9.1096(7)$ Å
$c = 5.3071(6)$ Å
$\beta = 111°\,37'(2')$
$V = 443.72(10)$ Å^3

[a] A few weak lines which could not be indexed were omitted.

It is to be remarked here that single crystals of the orthorhombic form of $ZnSiO_3$ pyroxene were picked up from the products at certain high temperature runs for Zn_2SiO_4. Since no stable region for this orthopyroxene could be found in the present study, the orthorhombic form of $ZnSiO_3$ pyroxene is suggested to be metastably formed.[1]

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[1] The clinopyroxene and orthopyroxene $ZnSiO_3$ which were reported to have been synthesized by Hayashi et al. (*14*) are now proved to be the mixture of Zn_2SiO_4 II + coesite and the clinopyroxene, respectively. Their phase diagram is not inconsistent with ours, if the above changes are taken into consideration.

TABLE VIII

POWDER DATA FOR THE HIGH PRESSURE FORMS OF Zn_2GeO_4 AND $ZnGeO_3$

Zn_2GeO_4 Spinel[a] (Cubic) ($Fd3m$)				Zn_2GeO_4 Distorted Spinel[b] (Tetragonal) ($I4_122$ or $I4_322$)				$ZnGeO_3$ Ilmenite[c] (Hexagonal) ($R\bar{3}$)			
$h\,k\,l$	d_{obsd}	d_{calcd}	I	$h\,k\,l$	d_{obsd}	d_{calcd}	I	$h\,k\,l$	d_{obsd}	d_{calcd}	I
1 1 1	4.823	4.821	20	1 0 1	4.820	4.820	20	0 0 3	4.616	4.618	30
2 2 0	2.9520	2.9521	50	2 0 0	2.967	2.969	40	0 1 2	3.648	3.649	30
3 1 1	2.5169	2.5176	100	1 1 2	2.942	2.943	20	1 0 4	2.695	2.696	100
2 2 2	2.4105	2.4104	20	2 1 1	2.529	2.528	100	1 1 0	2.478	2.479	60
4 0 0	2.0873	2.0875	50	1 0 3	2.497	2.496	60	0 1 5	2.329	2.328	20
4 2 2	1.7045	1.7044	15	2 0 2	2.409	2.410	30	0 0 6	2.310	2.309	10
5 1 1 3 3 3	1.6068	1.6069	50	2 2 0	2.100	2.099	20	1 1 3	2.185	2.184	10
				0 0 4	2.063	2.063	10	0 2 4	1.8249	1.8247	30
4 4 0	1.4761	1.4761	55	3 1 2	1.7095	1.7090	10	1 1 6	1.6894	1.6897	40
5 3 1	1.4114	1.4114	5	2 0 4	1.6946	1.6943	5	0 1 8	1.6060	1.6063	10
6 2 0	1.3203	1.3202	5	3 2 1	1.6148	1.6149	20	0 0 9	1.5398	1.5396	10
5 3 3	1.2734	1.2734	10	3 0 3	1.6065	1.6066	10	2 1 4	1.4696	1.4695	20
6 2 2	1.2588	1.2588	5	1 0 5	1.5903	1.5904	10				
7 3 1	1.0870	1.0871	15	4 0 4	1.4841	1.4843	50				
				2 2 4	1.4714	1.4715	30				
$a = 8.3499(3)$ Å $V = 582.16(6)$ Å^3 $Z = 8$				$a = 5.937(1)$ Å $c = 8.254(1)$ Å $V = 290.95(7)$ Å^3 $Z = 4$				$a = 4.958(1)$ Å $c = 13.856(1)$ Å $c/a = 2.795(1)$ $V = 294.93(8)$ Å^3 $Z = 6$			

[a] Synthesized at 30 kbar and 1600°C.

[b] Synthesized at 72 kbar and 930°C.

[c] Synthesized at 76 kbar and 1150°C.

(h) Zn_2GeO_4 and $ZnGeO_3$

High pressure polymorphs of Zn_2GeO_4 and $ZnGeO_3$ were synthesized and analyzed by means of powder X-ray analysis. The results are summarized in Table VIII. High pressure polymorphs of Zn_2GeO_4 and $ZnGeO_3$ have the spinel structure and the ilmenite structure respectively. This is consistent with the results reported by Ringwood and Major (*13*) and Rooymans (*18*). Zn_2GeO_4 spinel is dimorphous. The cubic form is synthesized at 30 kbar and 1600°C, whereas the tetragonal form is stable at 30 kbar and 1450°C and 72 kbar and 930°C. The tetragonal distortion is most probably due to the ordering of Zn^{2+} and Ge^{4+} ions in the octahedral sites of the spinel lattice as found in Zn_2TiO_4 (*28*) and Mn_2TiO_4 (*29*) spinels, although the superstructure lines could not be found owing to the similarity between the atomic scattering factors of Zn and Ge. Volume decreases accompanied by the transformation in Zn_2GeO_4 from the phenacite structure to the spinel structure and by the synthesis of $ZnGeO_3$ ilmenite from Zn_2GeO_4 spinel plus GeO_2 rutile are estimated to be 21.8 and 2.0% respectively.

