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HIGH-PRESSURE SYNTHESIS OF A "MODIFIED" SPINEL AND SOME GEOPHYSICAL IMPLICATIONS

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Stability relations of Mn_2GeO_4 have been studied over the temperature range 790 to 1240 °C in the pressure range 31 to 70 kb. β-Mn_2GeO_4 with a "modified" spinel structure was observed in a large synthesis field between the fields of the olivine polymorph (α-Mn_2GeO_4) and another high-pressure polymorph (δ-Mn_2GeO_4) with Sr_2PbO_4-type structure. Density increases associated with the α-β transformation and the β-δ transformation were estimated to be 7.1% and 10.7%. The mean volume thermal expansivity for β-Mn_2GeO_4 has been determined to be $(30 \pm 1) \times 10^{-6}$ °C^{-1} in a temperature range of room temperature to 460 °C and at ambient pressure.

A high-pressure transformation diagram in $(Mg, Co)_2SiO_4$ solid solutions ranging in composition from pure Co_2SiO_4 to $(Mg_{0.5}Co_{0.5})_2SiO_4$ has been studied over the pressure range 61 to 94 kb at 800, 1000 and 1200 °C. The phase relationships of the system were found to be strongly influenced by temperature; at 800 °C any indication of the phases other than olivine and spinel solid solution was not found, but at 1200 °C the formation of the "modified" spinel solid solutions was distinguishable in a pressure range between the fields of the olivine and the true spinel solid solutions.

It is plausible from these experimental results to conclude that the "modified" spinel solid solutions synthesized by Ringwood and Major for compositions more magnesian than $(Mg_{0.85}Fe_{0.15})_2SiO_4$ in the Mg_2SiO_4–Fe_2SiO_4 system may represent a thermodynamically stable phase and not a metastable phase formed during quenching. If the mantle olivine transformed stepwise to the true spinel phase through the "modified" spinel phase, the previous estimates of the constitution and width of the transition zone of the mantle should be reexamined.

1. Introduction

It has recently been accepted that high-pressure transformations in $(Mg, Fe)_2SiO_4$ are responsible for the formation of the high-gradient zone of seismic-wave velocities at a depth of about 350 to 1000 km in the Earth's mantle. Successful interpretation of the sharp velocity increase around 370 km has been given by ANDERSON (1967) and FUJISAWA (1968) on the basis of the simple olivine-spinel equilibrium diagram which was established for the $(Mg, Fe)_2SiO_4$ solid solutions ranging in composition from pure Fe_2SiO_4 to $(Mg_{0.8}Fe_{0.2})_2SiO_4$ (AKIMOTO and FUJISAWA, 1966 and 1968). However, some complexity in the transformation in more magnesian olivines than $(Mg_{0.85}Fe_{0.15})_2SiO_4$ was pointed out by RINGWOOD and MAJOR (1966). They synthesized another non-cubic high-pressure phase (β phase*) at 900° to 1000 °C and at pressures just above the stable range of olivine. An X-ray powder diffraction pattern of this β phase showed a marked resemblance to spinel but contained many extra lines. RINGWOOD and MAJOR (1966) suggested that the β phase may be a "distorted" or "modified" spinel, and that the distortion occurred during quenching of an original true spinel. The crystal structure of the β phase, however, has been remained unknown on account of the lack of a suitable single crystal for the structure analysis.

In these situations, it is of great importance to determine what is the crystal structure of the β phase and to examine whether or not the β phase is a metastable phase formed during quenching from high-pressure and high-temperature conditions. We have recently found the occurrence of a new high-pressure polymorph of Co_2SiO_4 which is the isotype of the β phase of Mg_2SiO_4. The stability relationships between this new polymorph and olivine and spinel polymorphs of Co_2SiO_4 at high-pressures and high-temperatures have been reported in our recent paper (AKIMOTO and SATO, 1968). Further, successful synthesis of a single crystal of the β phase of Co_2SiO_4 made it possible to determine

* In the present paper, the terms, α, β, γ and δ phase in R_2MX_4 type compounds are used for olivine, "modified" spinel, true spinel, and Sr_2PbO_4-type polymorph respectively.

the crystal structure of the β phase. Structure analysis carried out by MORIMOTO *et al.* (1969) revealed that the β phase of Co_2SiO_4 could be assigned an orthorhombic structure with space group of *Imma*, and justified that the β phase is termed "modified" spinel. Detailed report is given elsewhere in this volume (MORIMOTO *et al.*, 1970).

