

THE SYSTEM $\text{Fe}_3\text{O}_4-\text{Mn}_3\text{O}_4$ *

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ABSTRACT

Investigation of the system $\text{Fe}_3\text{O}_4-\text{Mn}_3\text{O}_4$ was carried out on mixtures prepared in evacuated silica glass tubes to ensure the desired stoichiometric proportions. Runs at liquidus temperatures were made on prepared charges sealed in platinum tubes so as to avoid compositional change resulting from reaction with the furnace atmosphere. Sub-solidus relationships were determined mainly by x-ray diffraction studies of mixtures which had been heated to temperatures between 400° and 1100° C. under conditions which permitted the synthesis and stable coexistence of the cubic and tetragonal phases.

The liquidus exhibits a minimum at 67% Mn_3O_4 and 1543° C. Complete solid solution exists between Fe_3O_4 and Mn_3O_4 above the temperature of the tetragonal to cubic inversion of Mn_3O_4 , that is above about 1160° C. Below that temperature there is an immiscibility gap which increases in width at lower temperatures and is consistent with the compositions of the hausmannite and manganiferous magnetite found together in natural intergrowths. Inconsistencies of the interpretations of previous investigators for the intermediate-temperature portion of the diagram are attributed to their failure to allow for the extreme sluggishness of unmixing of the cubic and tetragonal phases.

INTRODUCTION

One of the common oxide structures encountered in minerals and synthetic materials formed at higher temperatures is the spinel structure, which permits substitution of many metallic elements within wide limits. The most abundant natural spinels can be grouped in the magnetite series. Phase equilibria in systems involving Fe_3O_4 and oxides found in natural association with magnetite are important to petrology, to studies of the conditions of formation of iron ores, and to research on steel making processes.

In recent years the study of spinel oxides has received additional impetus from interest in the unusual magnetic properties which certain of these compounds possess. Manganese-iron spinels are particularly interesting in this respect (Economos, 1955; Romeijn, 1953) and have important technical application as ferromagnetic components in electronic devices.

Previous experimental studies of the system $\text{Fe}_3\text{O}_4-\text{Mn}_3\text{O}_4$ using materials prepared at high temperatures gave inconsistent interpretations concerning the extent of the region of solid immiscibility (Mason, 1943; McMurdie *et al.*, 1950). In the present study the extent of immiscibility was determined by preparing and quenching oxide compositions at temperatures within the two-phase region.

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Stability and Structure of Fe_3O_4 — Mn_3O_4

Fe_3O_4 is stable in air above 1388° C. (Greig *et al.*, 1935); below that temperature α - Fe_2O_3 is the stable form. A cation deficient oxide, γ - Fe_2O_3 , having the same structure as Fe_3O_4 can be prepared by various methods (Verwey, 1935).

Verwey and Heilmann (1947) concluded on the basis of a careful x-ray diffraction study that Fe_3O_4 is probably an inverse spinel. More recent neutron diffraction studies of Shull *et al.*, (1951) confirm that observation. The structural formula is given as $Fe^{+3}[Fe^{+3}Fe^{+2}]O_4$.

Mn_3O_4 is the stable oxide of manganese in air above about 940° C. (Sidgwick, 1950; Mason, 1943). The structure was first determined by Aminoff (1926); although tetragonal at room temperature, the structure is similar to that of the spinels and may be described as a distorted spinel structure. Cation valencies and distribution have been discussed by Mason (1943), von Eckermann (1943), Verwey (1947), Aminoff (1926), and Montoro (1938). Two possible cation combinations for Mn_3O_4 are: $Mn^{+2}[Mn^{+2}Mn^{+4}]O_4$ and $Mn^{+2}[Mn_2^{+3}]O_4$. Mn_3O_4 occurs in nature as the mineral hausmannite. It is not common but in some places occurs in considerable amounts: at Långban, Sweden, it is an important ore of manganese.

The oxide Mn_2O_3 has two established polymorphic forms. The stable form α - Mn_2O_3 has a "C" type cubic structure. It occurs naturally as the mineral bixbyite, generally containing considerable iron in solid solution (Mason, 1943). A cation deficient form, γ - Mn_2O_3 having the same structure as Mn_3O_4 has been reported (Verwey, 1935). Extensive solid solution between Mn_3O_4 and γ - Mn_2O_3 seems probable, analogous to that reported to take place between Fe_3O_4 and γ - Fe_2O_3 (Greig *et al.*, 1935).