Discussion

Olivine and Pyroxene in Zinc Silicates

It is a well-known fact that the Zn^{2+} ion strongly prefers the tetrahedrally coordinated sites compared with other divalent cations with similar ionic radius. This fact has been explained as a result of a covalent character of Zn^{2+} ions which form sp^3-type hybrid bonding in the crystal. Peculiar crystal structures realized in ZnO and Zn_2SiO_4 are typical examples for such strong tetrahedral preference of the Zn^{2+}

ion. The present study on the high-pressure phase transformation in Zn_2SiO_4 demonstrates another example of such a tetrahedral preference of Zn^{2+}. All new phases Zn_2SiO_4 II–IV appearing below 100 kbar seem to have Zn^{2+} ions in four coordinated positions in the crystal structure, because these three polymorphs have almost the same molar volume, which is much larger than those of the modified spinel or "virtual" olivine with Zn^{2+} ions at six coordinated sites. (The relatively larger density increase found in the Zn_2SiO_4 I–II transformation can be explained by the discrepancy between the open structure of willemite and the more closely-packed structure of Zn_2SiO_4 II.) It is very remarkable that a pressure exceeding 130 kbar is necessary to bring Zn^{2+} ions in the octahedrally coordinated sites in Zn_2SiO_4. This is in marked contrast to other divalent cation orthosilicates which have the olivine structure at atmospheric pressure. The extreme instability of the olivine structure in Zn_2SiO_4 is particularly impressive.

Such a strong preference of Zn^{2+} ions for the tetrahedral sites appears to be somewhat reduced in the case of the octahedral sites in zinc pyroxene. The clinopyroxene form of $ZnSiO_3$ is stabilized at the relatively low pressure of 30 kbar. This formation pressure of $ZnSiO_3$ is only slightly higher than the pressures of $FeSiO_3$ or $CoSiO_3$ (*30*). However, no thermodynamically stable pressure-temperature region could be found for the orthopyroxene form of $ZnSiO_3$ in this case. Furthermore, the clinopyroxene form of $ZnSiO_3$ shows quite unusual cell parameters if compared with other clinopyroxenes $MSiO_3$ ($M = Mn$, Fe, Co, and Mg) (*31*, *32*). In particular, the value of 111° 37′ of the β angle is about 3.5° larger than values of around 108° for most clinopyroxenes. The dimensions of the a and c axes, and hence the cell volume, are also remarkably larger than those expected from the ionic radius (Table IX). These anomalous values are, of course, a reflection of the extraordinary structure of the zinc clinopyroxene and may have a close connection with the metastability of the orthorhombic form of $ZnSiO_3$. In this situation, it is worth while to discuss in some detail the nonexistence of zinc olivine and the existence of zinc pyroxene with such anomalous cell parameters.

Summarizing the above mentioned facts, it is concluded that the Zn^{2+} ion more strongly prefers the octahedral sites in the pyroxene structure to those in the olivine structure. This may partly be explained by the much higher concentration of Zn^{2+} ions in Zn_2SiO_4 than in $ZnSiO_3$; and stronger interaction among ZnO_4 tetrahedra would work against the stabilization of Zn^{2+} ions in octahedral sites in the former rather than in the latter. These results, however, are more reasonably related to the difference between the crystal structures of olivine and pyroxene. The olivine structure is basically formed by hexagonally close-packed arrangements of oxygen ions and the octahedrally coordinated sites are surrounded by more regular octahedra of oxygen ions, while the pyroxene structure is determined mainly by SiO_4 tetrahedra chains and has more irregular octahedral sites than those in olivine. The metal positions are more regularly coordinated, i.e., more symmetrical in the olivine structure than in the pyroxene structure. These considerations lead to the conclusion that the regulation of the shape of the octahedral site is strict in the olivine structure, while being rather flexible in the pyroxene structure. Therefore, it is plausible to consider that the Zn^{2+} ions are more stabilized or more easily adapted in the pyroxene structure than in the olivine structure, since Zn^{2+} ions tend to avoid the regular octahedral sites. Probably the anomalous unit cell parameters found in the clinopyroxene form of $ZnSiO_3$ are closely related to peculiar oxygen arrangements

TABLE IX

CRYSTAL DATA FOR SEVERAL CLINOPYROXENES

$MSiO_3$	r_M (Å)	a (Å)	b (Å)	c (Å)	β	V (Å^3)
$MnSiO_3$[a]	0.830	9.864(2)	9.179(2)	5.298(1)	108° 13′(1′)	455.6(2)
$FeSiO_3$[a]	0.780	9.716(2)	9.090(1)	5.239(2)	108° 27′(1′)	438.9(2)
$ZnSiO_3$[b]	0.750	9.8728(17)	9.1096(7)	5.3071(6)	111° 37′(2′)	443.72(10)
$CoSiO_3$[a]	0.745	9.655(1)	8.933(1)	5.199(1)	108° 32′(1′)	425.1(1)
$MgSiO_3$[c]	0.720	9.6065(11)	8.8146(7)	5.1688(6)	108° 20′(1′)	415.46(9)

[a] Unpublished data (*31*).