In the present paper, other examples of the high-pressure synthesis of the "modified" spinel are given in Mn_2GeO_4 and in $(Mg, Co)_2SiO_4$ solid solutions.

2. High-pressure transformations of Mn_2GeO_4

Preliminary reports of the phase relations of Mn_2GeO_4 have already been given by a few investigators. RINGWOOD and SEABROOK (1963) noted that olivine polymorph of Mn_2GeO_4 decomposed into $MnGeO_3$ ilmenite plus an additional phase (probably MnO) at about 90 kb and at 700 °C. Recently, above 90 kb and at 900 °C WADSLEY *et al.* (1968) synthesized a new high-pressure polymorph of Mn_2GeO_4 (δ phase) which was isomorphous with Sr_2PbO_4. In the present study we found that a third high-pressure polymorph of Mn_2GeO_4 was synthesizable in the pressure range intermediate between the olivine and Sr_2PbO_4-type field.

High-pressure and high-temperature experiments were done using the tetrahedral-anvil type of high-pressure apparatus. Two different sizes of cemented tungsten carbide anvils with 15 mm and 20 mm edge length were used, depending upon maximum pressure desired. Pressure values were calibrated at room temperature on the basis of the pressure scale proposed by JEFFERY *et al.* (1966).

Starting materials used in the ordinary runs are the olivine polymorph of Mn_2GeO_4 (α phase) which was prepared by sintering a stoichiometric mixture of MnO and GeO_2 sealed in an evacuated silica tube at 1000 °C for 40 hours. The unit cell dimensions of the Mn_2GeO_4 olivine are $a = 5.061 \pm 0.001$ Å, $b = 10.719 \pm 0.001$ Å and $c = 6.295 \pm 0.001$ Å. In order to determine the transition diagram of Mn_2GeO_4 accurately and to settle the question whether or not the newly found high-pressure polymorph of Mn_2GeO_4 (β phase) is a real stable phase in its synthesis field, a number of reverse runs, in which the β phase and the δ phase of Mn_2GeO_4 were used as starting materials, were also made.

Powder samples of starting materials were directly embedded in the tubular graphite furnace which was placed diagonally with the axis of the cylinder between opposite edges of the baked pyrophyllite tetrahedron. Temperatures were measured in the central part of the samples with a Pt/Pt-13% Rh thermocouple without any correction for the effect of pressure on the emf of the thermocouple.

The experimental method used in determining the stability diagram of Mn_2GeO_4 at high-pressures and high-temperatures was the usual quenching method. After pressure was applied to the sample, the temperature was brought to the desired value and held for the desired interval of time. Then the sample was quenched under the working pressure by turning off the heating power. After relaxation of pressure, the phases present in the central part of the quenched samples were examined by the X-ray diffraction technique.

Results of runs on the high-pressure and high-temperature phase transformations in Mn_2GeO_4 are summarized in table 1. The high-pressure synthesis of the δ phase of Mn_2GeO_4 was confirmed in the present study over the wide temperature range. Unit cell dimensions and the calculated density of the δ-Mn_2GeO_4; $a = 5.262 \pm 0.001$ Å, $b = 9.274 \pm 0.001$ Å, $c = 2.954 \pm 0.001$ Å and $\rho_\delta = 5.676$ g/cm^3, are in good agreement with the values reported by WADSLEY *et al.* (1968). However, a new high-pressure polymorph of Mn_2GeO_4 with greyish-blue colour was observed in the pressure range intermediate between the α and δ phase field. X-ray diffraction data of the newly found high-pressure polymorph of Mn_2GeO_4 were found to be successfully indexed by the β-Co_2SiO_4 structure. Structure analysis carried out bij MORIMOTO *et al.* (1969 and 1970), using single crystals of Mn_2GeO_4 synthesized at 64 kb and at 1240 °C, established that the new high-pressure polymorph of Mn_2GeO_4 was assigned the "modified" spinel structure with space group of *Imma*. Unit cell dimensions and the calculated density of this β-Mn_2GeO_4 were determined to be $a = 6.025 \pm 0.002$ Å, $b = 12.095 \pm 0.004$ Å, $c = 8.752 \pm 0.002$ Å and $\rho_\beta = 5.13$ g/cm.