Previous Experimental Work

An x-ray study of synthetic manganese-iron spinels was made by Verwey and von Bruggen (1935). Mixtures of MnO and Fe_2O_3 in equal mole proportions heated in air at 1250° C. were found to have absorbed an amount of oxygen exactly equal to conversion of MnO to Mn_3O_4 . The oxide formed was believed to have the composition $Mn_3O_4 \cdot 3Fe_2O_3$ and a spinel-type structure related to γ - Fe_2O_3 . Other mixtures were cooled rapidly from temperatures between 900° and 1300°, a temperature interval considered to be one in which Mn_3O_4 is the stable oxide of manganese (in air) and Fe_2O_3 is the stable oxide of iron. It was apparently assumed that solid solution has no effect on the respective stability ranges of these oxides. The several compositions prepared in this manner were found to exhibit a continuous transition from cubic to tetragonal symmetry. A

sample containing 60 mol % Mn_3O_4 and 40 mol % Fe_2O_3 was found to be cubic, whereas a sample with 67 mol % Mn_3O_4 was tetragonal ($c/a=1.05$). Increasing relative amounts of manganese increased the tetragonal character to a maximum axial ratio of $c/a=1.16$ for the end member, Mn_3O_4 .

Verwey and von Bruggen described the system as showing solid solution of Mn_3O_4 in $\gamma-Fe_2O_3$. The observed cell dimensions agree very closely, however, with those of more recent workers who considered their preparations as a solid solution series $Fe_3O_4-Mn_3O_4$. In Fig. 1 a graphical comparison of cell variation with composition demonstrates this similarity. Since $\gamma-Mn_2O_3$, which is cation deficient, is an established form of manganese oxide, the assignment of cation deficiency to the Fe component in homogeneous Fe, Mn spinels is artificial, although possible.

Montoro (1938) prepared oxide mixtures in the system $Fe_3O_4-Mn_3O_4$ by co-precipitating manganese and iron hydroxide from solutions of the sulfates. The hydroxides were sintered in air at $1200^\circ C.$ and quenched. Montoro reported that samples prepared in this manner are cubic up to 67% $Mn_3O_4^*$ and tetragonal for higher percentages. He related the change from cubic to tetragonal structure to the formation of a supposed compound $FeO \cdot Mn_2O_3$.

A major contribution to understanding the system $Fe_3O_4-Mn_3O_4$ was made by Brian Mason (1943). Mason had access to specimens of relatively pure $(Mn,Fe)_3O_4$ minerals from the ore districts of central Sweden. Microscopic and x-ray examination revealed the existence of vredenbërgite, an intergrowth of Mn-rich magnetite and hausmannite.

In order to determine the compositional limits of the phases in vredenbërgites Mason prepared a series of oxide compositions from co-precipitated hydroxides sintered at temperatures ranging from 1100° to $1300^\circ C.$ Again a continuous variation of cell parameters was observed after quenching. Mason concluded: " Fe_3O_4 and Mn_3O_4 are completely miscible at high temperatures in spite of the difference in symmetry between them. The cubic lattice of Fe_3O_4 changes to a tetragonal lattice at about 60 mol. % Mn_3O_4 ." He compared the cell dimensions of the synthetic preparations with those of natural vredenbërgites and fixed the compositional limits of the two-phase region at low temperatures at 54% and 91% Mn_3O_4 .

Mason heated several of his sintered oxide samples in evacuated silica glass tubes at lower temperatures to induce exsolution; the results were generally negative except for a sample with 80% Mn_3O_4 which exsolved into two tetragonal phases at $750^\circ C.$ but remained unchanged at $900^\circ C.$

* % Mn_3O_4 indicates calculated mol.% Mn_3O_4 . The difference from 100% equals mol.% Fe_3O_4 .

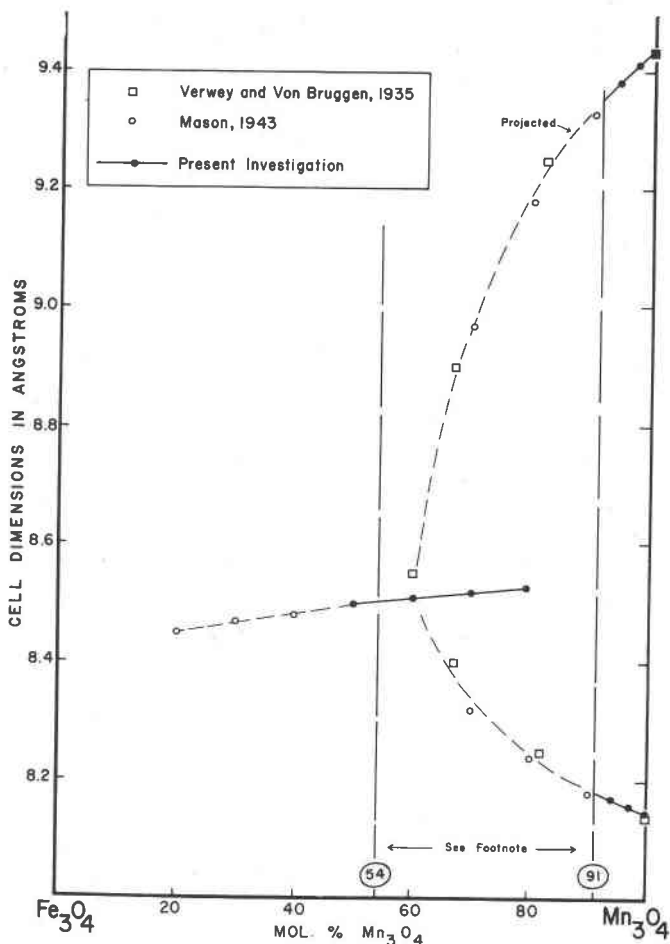


FIG. 1. Variation of cell dimensions with composition.

