

## The $\text{SrMnO}_{3-x}\text{-Mn}_3\text{O}_4$ System

T. NEGAS

National Bureau of Standards, Washington, D.C. 20234

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Phase relations were determined in the  $\text{SrMnO}_{3-x}\text{-Mn}_3\text{O}_4$  system at elevated temperatures in air using quenching, gravimetric, and X-ray diffraction techniques. The system contains one intermediate compound,  $\text{SrMn}_3\text{O}_{6-x}$  ( $0 \leq x \leq 0.10$  between  $900\text{-}1200^\circ\text{C}$ ), which decomposes to  $\text{SrMnO}_{3-x}$  plus  $\text{Mn}_3\text{O}_4$  near  $1215^\circ\text{C}$ . The existence of an oxygen deficient  $\text{SrMnO}_{3-x}$  having the hexagonal 4-layer structure was confirmed. Crystals of perovskite-like  $\text{SrMnO}_{3-x}$  ( $x > 0.25$ ) were grown from its primary field located in the system.

An investigation of phase relations in the manganese-rich portion of the Sr-Mn-O system at elevated temperatures in air was initiated primarily to further elucidate and substantiate phase relations at the 1:1 Sr:Mn ratio. Negas et al. (1, 2) reported that stoichiometric  $\text{SrMnO}_3$  is stable in air only below  $\sim 1035^\circ\text{C}$ . The compound has the so-called 4H (four layer, hexagonal) structure (1-4). Within the  $1035\text{-}1400^\circ\text{C}$  range this phase is nonstoichiometric,  $\text{SrMnO}_{3-x}$ , with  $0 < x < 0.11$  (2). The 4H, nonstoichiometric modification transforms at  $\sim 1400^\circ\text{C}$  to a perovskite-type phase near  $\text{SrMnO}_{2.74}$  stoichiometry. This phase is stable to about  $\text{SrMnO}_{2.62}$  near a melting point at  $\sim 1740^\circ\text{C}$  (2). Preliminary experiments using compositions with Sr:Mn ratios less than 1:1 suggested that the data from the  $\text{SrMnO}_{3-x}$  system must be utilized to correctly define phase relations in this portion of the system.

### Experimental Methods

Weighed amounts of spectrographic grades of  $\text{SrCO}_3$  and  $\text{Mn}_3\text{O}_4$  were mixed under acetone, packed in Au envelopes, and calcined in air at  $900^\circ\text{C}$  for 1 week followed by 1 week at  $1000^\circ\text{C}$  and 4 days at  $1100^\circ\text{C}$  with periodic remixing. Calcined specimens were equilibrated at selected temperatures in Pt-tubes and quenched in water or liquid nitrogen. Furnaces and temperature control used are described in (2).

Gravimetric data were obtained using 2.0-2.5 g of calcined specimens which were pressed into

$\frac{1}{2}$  in. diameter discs at 10,000 psi, suspended within a Pt-wire basket in a quench furnace, and equilibrated at  $1275 \pm 5^\circ\text{C}$  for 3 days. These specimens were quenched in liquid nitrogen, weighed at room temperature using a semi-microbalance, then heated in air to about  $900^\circ\text{C}$ . They were periodically removed from the furnace and reweighed until a constant weight was achieved, generally within 8 days. All measurements thus involve a weight gain from a high-temperature to a lower-temperature, more oxidized, phase assemblage. A similar procedure was followed to determine the extent of oxygen loss for a compound to be herein reported. Single phase powders (1.5-2.0 g) were equilibrated at various temperatures ( $< 1200^\circ\text{C}$ ) for 5 days, quenched, and weighed. These were also oxidized to constant weight at  $900^\circ\text{C}$ .

Phases were identified at room temperature using an X-ray diffractometer and Ni-filtered Cu radiation. Melting was detected by microscopic examination of quenched specimens. Liquid plus solid fields were particularly easy to determine as the primary solid phase usually grew in single crystal form. The liquidus, however, was difficult to delimit as the liquids are extremely mobile and tended to flow out of their container.