A true spinel phase could not be synthesized in the Mn_2GeO_4 sample at the pressure-temperature condition studied in this work. This is a marked difference from the high-pressure transformations in Co_2SiO_4. Further, any evidence suggesting a decomposition of

TABLE 1

Results of runs on the high-pressure and high-temperature phase transformations in Mn_2GeO_4

Run no.	Pressure*, kb	Temperature, °C	Time, min	Phases present
		Starting material, α-Mn_2GeO_4 (Olivine type)		
6	31	810 ± 5**	50	α phase
7	35	790 ± 10	50	α phase
9	39	1100 ± 20	18	α phase
8	40	800 ± 10	50	β phase
10	42	1100 ± 20	15	α phase
11	47	1100 ± 20	15	β phase + α phase
15	49	900 ± 5	40	β phase
4	54	930 ± 5	25	β phase
13	54	1030 ± 20	30	β phase
12	56	810 ± 5	31	β phase
1	63	1200 ± 20	20	β phase
3	64	840 ± 5	45	δ phase
2	64	1240 ± 20	20	β phase
5	68	1200 ± 20	20	δ phase
16	70	900 ± 5	40	δ phase
14	70	1030 ± 10	30	δ phase
		Starting material, β-Mn_2GeO_4 (Modified spinel type)		
21	41	1030 ± 15	25	α phase
22	66	1100 ± 10	20	δ phase
		Starting material, δ-Mn_2GeO_4 (Sr_2PbO_4 type)		
31	47	1130 ± 20	15	α phase
32	57	940 ± 5	30	β phase
33	60	930 ± 5	35	δ phase

* Precision of pressure control is about ±1 kb.
** Precision of temperature control.

Mn_2GeO_4 into $MnGeO_3$ ilmenite and MnO was not observed at pressures below 70 kb.

Experimental runs using δ-Mn_2GeO_4 as starting material revealed that the β-Mn_2GeO_4 could be formed not only from olivine but also from the Sr_2PbO_4-type polymorph. Further, complete conversion from β-Mn_2GeO_4 to δ phase or α phase was confirmed by the reverse reactions using β-Mn_2GeO_4 as starting material. These mutual transformation behaviors among the α, β, and δ phases of Mn_2GeO_4 may suggest that the β-Mn_2GeO_4 synthesized in this work is a real stable phase and not a metastable phase formed from a true spinel during quenching.

A possible stability field of Mn_2GeO_4 is shown in fig. 1, where the α–β and β–δ transformation curve at the temperature range from about 800 °C to 1200 °C is tentatively fitted by the linear relation P(kb) = 13 + 0.031 T(°C) and P(kb) = 39 + 0.022 T(°C) respectively.

In the course of high-pressure transformation of Mn_2GeO_4, the density increase was calculated to be

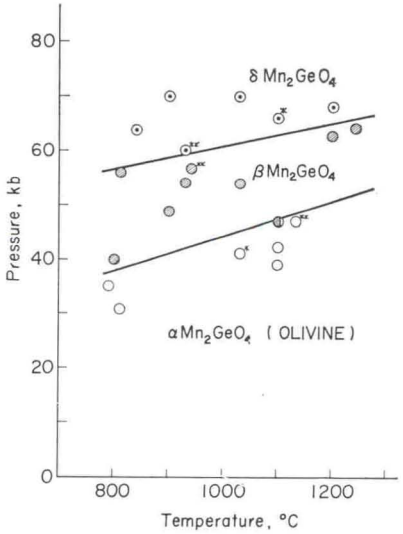

Fig. 1. Stability diagram for the high-pressure and high-temperature transformation of Mn_2GeO_4. * indicates the runs using β-Mn_2GeO_4 as the starting materials. ** indicates the runs using δ-Mn_2GeO_4 as the starting materials. Unless otherwise designated, the starting material is the olivine polymorph of Mn_2GeO_4 (α-Mn_2GeO_4).