NOTE: No single crystalline $(Fe, Mn)_3O_4$ phase with from 54% to 91% Mn_3O_4 is stable at room temperature. Cubic solid solutions in that compositional range were obtained only by quenching from higher temperature and are metastable at room temperature. Tetragonal solid solutions which can be prepared in air, probably have a lower cation: oxygen ratio than R_3O_4 and are to be compared with the R_3O_4 - R_2O_3 solid solutions of Verwey and Van Bruggen (1935), whose data are projected (open squares) onto the R_3O_4 plane of Figure 1.

On the basis of this "admittedly meager evidence" for a subsolidus maximum, Mason proposed a tentative phase diagram which is reproduced in Fig. 2, (dashed line).

In 1948 McMurdie and Golovato reported that Mn_3O_4 undergoes a reversible tetragonal to cubic transition at 1170° C. However, they record

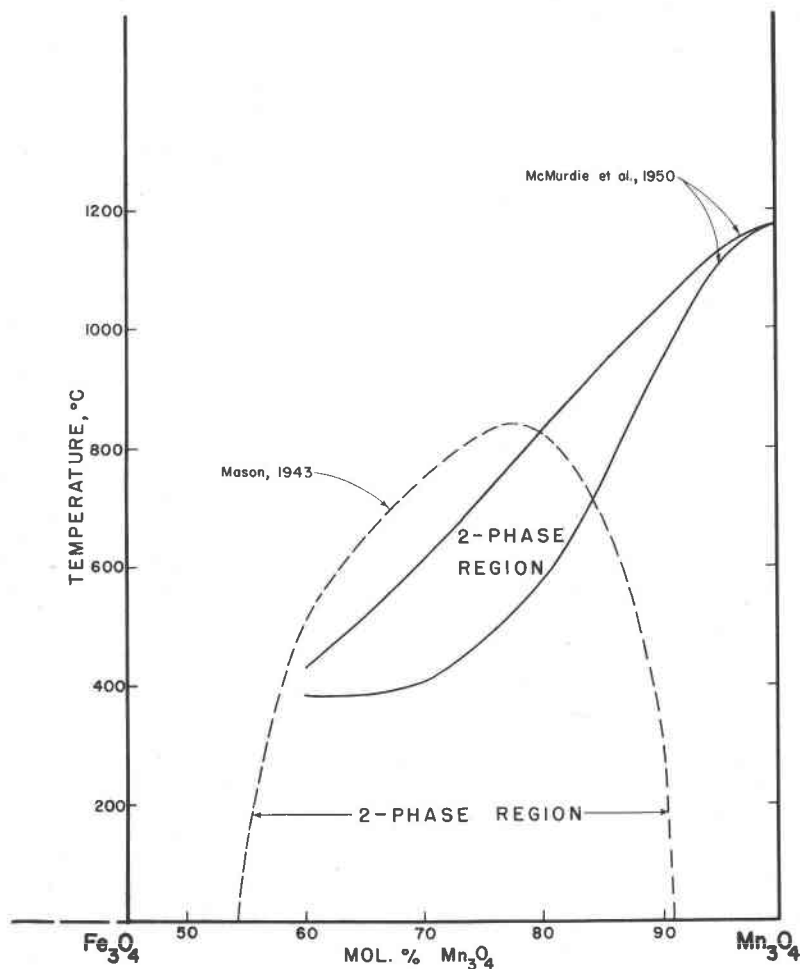


FIG. 2. Previous interpretations of the system $\text{Fe}_3\text{O}_4\text{--Mn}_3\text{O}_4$.

(op. cit. p. 597) that on cooling, "... an exothermic break took place near 1100°C . with samples of high purity." The transition previously had been estimated from heat content data as $1172^\circ \pm 40^\circ\text{C}$. (Southard and Moore, 1942).

Further high temperature x -ray studies were conducted (McMurdie et al., 1950) on the system $\text{Fe}_3\text{O}_4\text{--Mn}_3\text{O}_4$. The hydroxides were prepared and sintered by the same methods employed by Mason. A continuous change in symmetry was again observed, the lattice dimensions showing agreement with Mason's results (Fig. 1). X -ray patterns were then recorded at elevated temperatures. It was observed that some composi-

tions showed cubic and tetragonal phases occurring together over a range in temperature. The partial phase diagram of the system according to McMurdie *et al.* (1950) is reproduced in solid lines in Fig. 2.

