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THE OCCURRENCE OF AN ENSTATITE PHASE IN THE SUBSYSTEM GeO_2-$MnGeO_3$

A. TAUBER, J. A. KOHN, C. G. WHINFREY[1] AND W. D. BABBAGE,
U. S. Army Electronics Research and Development Laboratory
Fort Monmouth, New Jersey.

ABSTRACT

A phase diagram for the subsystem GeO_2-$MnGeO_3$ has been determined by using three different thermal methods together with optical and *x*-ray diffraction analysis. Only one compound was found, $MnGeO_3$: orthorhombic *Pbca*, $a=19.29$ Å, $b=9.25$, $c=5.48$, $Z=16$. It is isostructural with enstatite, $MgSiO_3$. $MnGeO_3$ melts congruently at $1290 \pm 10°$ C. The phase diagram shows a region of two immiscible liquids. Polymorphism similar to that in $MgSiO_3$ and $MgGeO_3$ was sought but was not detected. Optical and *x*-ray data for $MnGeO_3$ are given.

INTRODUCTION

During the investigation of the melting in air of garnets containing germanium and manganese, Tauber *et al.* (1961) found that spinel and an unidentified second phase were persistent decomposition products. After some preliminary experiments directed towards the identification of the unknown phase in ternary systems containing GeO_2 and MnO, an examination of the binary system GeO_2-MnO was undertaken. When the composition $MnO \cdot GeO_2$ was prepared, its *x*-ray diffraction powder pattern gave an excellent match with the line positions of the unknown phase. Accordingly, single crystals were grown; characterization of the unit cell and space group by single-crystal *x*-ray diffraction subsequently established the fact that $MnGeO_3$ is isostructural with enstatite. This should not be surprising, since it has been known for some time that enstatite or substituted enstatite is a product in the thermal decomposition of garnets (*e.g.*, Winchell and Winchell, 1951). The result, however, requires a revision in Roth's (1957) classification diagram for $A^{2+}B^{4+}O_3$-type compounds based on constituent ionic radii, in which he indicates that no compound of the type $MnGeO_3$ is expected.

Only one other system, MgO-GeO_2, has yielded an end-member metagermanate isostructural with enstatite (Roth, 1957; Robbins and Levin, 1959). In the present article the subsystem GeO_2-$MnGeO_3$ is examined in order to compare it with the GeO_2-$MgGeO_3$ subsystem and to detect the presence of polymorphism in $MnGeO_3$.

EXPERIMENTAL PROCEDURES

Twelve different compositions between GeO_2 and $MnGeO_3$ were studied. Two or three grams of each composition were prepared by mix-

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[1] Deceased.

ing $MnCO_3$ with GeO_2 and pressing into ½-inch-diameter pellets at about 10,000 psi. The compacts were slowly heated to 1000° C. in air and held for two hours at temperature. Subsequently, they were cooled in air to room temperature, reground and pressed. In order to ensure sample homogeneity in the equilibrium experiments, compositions near phase boundaries were subjected to at least one, and in most cases two additional pre-calcinations. The latter were of five hours duration at 1000° C. and involved regrinding and pelletizing between firings. A maximum of 0.15% loss in weight was found for the calcined compacts. For further assurance of homogeneity, all samples were examined microscopically and by powder *x*-ray diffraction at each stage of preparation. The $MnCO_3$ used in these preparations was Fisher reagent grade and the GeO_2 was electronic grade obtained from Eagle-Picher Company. Over 100 samples, in the form of small chips, were prepared and studied. Samples prepared in a Baker E-2 platinum-wound furnace were heated below 1000° C. and quenched in air. Equilibrium samples prepared above 1000° C. were sealed in platinum tubes, heated in a Tem-Pres platinum-wound quench furnace and quenched in ice water. The temperature was measured with a calibrated Pt-Pt 10% Rh thermocouple.

The liquidus was first measured, approximately, by heating small chips on a platinum strip furnace in air (Keith and Roy, 1954). The sample temperature was read with a calibrated optical pyrometer. A second and somewhat better approximation was obtained by heating small chips in a boat in a horizontal tube furnace and observing the sharp-cornered specimens with a telescope. The furnace was first raised to within 10° C. of the previously observed melting point; the sample was then introduced into the hot zone and heated to the melting point within five to ten minutes. The liquidus was finally delineated by examining equilibrium quenched samples heated in sealed platinum tubes 5 to 20° C. above and below the liquidus as defined by observation in air. Although samples heated in air were found to undergo a 1–4% weight loss, the melting points thus determined never differed by more than 20° C. from those found with equilibrium samples. The upper value, however, was outside the limits of experimental error which range from ±10 to ±15° C.