### Experimental Results and Discussion

Phase relations in the manganese-rich portion of the Sr-Mn-O system at ambient atmospheric pressure are shown as a function of Sr:Mn ratio and temperature in Fig. 1. The system is not truly

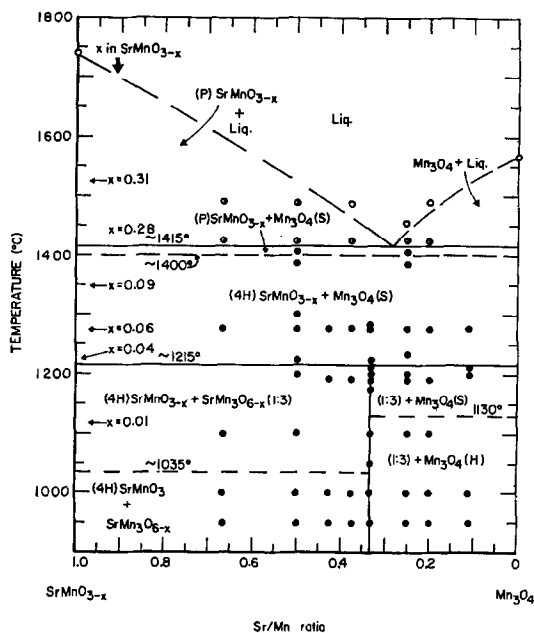


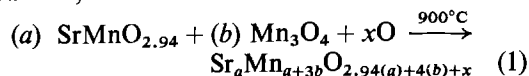
FIG. 1. Phase relations at ambient atmospheric pressure in the  $\text{SrMnO}_{3-x}\text{-Mn}_3\text{O}_4$  system. The composition variable is plotted in terms of Sr/Mn ratio as the system is not truly binary because of reactions with atmospheric oxygen. Values of  $x$  in  $\text{SrMnO}_{3-x}$  are after Ref. 2. The phase  $\text{SrMn}_3\text{O}_{6-x}$  (1:3) has  $0 \leq x \leq 0.10$  between 900–1200°C. Abbreviations used: H = hausmannite; S = spinel; P = perovskite-like phase (Refs. 1, 2); 4H = 4-layer, hexagonal (Refs. 1, 2); Liq. = liquid.

binary because of reactions with atmospheric oxygen. Data for the air isobar in the  $\text{SrMnO}_{3-x}\text{-Mn}_3\text{O}_4$  system were taken from Negas and Roth (2). Several values of  $x$  are shown at various temperatures for the 1:1 Sr:Mn ratio. The dashed line at  $\sim 1035^\circ\text{C}$  represents the beginning of oxygen loss from the 4H  $\text{SrMnO}_3$  phase. The dashed line at  $\sim 1400^\circ\text{C}$  is the transition from nonstoichiometric, 4H,  $\text{SrMnO}_{2.89}$  to a nonstoichiometric,  $\text{SrMnO}_{2.74}$ , perovskite-like phase (1, 2). The hausmannite to spinel transition at  $1130 \pm 10^\circ\text{C}$  of  $\text{Mn}_3\text{O}_4$  was taken from Driessens (5) while the melting point at  $1567^\circ\text{C}$  of  $\text{Mn}_3\text{O}_4$  is from Muan (6). An "invariant" condition at  $\sim 1415^\circ\text{C}$  was established among  $\text{SrMnO}_{3-x}$  (perovskite), liquid and  $\text{Mn}_3\text{O}_4$  phases. Compositions of liquids at liquidus temperatures within the Sr-Mn-O ternary, however, were not determined.