The conclusion of McMurdie *et al.* that there is no region of immiscibility at low temperatures (below 380° C.) is inconsistent with coexistence (at any temperature) of phases of the compositional limits found in vredenbergit, namely 54% to 91% Mn_3O_4 (Mason, 1943).

EXPERIMENTAL PROCEDURE

SUB-SOLIDUS INVESTIGATION

High Temperature Preparations

In the preliminary investigation MnO_2 and Fe_2O_3 were mixed together and fired in covered platinum crucibles for 2-hour periods in a gas furnace at 1400° C. The crucibles were then removed from the furnace and cooled in air. This treatment yielded homogeneous spinel phases for all compositions from Fe_3O_4 to about 80% Mn_3O_4 . X-ray diffraction studies showed both tetragonal and cubic reflections in the 90% Mn_3O_4 sample, tetragonal reflections alone in the 100% Mn_3O_4 sample.

The preparation procedure adopted by Mason was repeated with results identical to his. Mixtures co-precipitated as hydroxides and subsequently sintered in air at 1250° C. produced materials which are cubic if the Mn_3O_4 content is less than 60%, tetragonal if the Mn_3O_4 content is higher. All mixtures prepared by this method gave poor x-ray patterns, progressively poorer with increasing iron content.

The high temperature preparations described above showed no tendency to exsolve into separate phases. Fired oxide and hydroxide preparations remained unaffected after heating in evacuated silica tubes for one month at 750° C. It was therefore evident that in order to confirm or disprove a low temperature two-phase region, an attempt should be made to form the R_3O_4 phase or phases at low temperatures.

Preparations in Vacuo and in Controlled Atmosphere

Manganese dioxide and powdered manganese and iron metals were used as starting materials for preparing $(\text{Fe},\text{Mn})_3\text{O}_4$ compositions within the range 67% to 100% Mn_3O_4 . This mixture proved particularly suitable for synthesis in evacuated silica glass tubes. MnO_2 decomposes below 500° C. in the presence of the metals and they readily take up the available oxygen. In runs made as low as 500° C., $(\text{Mn},\text{Fe})_3\text{O}_4$ phases could be prepared with no other recognizable phases present. At 400° C. some $(\text{Mn},\text{Fe})_2\text{O}_3$ reflections were encountered. For compositions with less than 67% Mn_3O_4 , Fe_2O_3 was used, of necessity, as one of the com-

ponent oxides. It is less desirable than MnO_2 as a starting material because it has a higher temperature of decomposition.

An inherent uncertainty in this procedure is in the difficulty of preparing a homogeneous sample. The starting materials were weighed in amounts totaling one gram, then thoroughly mixed and ground together. An aliquot of approximately one-tenth of the total sample was used for each run. The error introduced by any inhomogeneity was apparently small since samples of different compositions heated at the same temperature produced consistent results.

A few runs were made in a controlled-atmosphere furnace. Experimental thermodynamic data delimiting the stability fields of Mn_3O_4 (Ishihara and Kigoshi, 1953) and of Fe_3O_4 (Darken and Gurry, 1945) indicate that any ratio of CO_2/CO from 10 to 10^4 should be in equilibrium with those oxides at the temperatures used. The optimum gas ratio of CO_2/CO for preparing oxides in the desired temperature-composition range was found empirically to be 300/1. This gas ratio was attained by mixing the gases at low pressures in a tank. The gas mixture was passed slowly through a vertical tube furnace designed for controlled atmosphere experiments.

Determination of Two-Phase Region

With the exception of confirmatory runs at 800° C., 900° C., and 1000° C. in a controlled atmosphere, all subsolidus data are based on runs made in evacuated silica glass tubes. The determination of the existing phases and their respective cell dimensions was made after quenching to room temperature. The boundary curves limiting the two-phase region were determined by two methods.

- 1) The compositions of co-existing cubic and tetragonal phases were determined from their cell dimensions by using extrapolated curves giving cell variation versus composition.
- 2) Each boundary curve was bracketed by runs made at different compositions and temperatures. This method was used in particular to check the boundary between the two-phase area and the cubic-phase area because the variation of the cubic parameter with composition is small.

Determination of Mn_3O_4 Inversion

Mn_3O_4 previously prepared from MnO_2 was packed in a platinum sample holder and mounted within a heating unit* in air on a G. E. -XRD 3 geiger counter spectrometer. A Pt vs 10% Rh Pt reading couple

* Heating unit designed by H. McKinstry, Pennsylvania State University.

and Pt Rh vs. Au Pd control couple were used. X-ray diffraction patterns were taken at room temperature and at successive temperature intervals up to 1270° C. In each case, the x-ray pattern was taken after the temperature had reached a steady state. The x-ray furnace thermocouple was calibrated with barite from Stoneham, Colorado, heating inversion 1180° C. (Gruver, 1951).