All polycrystalline samples were examined with a binocular microscope. Many were also studied with the petrographic and metallurgical microscopes. Powder *x*-ray diffraction films were prepared for all subliquidus samples, using FeK filtered radiation. In addition a Geiger diffractometer was used to obtain powder data on $MnGeO_3$.

To confirm the enstatite stoichiometry and establish the absence of Mn^{3+}, chemical analysis was performed on selected samples of six different compositions in the equilibrium studies. Total Mn was determined by the

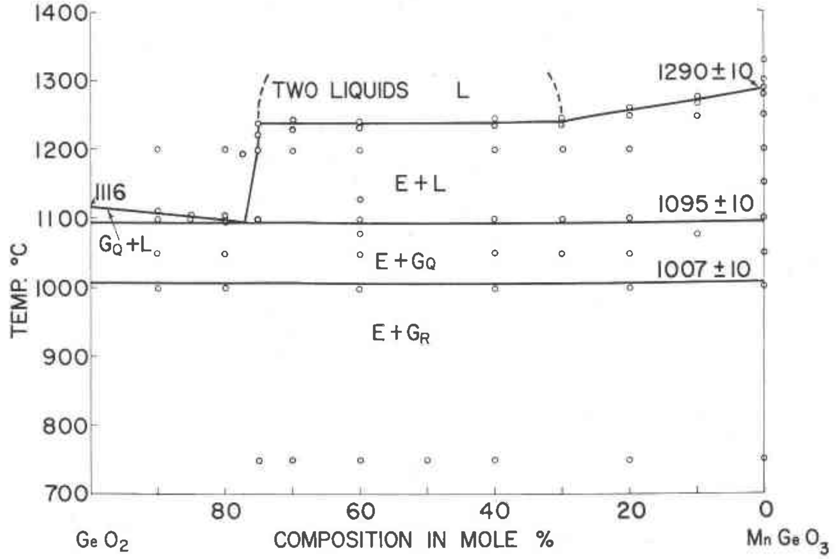

FIG. 1. Phase diagram for the subsystem GeO_2-$MnGeO_3$.

Symbol (Robbins and Levin, 1959)	Composition and Structure Type	
E	$MnGeO_3$	Enstatite
G_R	GeO_2	Rutile
G_Q	GeO_2	Quartz
L	—	Liquid

bismuthate method (Kolthoff and Sandell, 1946) and Ge by tannic acid precipitation (Hillebrand *et al.* 1953) on samples yielding single-phase enstatite. Analysis for Mn^{3+} was performed with vanadyl sulfate titrating with $KMnO_4$ (Wickham, 1957) on all samples assayed. No change in stoichiometry was detected for single-phase enstatite samples. The presence of Mn^{3+} was not detected in any samples examined within the limits of analysis, $\pm 0.5\%$.

Single crystals of $MnGeO_3$ were grown by heating powdered $MnGeO_3$ in a sealed platinum tube 30° C. above the melting point and cooling at a rate of 2.5° C. per hour to 100° C. below the melting point. Crystal bundles up to 3 mm on an edge were thus obtained. These were studied with single-crystal x-ray diffraction cameras, the two-circle optical goniometer, and the petrographic microscope.

RESULTS AND DISCUSSION

Phase equilibria. A phase diagram of the subsystem GeO_2-$MnGeO_3$ is given in Fig. 1. The melting point of GeO_2 is that determined by Laubengayer and Morton (1932), and the inversion temperature of GeO_2 was obtained from Schafer and Roy (1956). The points indicated are the best values used in determining phase boundaries obtained from sealed-tube quench experiments (above 1000° C.).

Liquid $MnGeO_3$ could not be quenched to a glass. Robbins and Levin (1959) experienced the same difficulty with $MgGeO_3$. All samples of $MnGeO_3$ quenched from above the liquidus showed only the enstatite phase. In two instances when the tubes leaked, GeO_2 was lost as indicated by the loss in weight measurements. Examination of the contents of these tubes indicated the presence of a second phase identified from *x*-ray diffraction patterns as a spinel. Therefore, congruent melting of $MnGeO_3$ is inferred when no loss of GeO_2 is observed. The indicated melting point is $1290 \pm 10°$ C.