7.1% for the α–β transformation and 10.7% for the β–δ transformation, using the lattice dimensions of the quenched α, β and δ phase. The total density increase from α phase to δ phase amounts to 18.4%.

The thermal expansion of the α, β and δ phase of the Mn_2GeO_4 sample was determined in a temperature range of room temperature to 460 °C and at ambient pressure by means of an X-ray diffractometer equipped with a heating device. Six to seven strong diffraction lines were used in determining the lattice dimensions of each phase at high temperatures. No indication of the phase transformation was observed in the β and δ phase of Mn_2GeO_4 after 60 minutes at 460 °C. The mean thermal expansivity, $\Delta V/(V_0 \times \Delta T)$, was determined to be $(36 \pm 1) \times 10^{-6}\ °C^{-1}$ for α-Mn_2GeO_4, $(30 \pm 1) \times 10^{-6}\ °C^{-1}$ for β-Mn_2GeO_4 and $(39 \pm 3) \times 10^{-6}\ °C^{-1}$ for δ-Mn_2GeO_4 respectively. It is interesting to note that the thermal expansivity of the δ-Mn_2GeO_4 with the highest density shows the largest value among the three polymorphs of Mn_2GeO_4.

3. High-pressure transformation in the system Mg_2SiO_4-Co_2SiO_4

High-pressure transformation mode in Co_2SiO_4 olivine is known to be so temperature-dependent that the occurrence of the β phase is restricted in a relatively high temperature range (AKIMOTO and SATO, 1968). This motivated us to investigate the transformation diagram of the Mg_2SiO_4–Co_2SiO_4 system over the wide range of temperature and pressure. A knowledge obtained from such a study may help towards the better understanding of the high-pressure transformation behavior of pure Mg_2SiO_4, which is still in controversy.

Microcrystalline olivines prepared at the interval of 12.5 mole percent in the compositional range from pure Co_2SiO_4 to $(Mg_{0.5}Co_{0.5})_2SiO_4$ were used as starting compound in the present high-pressure experiments. Olivine solid solution of $(Mg_{0.05}Co_{0.95})_2SiO_4$ was also used as starting material with a view to investigate the detailed transformation behavior of the extremely cobalt-rich side of the system. In the synthesis of the olivine solid solutions intimate powder mixtures of forsterite and Co_2SiO_4 olivine, which had been prepared in advance, were made to react in air at temperatures ranging from 1300 °C to 1400 °C for more than 8 hours. Formation of uniform olivine solid solutions was justified from well-defined X-ray diffraction peaks.

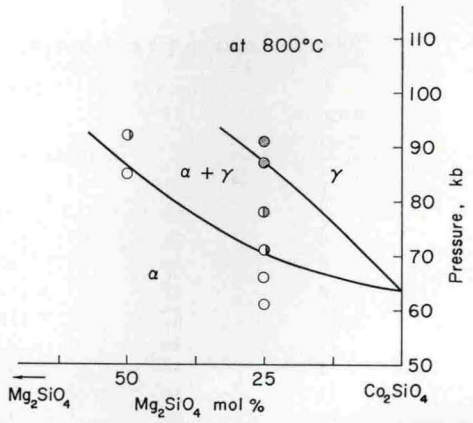

Fig. 2. Phase diagram for the high-pressure transformation of the system Mg_2SiO_4–Co_2SiO_4 at 800 °C.

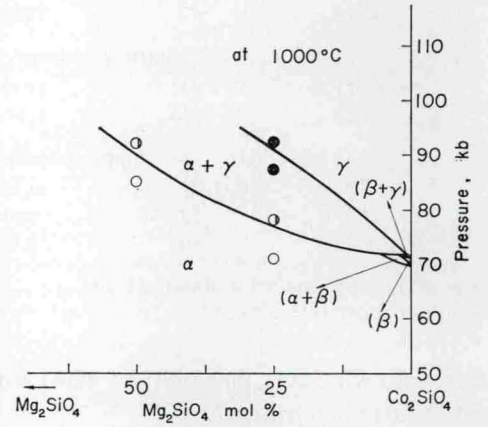

Fig. 3. Phase diagram for the high-pressure transformation of the system Mg_2SiO_4–Co_2SiO_4 at 1000 °C.