The Mn_3O_4 inversion was also investigated by differential thermal analysis, using a heating rate of 2° to 3° per minute and a cooling rate of about 1.5° per minute. D.T.A. runs were made on initially stoichiometric Mn_3O_4 in air and in evacuated silica glass. The temperature standard used was $Na_2O \cdot 3 TiO_2$, melting point 1128° C. (Shafer and Roy 1956). The inversion on cooling could not be determined using the sodium titanate standard due to an overlap of its freezing-point thermal effect with that due to the Mn_3O_4 inversion. Therefore granular alumina was substituted for sodium titanate for the cooling run.

LIQUIDUS INVESTIGATION:

Charges for investigation of equilibria at liquidus temperatures were prepared from metal plus oxide mixtures heated in platinum foil envelopes in evacuated silica glass tubes for four days at 650° C., then 17 hours at 950° C. Sintered charges prepared in this manner at 10 mol% intervals were ground, and portions of each were packed in platinum tubes which were then sealed by welding. The sealed charges were heated for 10 hours or longer, in a vertical tube furnace and then quenched in mercury. Quenched charges were polished and examined microscopically under reflected light for the presence of primary crystals, well-formed octahedra easily distinguished from the fine-grained mass representing quenched liquid. Temperatures were measured with a Pt vs. 10% Rh Pt thermocouple calibrated at the melting point of pseudowollastonite, $CaSiO_3$ (1544°).

Controlled atmosphere runs and runs at liquidus temperatures were quenched by dropping the envelopes or tubes directly into a mercury container connected to the bottom of the vertical tube furnace.

EXPERIMENTAL RESULTS

Tables 1, 2 and 3 below summarize the critical runs and experimental data and the results are shown in diagrammatic form in Figure 3.

Sub-Solidus Equilibria

The inversion of Mn_3O_4 from the tetragonal hausmannite form to a cubic high-temperature form with spinel structure was confirmed; we propose that the cubic form be called high hausmannite and the tetragonal form, low hausmannite.

Determination of the inversion temperature of Mn_3O_4 was found to be complicated by the fact that H , (the beginning of inversion on heating) is at a higher temperature than C , (the beginning of inversion on cooling). The inversion has been described as a readily reversible inversion at $1170^\circ C.$, (McMurdie and Golovato 1948). However our results lead us to suspect that the "exothermic break" which they obtained at a temperature near $1100^\circ C.$ on cooling, probably is due to the inversion on cooling.

TABLE 1. LATTICE DIMENSIONS OF Mn_3O_4 IN AIR

	Temp., $^\circ C.$	a_0	c_0
Tetragonal Form	20	8.136 Å	9.422 Å
	250	8.14	9.45
	450	8.15	9.47
	625	8.16	9.49
	800	8.175	9.50
	1000	8.20	9.49
	1160	8.22	9.46
	1162—(first cubic reflections on heating)		
Cubic Form	1270	8.57	
	1220	8.56	
	1144—(first tetragonal reflections on cooling)		
	1140	8.54	

Our results by two different methods are summarized below and compared with the data of McMurdie and Golovato.

<i>Inversion Break, Degrees C.</i>			<i>Method</i>
<i>Heating</i>	<i>Cooling</i>	<i>H-C</i>	
1170	(1100±)	(70±)	D.T.A. in air at $8^\circ/min.$ (McMurdie and Golovato)
1167	1130	37	D.T.A. in air at $2^\circ/min.$
1162	1144	18	x-ray diffraction and slow step-wise heating in air.

It is apparent that the Mn_3O_4 inversion can be inhibited or delayed and that the measured inversion break is a function of the rate of heating or cooling. If $H-C$ is plotted against H and separately against C , extrapolation yields a temperature of about $1160^\circ C.$ at $H-C = \text{zero}$. We propose to use $1160^\circ C.$ as an estimate of the equilibrium inversion temperature of Mn_3O_4 in air.

Differential thermal analysis at about 2° per minute, of a sample of Mn_3O_4 contained in an evacuated silica glass tube* showed at 26° hys-

* The calculated amount of oxygen in the silica glass tube at 1160° is less than 1 part per million of the oxygen in the sample.