The general features of the phase diagrams for GeO_2-$MgGeO_3$ (Robbins and Levin, 1959) and GeO_2-$MnGeO_3$ are similar with one exception: a clinoenstatite analogue was detected in $MgGeO_3$ and not in $MnGeO_3$.

Attempts to detect polymorphism consisted of long heat treatment over a range of temperature and the application of a mineralizer and a stabilizer. The results of these experiments are given in Table 1. Atlas (1952) has used LiF to accelerate reactions in the investigation of polymorphism in $MgSiO_3$. He also indicated that if sufficient Ca^{2+} is present, clinoenstatite is stabilized as the high-temperature phase in magnesium metasilicate. In the present study, $MnGeO_3$, isostructural with orthorhombic enstatite, was the only phase detected when LiF was used as a mineralizer and also when CaO up to 5 weight per cent was used as a possible stabilizer. When 10 weight per cent of CaO was used, a new phase resembling diopside appeared. The failure to detect polymorphism in $MnGeO_3$ may be due to the accommodation of Mn^{2+}. This is the largest cation known in an end-member enstatite structure.

Crystallography of $MnGeO_3$. Single crystals most commonly were prismatic along the *c* axis. Occasionally, lath-shaped specimens were observed, with the lath face (210) and the elongation parallel to *c*. Crystals were generally multiple, occurring in extremely brittle, prismatic bundles; specimens ranged from colorless to yellow to red with increasing thickness. An easy, good prismatic cleavage was observed along {210}, yielding crystals with a pseudo-orthogonal cross-section.

Optical extinction was observed with light vibrating normal and parallel to the *c* axis. Indices of refraction were all noted to be greater than 1.81.

Three crystals were examined on a two-circle optical goniometer, two having a prismatic habit and the third being lath-shaped. The forms in-

TABLE 1. EXPERIMENTAL DATA FOR THE DETECTION OF POLYMORPHISM

Initial Composition	Heat Treatment[1]	Phase Detected and Remarks
$MnO \cdot GeO_2$	1315° C. for 1 hr	Enstatite (small crystals)
$MnO \cdot GeO_2$	1315° C. for 1 hr. cooled at 10° C./hr. to 1200° C.	Enstatite (small crystals)
$MnO \cdot GeO_2$	1315° C. for 1 hr. cooled at 2.5° C./hr. to 1100° C.	Enstatite (2–3 mm ×1 bundles)
$MnO \cdot GeO_2$	1263° C. for 24 hrs.	Enstatite
$MnO \cdot GeO_2$	1226° C. for 67 hrs.	Enstatite
$MnO \cdot GeO_2$	1100° C. for 2 hrs. in air and air quenched	Enstatite
$MnO \cdot GeO_2$	1100° C. for 20 hrs. in air and air quenched	Enstatite
$MnO \cdot GeO_2$ with 2 wt % LIF	1100° C. for 1 hr. in air and air quenched	Enstatite (lattice contracted)
$MnO \cdot GeO_2$ with 2 wt % LiF	1224° C. for 4 hrs.	Enstatite (lattice contracted)
$MnO \cdot GeO_2$ with 2 wt % CaO	1100° C. for 1 hr. in air and air quenched	Enstatite (lattice expanded)
$MnO \cdot GeO_2$ with 2 wt % CaO	1200° C. for 3 hrs.	Enstatite (lattice expanded)
$MnO \cdot GeO_2$ with 5 wt % CaO	1236° C. for 3 hrs.	Enstatite (lattice expanded)
$MnO \cdot GeO_2$ with 10 wt % CaO	1230° C. for 3 hrs.	Diopside-like phase

[1] All samples were heated in sealed platinum tubes and quenched in ice water, unless otherwise indicated.

dexed were the prisms {210} and {110}, and the bipyramid {221}. One crystal showed an indication of {010} and {211}. Morphological data are summarized in Table 2.

Single-crystal *x*-ray diffraction revealed orthorhombic symmetry.

