VERIFICATION OF THE STABILITY OF THE MODIFIED SPINEL BY MEANS OF HIGH-PRESSURE AND HIGH-TEMPERATURE X-RAY ANALYSIS

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Modified spinel (β-phase), a high-pressure polymorph of olivine, has hitherto been found in Mn_2GeO_4(1), Co_2SiO_4 (2), Zn_2SiO_4(3) as well as in the magnesium rich side of the Mg_2SiO_4-Fe_2SiO_4 system(4),(5). Since $(Mg,Fe)_2SiO_4$ olivine is believed to be the most abundant minerals in the upper mantle, the stability of the modified spinel phase is greatly relevant to the phase changes in the mantle.

Structure analysis(6) carried out on the single crystals of βMn_2GeO_4 and βCo_2SiO_4 revealed that the oxygen atoms in the modified spinel are approximately in cubic close packing as in normal spinel. The modified spinel,however, partly violates Pauling's electrostatic valence rule : Two GeO_4 or SiO_4 tetrahedra, which would be isolated in the normal spinel structure, share one of their oxygen atoms resulting in a Ge_2O_7 or Si_2O_7 group and an oxygen atom not bonded to any Ge or Si atom. It was further shown that the structure of the modified spinel phase of Co_2SiO_4 could be derived from the normal spinel structure of γCo_2SiO_4 by displacing four Si and four Co atoms out of the eight Si and sixteen Co atoms in the cell. These particularities of the crystal structure aroused much discussion on the stability of the modified spinel. Since all the modified spinel phases have been obtained as quench products, the possibility of the meta-stable phase, which would be produced during quenching of an original normal spinel, has not yet been completely denied.

In the present investigation, stability of the modified spinel was examined _in situ_ by a high-pressure and high-temperature X-ray diffraction technique. A cubic anvil type of high pressure apparatus was used. The pressure cell attached to the 250-ton uniaxial hydraulic ram is designed so as to converge the six cemented tungsten carbide anvils with square face of 4mm edge length towards the center of the cubic pressure medium. Amorphous boron mixed with polyester resin in the ratio of boron/resin = 1/2 (in weight) was used as a pressure medium.

Powder samples of αMn_2GeO_4 with olivine structure was shaped into a thin plate with thickness of 0.1 - 0.2 mm and sandwiched by boron nitride blocks and settled into the center hole of the pressure medium with 6 mm edge length. A pair of stainless steel disk heater 0.05 mm in thickness and 2.5 mm in diameter was used as a high-temperature furnace. D. C. power was supplied to the heater through Au electrodes which were faced to one pair of cubic anvils. Temperature was measured with Pt/Pt-Rh13% thermocouple which was placed in the upper part of the furnace not to screen the X-ray path.

Thermocouple leads were brought out to the faces of another pair of anvils, which were insulated electrically from the anvil pair used for D.C. power supply.

Samples in the pressure medium were first subjected to the desired pressure and then heated to the desired temperature. Pressure values are calibrated at room temperature on the basis of the volume change of NaCl using the same pressure medium. Phase change of the sample was detected by the X-ray diffraction method.

A finely collimated molybdenum X-ray beam was entered through the gap of the two cubic anvils, and the X-ray diffracted by the sample was passed through the opposite gap of the anvils. The diffracted X-rays were measured in fixed-time step-scanning method using a scintillation counter. The angle width of one step was 0.1° and the fixed time for one-step was controlled in the range from 40 seconds to 200 seconds depending upon the gap width of anvils.

Examples of the X-ray diffraction pattern obtained in the present investigation are shown in Figs.1 and 2. Fig.1 shows the diffraction pattern of αMn_2GeO_4 at 45 kbar and at room temperature. The very strong peak of the (002) line of boron nitride masked the (130) line of αMn_2GeO_4 with olivine structure. 2θ angles of α-Mn_2GeO_4 at atmospheric pressure and at room temperature are shown by black arrows. No diffraction peaks assigned to the modified spinel were observed. Fig.2 shows the diffraction pattern at 45 kbar and at 780° C. The diffraction line (002) of boron nitride moved remarkably to the lower angle side owing to the effect of the thermal expansion. White arrows in the figure indicate the 2θ angle to be observed on the β-Mn_2GeO_4 with the modified spinel structure at atmospheric pressure and at room temperature. Diffraction peaks assigned to the modified spinel structure are easily distinguished in the figure.

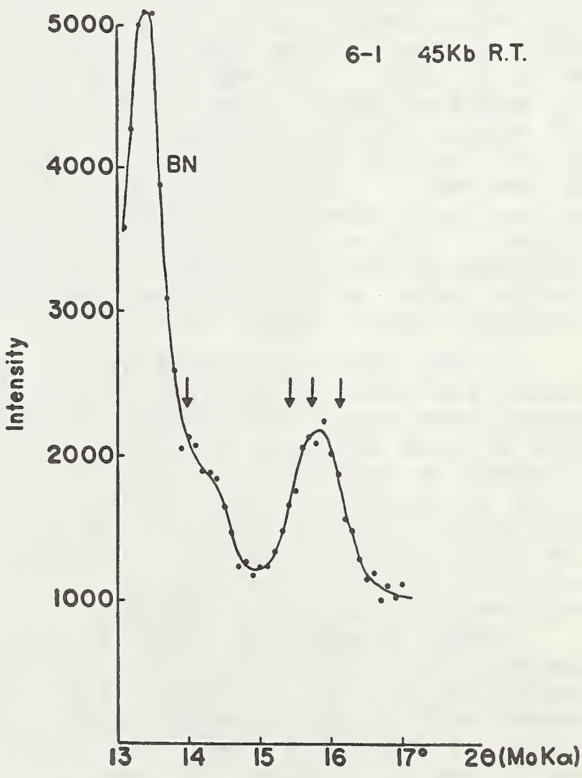

Fig. 1
X-ray diffraction pattern of Mn_2GeO_4 at 45 kbar and at room temperature.