[b] Present study.

[c] Stephenson *et al.* (1966) (*32*).

around Zn^{2+} ions in the crystal. Detailed crystal structure analysis is, therefore, of great interest.

These situations in zinc silicates are in great contrast to those in nickel silicates. It has already been mentioned that, due to the strong crystal field stabilization, Ni ions prefer more regular octahedral sites in the crystal, so that octahedral sites in olivine are much more favorable than the severely distorted sites in pyroxene. This explains why nickel pyroxene shows an extreme instability even at high pressure, while nickel olivine can be synthesized at atmospheric pressure (*25*, *33*).

"Nonstoichiometry" in Zn_2SiO_4 III & IV

Two high-pressure polymorphs Zn_2SiO_4 III and IV are proved to have the reduced atomic ratio of Zn:Si from the stoichiometric value of 2. Since the intensity of X-ray diffraction lines decay rapidly with increasing Bragg angle in the case of Zn_2SiO_4 III and IV, indicating relatively large temperature factors, and since the diffraction spots are also very diffuse, the crystal is suggested to suffer from severe thermal vibration of the lattice caused by the disorder such as defects or interstitials. Although definite conclusions should not be made unless the complete structure analysis is carried out, these polymorphs may probably be nonstoichiometric. This is quite different from the mode of the high-pressure transformation in other orthosilicates M_2SiO_4 in which only stoichiometric polymorphs are found.

Comparison with Germanates

In the early stage of the work on the high-pressure transformation in silicates, the most useful guiding principle was the analogous structure types of corresponding silicates and germanates. It has been thought that the high-pressure phase transformation in silicates can be predicted by the analogy of the structure type known for germanates (*34*). However, recent progress in high-pressure work has revealed that this analogy does not hold in all cases, e.g., $MnSiO_3$ and $MnGeO_3$, $CaSiO_3$ and $CaGeO_3$, Mg_2GeO_4 and Mg_2SiO_4, etc. (*35*).

In the case of zinc silicates and germanates, this analogy was proved to be of little use. Zn_2SiO_4 finally transforms to the modified spinel structure, passing through three four-coordination structures, while Zn_2GeO_4 directly transforms to the spinel structure, although both compounds crystallize in the same phenacite structure at atmospheric pressure. This dissimilarity is mainly due to the fact that the cationic distribution is of a normal spinel type in Zn_2SiO_4, while an inverse spinel type in Zn_2GeO_4. In other words, the tetrahedral preference among relevant ions is in the order of Si^{4+}, Zn^{2+} and Ge^{4+}. It is to be noted that ilmenite type $ZnGeO_3$ was formed at relatively low pressure, while the only known compound for $ZnSiO_3$ is clinopyroxene, and metastable orthopyroxene, and it disproportionates to Zn_2SiO_4 plus stishovite at high pressure. This discrepancy can be explained on the basis that the difference in the ionic radii in Zn^{2+} and Si^{4+} is too large to form the ilmenite structure, while that in Zn^{2+} and Ge^{4+} is tolerable (*36*).

The discrepancy between the high-pressure polymorphs of zinc silicates and germanates suggests that the analogy between silicates and germanates should be applied carefully in discussing high-pressure phase transformations. Important factors controlling the crystal structure type such as ionic radius ratio, electrostatic energy, and crystal field effects in the transition metal ions have to be taken into consideration. From this aspect, hypotheses such as the existence of Mg_2SiO_4 cubic spinel and $MgSiO_3$ ilmenite at extreme high pressure should be reexamined.

Stability of Modified Spinel

The newly found modified spinel of Zn_2SiO_4 V is the third example in orthosilicates. The modified spinel structure has peculiar atomic arrangements, i.e., two SiO_2 tetrahedra share one of their oxygen atoms resulting in a Si_2O_7 group, and Pauling's electrostatic balance rule fails for certain oxygen atoms in the structure (*12*, *37*). Therefore, some questions have been thrown upon the structural stability of the modified spinel. However, recent calculation on the electrostatic energy of the modified spinel and the cubic spinel of Co_2SiO_4, based on the accurate atomic coordinates, revealed that the modified spinel is not particularly unstable as compared with the spinel structure (*38*, *39*).

This result seems to be supported by the existence of Zn_2SiO_4 with the modified spinel structure. It is to be noted that four modified spinel isomorphs, Mg_2SiO_4, Co_2SiO_4, Zn_2SiO_4 and Mn_2GeO_4 are composed of such metal ions as are not sensitive to the crystal field effect, except for the case of Co^{2+} ions. On the contrary, transition metal silicates and germanates are known to take the cubic spinel structure. This implies that the contribution from the crystal field stabilization energy might play an important role in the stabilization of the cubic spinel structure and the modified spinel would be more stable than the cubic spinel without this contribution. Detailed discussion on the crystal field effect on the olivine-spinel transformation will be given elsewhere (*40*).

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