

NOTE

The System $\text{GeO}_2\text{-MnO-Mn}_2\text{O}_3$ at 900°C

In a previous paper (1), we reported the phase diagram of $\text{GeO}_2\text{-FeO-Fe}_2\text{O}_3$. Some new compounds were found in the system, and the diagram is quite different from the corresponding one of $\text{SiO}_2\text{-FeO-Fe}_2\text{O}_3$. In the present work, we report the phase diagram of $\text{GeO}_2\text{-MnO-Mn}_2\text{O}_3$. Two ternary compounds, MnGeO_3 and Mn_2GeO_4 , are known and Mn_2GeO_4 has a olivine-type structure in contrast to the spinel-type structure of Fe_2GeO_4 (2, 3). Moreover, Mn_2O_3 is structurally different from Fe_2O_3 and Mn_3O_4 has a distorted spinel structure at the present experimental temperature (4). It is interesting to compare the present system with those of $\text{GeO}_2\text{-FeO-Fe}_2\text{O}_3$ and $\text{SiO}_2\text{-MnO-Mn}_2\text{O}_3$ (5) which have been already established.

GeO_2 (99.99%) and MnO_2 (99.9%) were used as starting materials. MnO and Mn_2O_3 were prepared from MnO_2 according to the method described previously (6). GeO_2 was calcined at 1000°C before using. The three materials, GeO_2 , MnO , and Mn_2O_3 , were mixed to desired ratios in an agate mortar with ethyl alcohol. The mixture (about 2 g) thus obtained was sealed in an evacuated silica tube and was allowed to react at $900^\circ \pm 2^\circ\text{C}$ in a tubular-type furnace. The empty space of the tube was made to be as small as possible relative to the amount of the sample. When MnO -rich samples were fired, the inner surfaces of the silica tubes devitrified strongly. These samples were reexamined by using Pt tubes. The powder X-ray patterns of the two kinds of samples were, however, identical with each other. Every sample was fired in the furnace until its powder X-ray pattern did not change any more. It took about 80 hr for the samples to react fully. The identification of the com-

pounds was carried out by means of powder X-ray data collected on the diffractometer described previously (1). About forty kinds of samples were fired and examined.

The phase diagram at 900°C is shown in Fig. 1. No ternary compounds were found in the system, except for MnGeO_3 and Mn_2GeO_4 . The experimental temperature was first set at 1000°C . Since equilibrium oxygen fugacities are very large in the two-phase region $\text{GeO}_2\text{-Mn}_2\text{O}_3\text{ss}$ ($\text{Mn}_2\text{O}_3\text{ss}$ shows the solid solution described below) and three-phase region $\text{GeO}_2\text{-MnGeO}_3\text{-Mn}_2\text{O}_3\text{ss}$ at 1000°C , the silica tubes sometimes burst when examinations were performed for these regions. The temperature was, therefore, lowered to 900°C . Even at this temperature, the equilibrium oxygen fugacities are larger than 1 atm in the above regions. This is related to the fact that MnGeO_3 is stable even in air at higher temperatures despite the divalent state of the manganese atoms. It is interesting to note that MnO is stable under oxygen fugacities less than about $10^{-8.9}$ atm at 900°C (6).

The solid solutions denoted by $\text{Mn}_{2-x}\text{Ge}_x\text{O}_3$ exist in the system, and the upper limit of x value is about 0.2. Along the solution line, the following cation substitution must occur.



Corresponding substitution has been found in the system $\text{SiO}_2\text{-MnO-Mn}_2\text{O}_3$ between Si^{4+} , Mn^{2+} , and Mn^{3+} (5). On the whole, the obtained phase diagram is geometrically identical with that of $\text{SiO}_2\text{-MnO-Mn}_2\text{O}_3$, and quite different from that of $\text{GeO}_2\text{-FeO-Fe}_2\text{O}_3$.

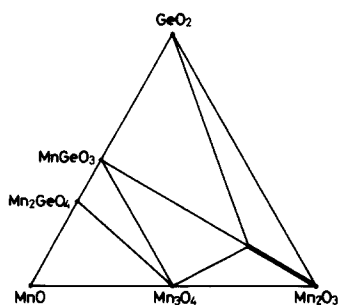


FIG. 1. The phase diagram of $\text{GeO}_2\text{-MnO-Mn}_2\text{O}_3$ at 900°C .

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E. TAKAYAMA

*National Institute for Research in Inorganic Materials
Sakura-mura, Niihari-gun,
Ibaraki-ken 305, Japan*

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