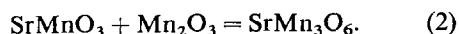
### The $\text{SrMn}_3\text{O}_{6-x}$ Phase

The system includes one compound with a composition  $\text{SrMn}_3\text{O}_{6-x}$  which was deduced by

a method to be described. Initially it was determined that this phase decomposed to 4H  $\text{SrMnO}_{3-x}$  plus  $\text{Mn}_3\text{O}_4$  near  $1215^\circ\text{C}$ . As the reaction is reversible, all pertinent Sr:Mn ratio compositions consisted of this compound plus  $\text{SrMnO}_{3-x}$  or  $\text{Mn}_3\text{O}_4$  below  $1215^\circ\text{C}$ . The Sr:Mn ratio of the compound was not certain because small amounts of  $\text{SrMnO}_{3-x}$  and especially  $\text{Mn}_3\text{O}_4$  are difficult to detect in the X-ray diffraction powder patterns of reacted materials. Furthermore, the oxygen content of the phase could not be established directly. Figure 2, based on gravimetric data, illustrates the method which was used to simultaneously solve both problems involving composition. The phase assemblage between 1215 and  $1400^\circ\text{C}$  consists of 4H  $\text{SrMnO}_{3-x}$  plus  $\text{Mn}_3\text{O}_4$  for all Sr:Mn ratios (Fig. 1). Assuming nearly stoichiometric  $\text{Mn}_3\text{O}_4$ , the bulk composition at any ratio for a given isotherm is determinable provided  $x$  in  $\text{SrMnO}_{3-x}$  is known. At  $1275^\circ\text{C}$  the  $\text{SrMnO}_{3-x}$  phase in equilibrium with  $\text{Mn}_3\text{O}_4$  has  $x \approx 0.06$  (2). This assemblage is shown in Fig. 2 by the limiting  $\text{SrMnO}_{2.94}\text{-Mn}_3\text{O}_4$  tie line. Phase assemblages consisting of the compound of interest plus stoichiometric  $\text{SrMnO}_3$  or  $\text{Mn}_3\text{O}_4$  are obtained by quenching Sr:Mn ratio compositions from  $1275^\circ\text{C}$  and reheating below  $1035^\circ\text{C}$  (Fig. 1). Tie lines, therefore, exist between the compound and  $\text{SrMnO}_3$  and  $\text{Mn}_3\text{O}_4$ , respectively. Thus, by measuring the weight gain associated with the reaction,



it is possible to obtain a final bulk composition. The values of (a) and (b) are known from the initial Sr:Mn ratio while  $x$  is related to the weight gain. If  $x = 0.06(a)$ , the bulk composition would lie on the  $\text{SrMnO}_3\text{-Mn}_3\text{O}_4$  tie line and the composition of the compound could then not be discerned. Mole percent oxygen contents measured for a number of starting Sr:Mn ratios are plotted in Fig. 2. The two tie lines that are established by the data intersect near a 1:3 Sr:Mn ratio which is that accepted for the compound. As the 1:3 compound- $\text{SrMnO}_3$  tie line is a portion of the  $\text{SrMnO}_3\text{-Mn}_2\text{O}_3$  tie line the oxygen content of the compound at  $900^\circ\text{C}$  is determinable according to:



The X-ray diffraction powder pattern of  $\text{SrMn}_3\text{O}_6$ , given in Table I, is of poor quality