TABLE 2. CRITICAL SUBSOLIDUS RUNS

Mn:Fe Ratio	Starting Materials	Time	Temp. °C.	Atmosphere	Product, and Cell Dimensions		
100:0	MnO ₂	2 hrs.	1400	gas furn.	Mn ₃ O ₄ , tetragonal		
90:10	MnO ₂ +Fe ₂ O ₃	2 hrs.	1400	gas furn.	Essentially cubic (some splitting of cubic reflections)		
80:20	MnO ₂ +Fe ₂ O ₃	2 hrs.	1400	gas furn.	Cubic		
				Ratio CO ₂ /CO	Cubic a ₀	Tetragonal a ₀ c ₀	
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	48 hrs.	1000	300	8.525	8.17	9.39
80:20	MnO ₂ +Mn ⁰ +Fe ⁰	48 hrs.	1000	300	8.53	8.17	9.40
70:30	MnO ₂ +Mn ⁰ +Fe ⁰	48 hrs.	1000	300	8.52	8.16	9.40
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	54 hrs.	900	300	8.52	8.17	9.38
80:20	MnO ₂ +Mn ⁰ +Fe ⁰	54 hrs.	900	300	8.52	8.17	9.38
70:30	MnO ₂ +Mn ⁰ +Fe ⁰	72 hrs.	900	300	8.52	8.17	9.38
60:40	MnO ₂ +Mn ⁰ +Fe ⁰	72 hrs.	900	300	8.51*		
	+Fe ₂ O ₃						
94:6	MnO ₂ +Mn ⁰ +Fe ⁰	48 hrs.	800	300		8.17	9.38
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	48 hrs.	800	300	8.51	8.17	9.38
70:30	MnO ₂ +Mn ⁰ +Fe ⁰	55 hrs.	800	300	8.515	8.17	9.38
60:40	MnO ₂ +Mn ⁰ +Fe ⁰	55 hrs.	800	300	8.51		
	+Fe ₂ O ₃						
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	24 hrs.	1100	in vacuo	8.535	8.16	9.40
80:20	MnO ₂ +Mn ⁰ +Fe ⁰	24 hrs.	1100	in vacuo	8.53		
100:0	MnO ₂ +Mn ⁰ +Fe ⁰	40 hrs.	1000	in vacuo		8.15	9.43
97:3	MnO ₂ +Mn ⁰ +Fe ⁰	40 hrs.	1000	in vacuo		8.16	9.41
94:6	MnO ₂ +Mn ⁰ +Fe ⁰	40 hrs.	1000	in vacuo		8.17	9.38
70:30	MnO ₂ +Mn ⁰ +Fe ⁰	45 hrs.	950	in vacuo	8.52		
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	36 hrs.	900	in vacuo	8.52	8.17	9.39
80:20	MnO ₂ +Mn ⁰ +Fe ⁰	36 hrs.	900	in vacuo	8.52	8.17	9.40
70:30	MnO ₂ +Mn ⁰ +Fe ⁰	36 hrs.	900	in vacuo	8.52	8.17	9.39
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	1 week	730	in vacuo	8.51	8.17	9.38
80:20	MnO ₂ +Mn ⁰ +Fe ⁰	1 week	730	in vacuo	8.51	8.16	9.38
60:40†	MnO ₂ +Mn ⁰ +Fe ⁰	1 week	730	in vacuo	8.51		
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	17 days	664	in vacuo	8.51	8.17	9.36
80:20	MnO ₂ +Mn ⁰ +Fe ⁰	17 days	664	in vacuo	8.51	8.17	9.37
70:30	MnO ₂ +Mn ⁰ +Fe ⁰	17 days	664	in vacuo	8.515	8.17	9.37
100:0	MnO ₂ +Mn ⁰ +Fe ⁰	30 days	610	in vacuo		8.16	9.43
97:3	MnO ₂ +Mn ⁰ +Fe ⁰	30 days	610	in vacuo		8.16	9.41
94:6	MnO ₂ +Mn ⁰ +Fe ⁰	30 days	610	in vacuo		8.17	9.39
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	32 days	600	in vacuo	8.51	8.17	9.36
80:20	MnO ₂ +Mn ⁰ +Fe ⁰	32 days	600	in vacuo	8.51	8.18	9.36
60:40†	MnO ₂ +Mn ⁰ +Fe ⁰	32 days	600	in vacuo	8.51	8.17	9.37
94:6	MnO ₂ +Mn ⁰ +Fe ⁰	25 days	600	in vacuo		8.17	9.39
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	60 days	500	in vacuo	8.51	8.17	9.36
80:20	MnO ₂ +Mn ⁰ +Fe ⁰	60 days	500	in vacuo	8.51	8.18	9.36
60:40	MnO ₂ +Mn ⁰ +Fe ⁰	60 days	500	in vacuo	8.51		
90:10	MnO ₂ +Mn ⁰ +Fe ⁰	85 days	400	in vacuo	8.5	8.18	9.35
80:20	MnO ₂ +Mn ⁰ +Fe ⁰	85 days	400	in vacuo			
70:30	MnO ₂ +Mn ⁰ +Fe ⁰	85 days	400	in vacuo			

* Italicized figures indicate cubic only or tetragonal only.

† Plus Fe₂O₃.‡ Some R₂O₃ present.