The appearance of the diffraction line (112) of βMn_2GeO_4 is most remarkable. Comparing Fig.1 with Fig.2, we can surely say that the βMn_2GeO_4 with the modified spinel structure realy exists as a stable phase at 45 kbar and at 780°C. The present results harmonize well with a previous study of the high-pressure and high-temperature stability diagram (Fig.3) of Mn_2GeO_4 which was determined using the usual quenching method.(1)

It was established through the present investigation that the modified spinel structure can exist stably as a high-pressure and high-temperature phase of olivine. It is plausible to conclude that in the earth's mantle the $(Mg, Fe)_2SiO_4$ olivine transforms to the modified spinel phase in the first step of its phase charge and this phase transformation corresponds to the rapid increase of seismic wave velocities at a depth near 400 km.

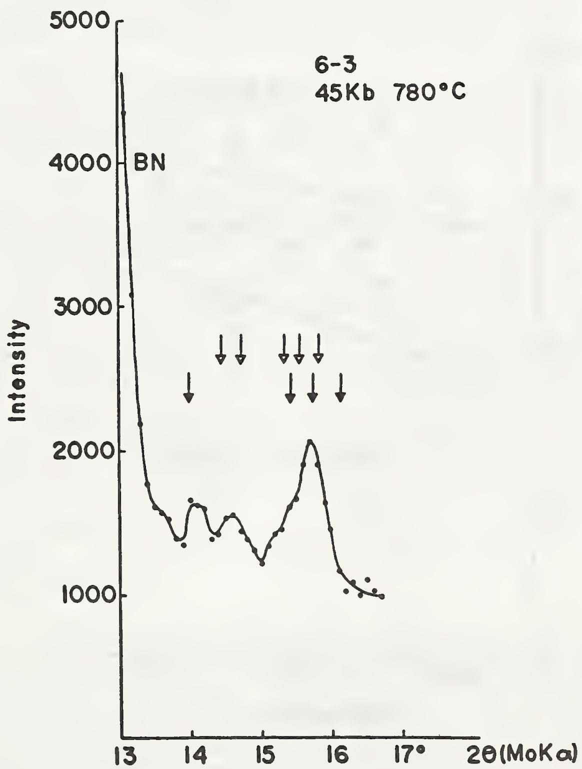

Fig. 2

X-ray diffraction pattern of Mn_2GeO_4 at 45 kbar and at 780°C.

References

(1) Akimoto,S. (1970) Phys. Earth Planet. Interiors 3, 189.
(2) Akimoto,S. and Y.Sato (1968) Phys. Earth Planet. Interiors 1, 498.
(3) Syono,Y., S.Akimoto, and Y.Matsui (1971) J. Sol. State Chem. 3, 369.
(4) Ringwood,A.E. and A.Major (1970) Phys. Earth Planet. Interiors 3, 89.
(5) Akimoto,S. (1972) Tectonophys., 13, 161.
(6) Morimoto,N., S.Akimoto, K.Koto and M.Tokonami (1970) Phys. Earth Planet. Interiors 3, 161.

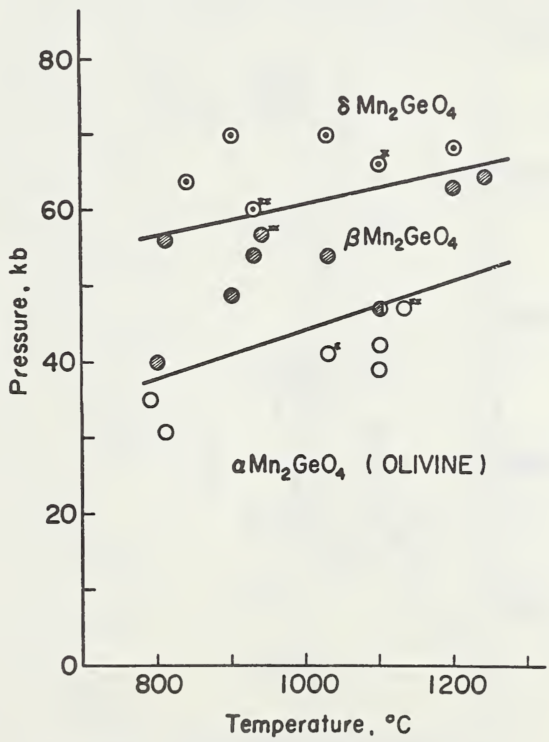

Fig. 3

Stability diagram for the high-pressure and high-temperature transformations of Mn_2GeO_4 (1)