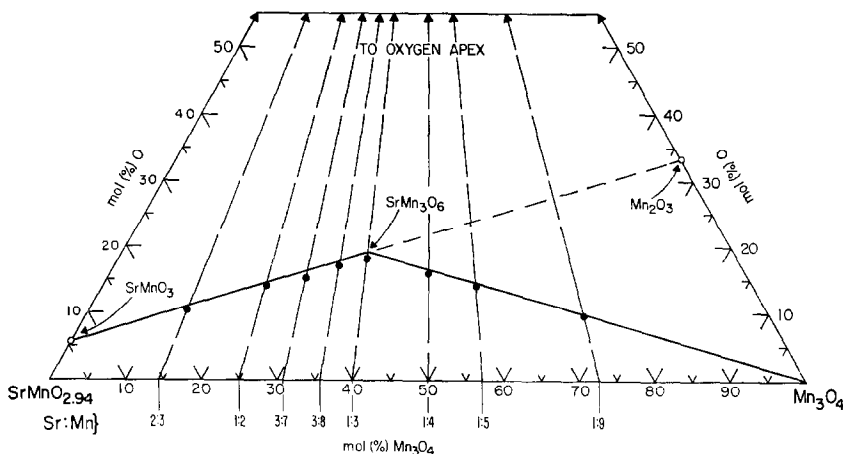


FIG. 2. Diagram illustrating the experimental method used to locate the composition of the  $\text{SrMn}_3\text{O}_{6-x}$  phase. The  $\text{SrMnO}_{2.94}\text{-Mn}_3\text{O}_4$  tie line is the 1275°C isotherm of Fig. 1. Specimens equilibrated at this temperature were oxidized at 900°C. Weight gains (mole percent oxygen) associated with the oxidation process are plotted along lines of constant Sr/Mn ratio (oxygen reaction lines). Two tie lines are established which intersect at Sr:Mn = 1:3. These tie lines correspond with phase relations along the 900°C isotherm in Fig. 1. Stoichiometric  $\text{SrMn}_3\text{O}_6$  (900°C) also lies on the  $\text{SrMnO}_3\text{-Mn}_2\text{O}_3$  join.

regardless of the heat treatment used to prepare or anneal the phase. Its general complexity probably suggests orthorhombic or lower sym-

TABLE I

SUMMARY OF X-RAY DIFFRACTION AND CHEMICAL DATA FOR THE PHASE  $\text{SrMn}_3\text{O}_{6-x}$ 

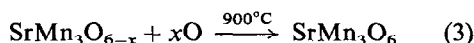
$d_{\text{obs}}$ (Å)	$I/I_1$	Temp. (°C)	$x$ in $\text{SrMn}_3\text{O}_{6-x}$
7.31	11	900	0.0
5.05	10 <sup>a</sup>	1050	0.04
3.65	20	1160	0.08
3.27	6 <sup>a</sup>	1200	0.10
3.027	95		
2.953	100		
2.875	50		
2.523	6	SrMn <sub>3</sub> O <sub>6</sub> prepared at 900°C, heated to 1200°C, oxidized at 900°C in air. Analysis for total Mn content by EDTA titration and atomic absorption <sup>b</sup> :	
2.467	17 <sup>a</sup>		
2.431	40		
2.358	21		
2.315	5 <sup>a</sup>		
2.235	22		
2.142	22	measured: 48.13 wt. %	
2.065	10 <sup>a</sup>	theoretical: 47.30 wt. %	
1.896	17		
1.844	11 <sup>a</sup>		
1.804	9		
1.708	11 <sup>a</sup>		
1.616	5 <sup>a</sup>		

<sup>a</sup> = broad.

<sup>b</sup> Performed by a company independent of the National Bureau of Standards. Average of four analyses.

metry. The pattern bears a strong resemblance to that of wadginite (7) which is monoclinic with  $a = 9.52$  Å,  $b = 11.46$  Å,  $c = 5.11$  Å, and  $\beta = 91^\circ 15'$ . The structure of wadginite is related to the ixiolite ( $\alpha\text{-PbO}_2$ ) and columbite-tantalite structures (8). Based on powder data alone, these are difficult to distinguish from structures having higher coordination environments for the cations (9). Although the powder data for  $\text{SrMn}_3\text{O}_6$  could not be indexed using a wadginite-type cell, most of the diffraction lines can be indexed on the basis of a related orthorhombic cell with  $a = 9.43$  Å,  $b = 11.51$  Å, and  $c = 5.06$  Å. As the entire powder pattern cannot be unambiguously indexed, the parameters above are either fortuitous or may represent, at best, a possible subcell. Single crystal data are required to prove conclusively the relationship with wadginite. Attempts to grow single crystals have not been successful. It is apparent, however, that the site occupied by Sr in  $\text{SrMn}_3\text{O}_6$  cannot tolerate a larger cation, as a Ba analogue does not exist.