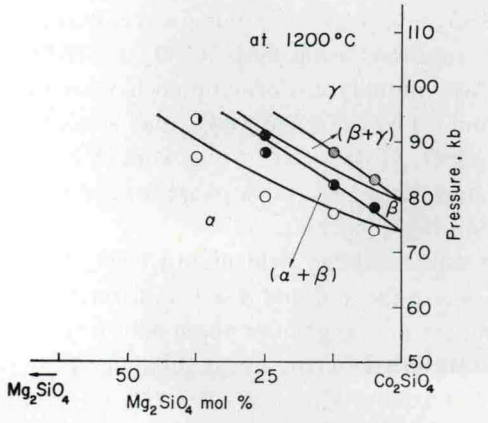

Fig. 4. Phase diagram for the high-pressure transformation of the system Mg_2SiO_4–Co_2SiO_4 at 1200 °C.

TABLE 2

Results of high-pressure and high-temperature experiments in the system Mg_2SiO_4–Co_2SiO_4

Run no.	Composition*, mole %	Pressure**, kb	Time, min	Phases present***	Lattice parameter of spinel s.s. (γ phase), Å
		Run temperature, 800 ± 10 °C			
2501	25M75C	61	60	α	
2502	idem	66	60	α	
2503	idem	71	60	$\alpha+\gamma$	8.134 ± 0.001
2505	idem	78	60	$\alpha+\gamma$	8.128 ± 0.001
2507	idem	87	60	γ	8.122 ± 0.001
2509	idem	91	60	γ	8.122 ± 0.001
5001	50M50C	85	60	α	
5003	idem	92	60	$\alpha+\gamma$	
		Run temperature, 1000 ± 10 °C			
2504	25M75C	71	40	α	
2506	idem	78	40	$\alpha+\gamma$	8.133 ± 0.002
2508	idem	87	40	$\gamma+\alpha$	8.124 ± 0.001
2510	idem	92	40	γ	8.122 ± 0.001
5002	50M50C	85	40	α	
5004	idem	92	40	$\alpha+\gamma$	
		Run temperature, 1200 ± 20 °C			
0503	5M95C	74	10	α	
0501	idem	78	10	β	
0502	idem	83	10	γ	8.136 ± 0.001
1251	12.5M87.5C	77	15	α	
1253	idem	82	15	$\beta+(\alpha)$	
1252	idem	88	15	γ	8.130 ± 0.001
2512	25M75C	80	20	α	
2514	idem	88	20	$\beta+(\alpha)$	
2513	idem	91	20	β	
3752	37.5M62.5C	87	20	α	
3751	idem	94	20	$\alpha+\beta$	

* M: Mg_2SiO_4, C: Co_2SiO_4;
** Precision of pressure control is about ±1 kb;
*** α: olivine solid solution, β: "modified" spinel solid solution, γ: true spinel solid solution.

High-pressure and high-temperature techniques used in determining the equilibrium diagram of the Mg_2SiO_4–Co_2SiO_4 system are essentially the same as described in the section of the high-pressure transformations in Mn_2GeO_4. Cemented tungsten carbide anvils with 9 mm edge length were used for the runs above 80 kb. Three discrete values of temperatures, 800°, 1000° and 1200 °C, were adopted as run temperatures.

Results of experimental runs are summarized in table 2. Diagrams showing the phases present and their stability field are given in figs. 2, 3 and 4 corresponding to 800°, 1000° and 1200 °C. Phases other than olivine and spinel solid solution were not observed in the run products at 800 °C (fig. 2). The equilibrium diagram at 1000 °C (fig. 3), in which a small stability field of the β phase was shown in a limited region close to Co_2SiO_4, was prepared in taking the transformation mode of pure Co_2SiO_4 into consideration (AKIMOTO and SATO, 1968). At 1200 °C, a remarkable expansion of the β phase region was established by the successful synthesis of the "modified" spinel solid solutions (fig. 4). In these figures, the olivine, spinel and "modified" spinel solvus curves were estimated from the relative content of each phase which was determined approximately from both the microscopic observation and the intensity ratio of the X-ray diffraction chart. Lattice parameters of the homogeneous spinel solid solutions synthesized in the present work were also given in table 2. Linear decrease of the lattice parameters with increasing amount of Mg_2SiO_4 was observed to $(Mg_{0.25}Co_{0.75})_2SiO_4$. This information also served for estimating the compositions of spinel solid solutions