TABLE 3. HIGH TEMPERATURE RUNS IN Pt TUBES

Mn:Fe Ratio	Time	Temp.	Product
50:50	10 hrs.	1556	crystals & liquid*
60:40	10 hrs.	1556	all liquid*
50:50	19.5 hrs.	1561	liquid > crystals
80:20	19.5 hrs.	1561	all liquid
50:50	14 hrs.	1566	all liquid*
90:10	14 hrs.	1566	all liquid*
100:0	14 hrs.	1566	all liquid*
60:40	10 hrs.	1545	crystals (80%+) & liquid
80:20	10 hrs.	1545	crystals (90%+) & liquid
60:40	16 hrs.	1550	crystals & liquid
70:30	16 hrs.	1550	all liquid
70:30	12 hrs.	1544	liquid > crystals
90:10	12 hrs.	1560	liquid > crystals
90:10	15 hrs.	1562	all liquid
100:0	15 hrs.	1562	liquid plus very rare crystals

* Sample tubes quenched in air (quench less rapid than mercury quench).

teresis between the thermal break on heating and on cooling, i.e., appreciably less than the 37° hysteresis indicated by D.T.A. in air at the same rate of heating and cooling. This suggests that part of the retardation, (superheating or undercooling) of the inversion in air may be due to an accompanying compositional change which requires diffusion of oxygen into or from the sample.

The low hausmannite structure tolerates a maximum of about 9 mole % of Fe_3O_4 in solid solution at room temperature (Mason, 1948); this decreases to 8% at $400^\circ C.$, and continues to decrease with rising temperature, to zero Fe_3O_4 at $1160^\circ C.$, the inversion temperature of Mn_3O_4 (See Fig. 3).

On the other hand, the magnetite-high hausmannite solid solution series contains a maximum of 54% Mn_3O_4 , at low temperatures and the maximum amount of Mn_3O_4 increases progressively with increasing temperature, to 100% Mn_3O_4 at $1160^\circ C.$ (See Fig. 3). There are no binary compounds, and intermediate members of the series can simply be described by giving the molecular percentage of Mn_3O_4 .

Single-phase tetragonal products with Mn:Fe ratio in the range of the 2-phase region can be prepared by heating in air; the compositions of such preparations apparently are off the join $Fe_3O_4-Mn_3O_4$ in the direction of excess oxygen. The basis of this conclusion is the experimental evidence that stoichiometric metal+oxide mixtures in the range from Mn:Fe approximately 60:40 to 90:10 yield cubic phases upon heating to $1200^\circ C.$ in evacuated silica glass tubes or in the slightly reducing

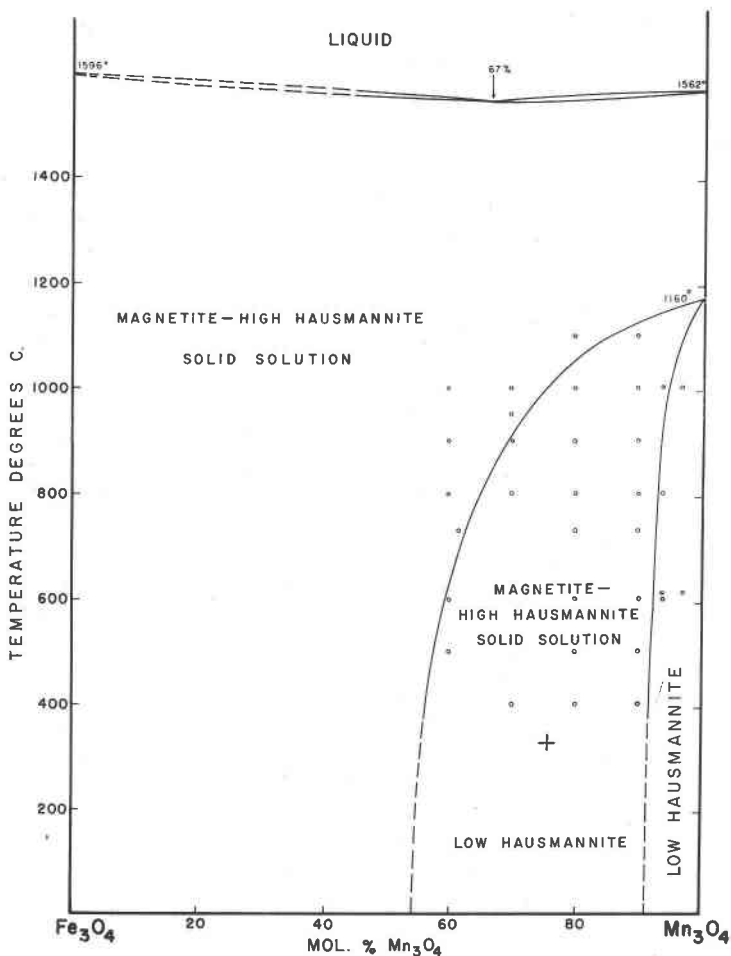


FIG. 3. Phase equilibria in the system Fe_3O_4 - Mn_3O_4 .

atmosphere of a gas furnace,¹¹ while similar materials fired at equivalent temperatures in air have a poorly developed tetragonal structure. Coprecipitated hydroxide starting materials promote formation of the tetragonal structure.