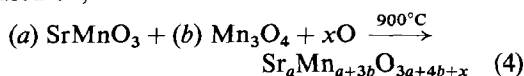
Single phase  $\text{SrMn}_3\text{O}_6$  was equilibrated at several temperatures below 1200°C and quenched. These materials were reheated at 900°C to measure a possible variation in the oxygen content according to:



These data as well as the results of chemical analyses for total Mn content of the starting

material used are summarized in Table I. It is apparent that  $\text{SrMn}_3\text{O}_6$  evolves oxygen above  $\sim 950^\circ\text{C}$  and has the stoichiometry,  $\text{SrMn}_3\text{O}_{5.9}$ , near the decomposition temperature at  $\sim 1215^\circ\text{C}$ .

The data shown in Fig. 2 further substantiate the evidence in (2) that 4H  $\text{SrMnO}_3$  is oxygen deficient at temperatures  $>1035^\circ\text{C}$  in air. If at  $1275^\circ\text{C}$  the 1:1 compound is stoichiometric, the component  $\text{SrMnO}_3$  rather than  $\text{SrMnO}_{2.54}$  would be located at the apex in Fig. 2. Mole percent oxygen calculated from weight gains based on,



would differ almost insignificantly from the values in Fig. 2. A tie line between  $\text{SrMnO}_3$  and the 1:3 ratio would not be evident. The  $\text{SrMnO}_3$ - $\text{Mn}_2\text{O}_3$  tie line, furthermore, would lie at lower mole percent oxygen contents (smaller weight gains). An extrapolation of the tie line established by the data points to the limiting  $\text{SrMnO}_3$  (if located at the apex in Fig. 2) -O tie line would suggest that  $\text{SrMnO}_3$  either contained excess oxygen or was cation deficient at  $900^\circ\text{C}$ . The close-packed nature of the 4H structure precludes an oxygen excess while cation deficiency is inconsistent with the cell expansion data of (2). Cation deficiency would also lead to formulations suggesting unreasonable oxidation states higher than 4+ for octahedrally coordinated Mn. When oxygen deficiency in the 4H structure is recognized, the data are consistent and can be interpreted in a simple, logical, manner.

### $\text{SrMnO}_{3-x}$ Perovskite Crystals

In the investigation of the  $\text{SrMnO}_{3-x}$  system (2) single crystals of the perovskite-like phase ( $x > 0.25$ ) could not be grown. Spherically shaped, 0.2-0.1-mm diameter, single crystals, some showing crystal faces, were grown, how-

ever, within the primary field of  $\text{SrMnO}_{3-x}$  perovskite (Fig. 1). The X-ray diffraction powder patterns of crystals grown near  $1490^\circ\text{C}$  show line splitting indicating a small distortion from cubic symmetry. The patterns are of poor quality as previously discussed (1, 2), but can be indexed on the basis of a simple orthorhombic cell or subcell with  $a = 5.44 \pm 0.01 \text{ \AA}$ ,  $b = 3.81 \pm 0.01 \text{ \AA}$  and  $c = 5.42 \pm 0.01 \text{ \AA}$ . The distortion could not be measured, however, in X-ray diffraction single crystal precession photographs. Evidence could not be found for weak superstructure spots that might indicate an ordering of oxygen vacancies. Similar with the results of Negas and Roth (1, 2), the crystals can be oxidized below  $300^\circ\text{C}$  for a few minutes to yield a cubic,  $\text{SrMnO}_3$ , perovskite ( $a = 3.806 \text{ \AA}$ ) characterized by an exceedingly sharp powder pattern. Based on the lattice parameters and the composition ( $x$ ) versus temperature data previously published (2), the  $\text{SrMnO}_{3-x}$  crystals grown at  $1490^\circ\text{C}$  have the stoichiometry  $\text{SrMnO}_{2.70}$  ( $x = 0.30$ ).

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