TABLE 2. MORPHOLOGICAL DATA FOR $MnGeO_3$

Face	No. of Times Observed	Angle with *a*		
		Range	Weighted Average	Calculated Value
(210)	12	46° 04′–46° 31′	46° 12′	46° 13′
(110)	6	64° 11′–64° 58′	64° 22′	64° 23′
		Angle with *c*		
(221)	3	52° 11′–52° 51′	52° 37′	52° 44′

Zero- and upper-level precession and Weissenberg data showed the following systematic absences:

$$\begin{aligned} 0kl,\ k &= 2n + 1 \\ h0l,\ l &= 2n + 1 \\ hk0,\ h &= 2n + 1 \end{aligned}$$

This conforms to the space group $P2_1/b\ 2_1/c\ 2_1/a$, identical to that shown by enstatite and its isotype $MgGeO_3$ (Roth, 1957).

Unit cell data for $MnGeO_3$ are given in Table 3 and compared with similar information for enstatite and orthorhombic $MgGeO_3$. The single-crystal cell dimensions were used to compute d spacings, which are compared in Table 4 with values observed using a Geiger diffractometer.

SUMMARY AND CONCLUSION

This study of the subsystem GeO_2-$MnGeO_3$ has shown that the unknown phase previously encountered in an investigation of garnets containing germanium and manganese is the compound $MnGeO_3$. The latter is isostructural with enstatite ($MgSiO_3$) and $MgGeO_3$ rather than with its silicate analogue, rhodonite ($MnSiO_3$). No polymorphism was observed in $MnGeO_3$. In view of the isostructural relationship noted herein, other

TABLE 3. UNIT CELL DATA FOR ENSTATITIC $MnGeO_3$, $MgGeO_3$ AND $MgSiO_3$

Lattice Parameter	$MnGeO_3$	$MgGeO_3$[1]	$MgSiO_3$[2]
a	19.29 Å	18.661	18.22
b	9.25	8.954	8.829
c	5.48	5.346	5.192

[1] Roth (1957).

[2] Swanson, H. E., *et al.* (1956); setting transformed for comparison purposes.

TABLE 4. *X*-RAY POWDER DIFFRACTION DATA FOR $MnGeO_3$[1]

hkl	$d_{obs.}$	$d_{calc.}$	I/I_1
400	4.81 Å	4.82 Å	10
020	4.62	4.63	42
121	3.47	3.48	55
420	3.33	3.34	82
221	3.315	3.318	89
321	3.097	3.097	70
610	3.034	3.036	100
511	2.982	2.982	27
421	2.848	2.851	56
131	2.660	2.662	49
202	2.633	2.636	60
521 112	2.607	2.606 2.603	68
231	2.580	2.588	34
302	2.518	2.521	18
312 800	2.429	2.432 2.411	10
404 711 621	2.377	2.382 2.379 2.378	17
040 412	2.309	2.313 2.307	12
502 630	2.229	2.233 2.225	10
721 512	2.171	2.173 2.171	7

[1] Unfiltered FeK radiation.

TABLE 4.—(*Continued*)

hkl	$d_{obs.}$	$d_{calc.}$	I/I_1
811 820	2.145	2.147 2.138	7
422 141	2.116	2.119 2.117	18
602 440	2.083	2.085 2.085	30
241	2.080	2.080	4
631	2.060	2.062	1
341	2.021	2.022	8
911 441	1.947	1.951 1.948	10
622 830 10,1,0	1.890	1.901 1.899 1.888	15
541	1.864	1.865	13
250 802	1.816	1.817 1.810	9
831 272	1.793	1.794 1.791	16
812	1.775	1.776	19
242	1.735	1.738	9
342 023	1.698	1.704 1.698	14
10,2,1 123 351 902	1.691	1.693 1.692 1.691 1.688	15
413 931 223	1.674	1.679 1.676 1.673	13

TABLE 4.—(*Continued*)

hkl	$d_{obs.}$	$d_{calc.}$	I/I_1
12,0,0	1.603	1.608	20
542		1.607	
650		1.603	
423		1.602	
10,3,1	1.565	1.567	31
133		1.566	
613		1.565	
832		1.561	
642	1.541	1.549	20
060		1.542	
651		1.539	
	1.468		21
	1.378		11
	1.370		10
	1.330		12
	1.317		6
	1.316		7
	1.298		6
	1.078		9
	1.036		8

studies involving GeO_2 and divalent oxides of the 3d transition metal cations are being carried out and will be described in another paper.

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