A tetragonal 80 Mn:20 Fe oxide composition prepared at 1200° C. from an hydroxide starting mixture, and a cubic 80:20 sample prepared at 1400° C. (gas furnace) from a metal+oxide starting mixture, were both heated above the liquidus temperature in air on a strip resistance furnace and quenched. Each sample recrystallized with the same structure it had before being melted, indicating that the difference in structure probably is due to a compositional difference.

Liquidus Temperatures

The melting point of Fe_3O_4 is taken as 1596° C. (Darken and Gurry, 1946), the melting point of Mn_3O_4 as 1562° C., (present investigation), in good agreement with the melting temperature, 1565° C., given by Wartenburg and Reusch (1932). Intermediate compositions exhibit solid solution with a liquidus minimum at about 67% Mn_3O_4 and 1543° C., (See Fig. 3).

CONCLUSIONS

The temperature of inversion of Mn_3O_4 from the tetragonal hausmannite form to the cubic high temperature form (here designated high hausmannite) is determined to be $1160^\circ \pm 5^\circ$ C.

Above 1160° C. there is complete solid solution between magnetite and high hausmannite. At lower temperatures there is a progressively widening region of solid immiscibility in which a cubic phase and a tetragonal phase can coexist in equilibrium. Compositional limits of the phases present at 400° C. are 57% Mn_3O_4 :43% Fe_3O_4 and 92% Mn_3O_4 :8% Fe_3O_4 . Extrapolation of the boundary curves (Figure 3) to room temperature gives composition limits in agreement with the results of Mason's work (op. cit., 1943) on natural intergrowths, namely 54% Mn_3O_4 and 91% Mn_3O_4 .

The name *jacobsite* has been used to refer to spinel-structure minerals with intermediate compositions in the system $Fe_3O_4-Mn_3O_4$ (Mason 1943, p. 158), and use of that name for the complete high temperature series could be defended, on the basis that the present work shows that the compositional range of jacobsite increases with increasing temperature. However, the upper limit of 54% Mn_3O_4 in the cubic series is a logical and useful point of subdivision for minerals, and we therefore propose to follow Mason for the most part, and to use the following definitions of minerals whose compositions fall in the system $Fe_3O_4-Mn_3O_4$:

<i>Mineral Name</i>	<i>Molecular % Mn_3O_4</i>
magnetite	0 to 10*
jacobsite (magnetite-high hausmannite solid solution)	10 to 54
vredenbergite (intergrowths of jacobsite and low hausmannite)	54 to 91
hausmannite	91 to 100

Results of the present investigation show that the compositional range of the tetragonal structure is much greater for cation deficient compositions, which may be written $(Mn,Fe)_{3-x}O_4$, than for stoichiometric

* Mason (op. cit. 1943a) set the boundary between magnetite and jacobsite at 16.7% Mn_3O_4 , a composition half-way between Fe_3O_4 and the hypothetical compound $MnFe_2O_4$. There is no evidence that such a compound exists and therefore it seems preferable to set the division arbitrarily at 10% Mn_3O_4 .

(Mn,Fe)₃O₄ preparations. Synthesis of stoichiometric (Mn, Fe)₃O₄ oxides requires that the partial pressure of oxygen be controlled or that the effect of furnace atmosphere be eliminated by use of sealed sample tubes.

It seems likely that the tetragonal mineral described by Mason (1943b) as alpha-vredenbergite is cation deficient. This would be consistent with its reported mode of origin, by alteration of bixbyite (Mn,Fe)₂O₃ and would explain the existence of the mineral as a single phase rather than as an intergrowth of cubic and tetragonal phases, as would be expected from its Mn:Fe ratio. The existence of single phase metastable minerals in the compositional range of vredenbergite is possible but we would expect them to be cubic rather than tetragonal if the cation:oxygen ratio is stoichiometric.

Fine-grained vredenbergite (oriented intergrowths of jacobsonite and iron-bearing hausmannite) may have originated by unmixing of a homogeneous magnetite-high hausmannite solid solution formed at temperatures above the two-phase region, as suggested by Mason. If an origin by unmixing could be proven to be the only means of producing such intergrowths, then it would be possible, for a vredenbergite sample of known composition, to estimate a minimum temperature of formation of the homogeneous solid solution by use of the equilibrium diagram (Fig. 3). However, there is no evident way of proving that such intergrowths do not originate from sedimentary iron-manganese deposits by thermal metamorphism at maximum temperatures *within* the two-phase region.

Unmixing of the cubic and tetragonal phases is so sluggish that it is practically useless in laboratory investigations of the system Fe₃O₄-Mn₃O₄ and that sluggishness, together with the difficulty of maintaining the stoichiometric proportions of preparations, probably is a principal reason for the inconsistencies of previous interpretations of the intermediate temperature portion of the system.

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