in the run products within the olivine-spinel transformation interval. Provisional estimate by linear extrapolation of the lattice parameter of the pure Mg_2SiO_4 spinel is 8.08 Å. This value agrees reasonably with the value estimated from the previous study of the Mg_2SiO_4–Fe_2SiO_4 system (RINGWOOD and MAJOR, 1966; AKIMOTO and FUJISAWA, 1968).

4. Discussion

The preceding experimental results demonstrate the high-pressure synthesis of the "modified" spinel phase in Mn_2GeO_4 and Mg_2SiO_4–Co_2SiO_4 solid solutions. The most notable feature of the high-pressure transformation in Mn_2GeO_4 is that there exists a large synthesis field of the β phase and that there is no indication of the occurrence of the γ phase. Reversibility of the phase transformations was also confirmed through the runs using the different polymorphs of Mn_2GeO_4 as starting material. These stability relations of Mn_2GeO_4 may strongly support the previous suggestion, obtained from the high-pressure and high-temperature study of Co_2SiO_4, that the "modified" spinel phase is a thermodynamically stable phase at the specified field of pressure and temperature (AKIMOTO and SATO, 1968). However, recent structure analysis of the β-Co_2SiO_4 and β-Mn_2GeO_4 revealed that from the crystalchemical viewpoint the crystal structure of the "modified" spinel seemed to be unusual compared with the structure of the true spinel on account of the existence of Si_2O_7 or Ge_2O_7 groups leaving oxygen atoms unbonded to any Si or Ge atoms (MORIMOTO *et al.*, 1969 and 1970). Thus the newly-added evidences for the stability of the β phase may still be insufficient to exclude the possibility that the β phase is a metastable quench product. Definite conclusion on the stability of the "modified" spinel structure will be obtained from a high-pressure and high-temperature X-ray diffraction study.

Since the present data on the high-pressure transformation of $(Mg, Co)_2SiO_4$ olivine are only limited to the composition range of the cobalt-rich side, it is still difficult to estimate the high-pressure transformation mode of pure forsterite. However, the present work showed that the phase relationships of the Mg_2SiO_4–Co_2SiO_4 system were strongly influenced by temperature. It is highly probable that pure forsterite transforms directly from olivine to true spinel at low temperatures around 800 °C, but at high temperatures above about 1000 °C it transforms from olivine to true spinel through the intermediate phase of the "modified" spinel. At the present stage of knowledge it is plausible to assume that the β phase solid solutions synthesized by RINGWOOD and MAJOR (1966) for compositions more magnesian than $(Mg_{0.85}Fe_{0.15})_2SiO_4$ in the Mg_2SiO_4–Fe_2SiO_4 system may possess a real stability field at high-pressures and high-temperatures.

If the mantle olivine transformed stepwise to the γ phase through the β phase, the previous estimates (ANDERSON, 1967; AKIMOTO and FUJISAWA, 1968; FUJISAWA, 1968) of the constitution and width of the transition zone of the mantle should be reexamined. Since all these estimates were based on the simple olivine–true spinel equilibrium diagram in the Mg_2SiO_4–Fe_2SiO_4 system, the transition width from olivine to true spinel would have been estimated at a considerably lower value. From the recent study of the high-pressure polymorphs of Co_2SiO_4 (AKIMOTO and SATO, 1968) the density increase associated with the olivine–"modified" spinel transformation is estimated to be about 80% of that for the olivine–true spinel transformation. This suggests that the sharp increase of the seismic wave velocities would be expected even if the "modified" spinel is the first high-pressure polymorph of the mantle olivine. Direct determination of the elastic wave velocities of both the "modified" spinel and the true spinel by ultrasonic method may hold the key for the more quantitative analysis of the transition zone in the Earth's mantle. The more detailed investigation of the high-pressure transformation diagram of the magnesium-rich side of the Mg_2SiO_4–Fe_2SiO_4 system at temperatures higher than 1000 °C is also indispensable for such analysis.

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