

Effect of Atmosphere on the Formation of Spinel Solid Solutions in $\text{Mn}_2\text{SnO}_4\text{-Mn}_3\text{O}_4$ System

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The formation of spinel solid solution in the system of $\text{Mn}_2\text{SnO}_4\text{-Mn}_3\text{O}_4$ was studied in flow of argon (99.99% pure) and in air. In argon, a wide region of spinel single phase was observed in the system, although no single phase of spinel at the composition of Mn_2SnO_4 was obtained below 1300°C. In air, only a narrow region of the spinel single phase was obtained in the composition near Mn_3O_4 above 1100°C. These experimental results are discussed in terms of both the stability of manganese ions in a given atmosphere and the existence of Sn^{4+} ions in the octahedral sites of the spinel structure.

Introduction

Hausmannite Mn_3O_4 and the related spinel-type compounds have been extensively studied mostly in relation to the Jahn-Teller effect of the Mn^{3+} ion in the octahedral sites. The critical content of Mn^{3+} ions for showing the tetragonal distortion due to their cooperation has been discussed on the basis of the experimental results on the binary systems between Mn_3O_4 and various spinel-type compounds (1-5).

Gilleo and Mitchel (6) synthesized the manganese-tin spinel containing 0.26 Mn^{3+} ions in the octahedral sites from a stoichiometric mixture of MnO and SnO_2 under purified nitrogen. Nogués and Poix (7) reported that the solid-state reaction between MnO and SnO_2 led to a nonstoichiometric compound of spinel type, and proposed to start from the mixture of SnO and Mn_2O_3 . They prepared the solid solutions in the $\text{Mn}_2\text{SnO}_4\text{-Mn}_3\text{O}_4$ system from the mixture of SnO , Mn_2O_3 , and Mn_3O_4 at 1100°C in a sealed silica tube, and discussed the cation distribution in the spinels (8).

It has also been known that the valence

state of manganese ions depends strongly on the partial pressure of oxygen (9, 10). Therefore, the structure of the solid solutions and also the solid solubility in the $\text{Mn}_2\text{SnO}_4\text{-Mn}_3\text{O}_4$ system have to be studied and understood in relation to the partial pressure of oxygen in the atmosphere where the compounds have been synthesized.

In the present work, the formation of solid solutions in the system was studied in the flow of argon and of air. Quite different solubility ranges were found in both atmospheres. The experimental results are discussed in terms of the stability of manganese ions and the effect of the existence of Sn^{4+} ions in the octahedral sites of spinel structure.

Experimental

The mixture of Mn_3O_4 and SnO_2 in the composition of $\text{Mn}_{2+x}\text{Sn}_{1-x}\text{O}_4$ was heated in platinum crucibles at 1050-1300°C in argon and in air under atmospheric pressure. The argon gas used had a purity of 99.99%. The samples were heated at each temperatures for 24 hr twice. At the end of heating, the samples were cooled in the furnace by cutting the

electric power of the furnace. The cooling rate was roughly 15°C/min. The starting Mn_3O_4 was prepared from the reagent grade $MnCO_3$ by heating up to 1000°C and SnO_2 from the reagent grade $SnCl_2$ by hydrolysis and subsequent heating at 800°C in a flow of oxygen.

The phases formed were identified from the X-ray powder pattern and, on the spinel phase, the lattice constants were measured from 404 and 440 or 511 and 115 diffraction lines, by referring to an internal standard of silicon. The X-rays used were $MoK\alpha$ radiation. The error for the determination of lattice constants was evaluated as $\pm 0.01 \text{ \AA}$, because of low diffraction angles of the lines and sometimes of the broadness of the lines. For the tetragonal spinels (hausmannite type), the parameter $a' (=2^{1/2}a_0)$ was used for the convenience of comparison with the cubic spinel. The existence of the second phase in more than 2% was detected on the X-ray powder pattern in the present work.

Results

The phases identified are summarized in Fig. 1a and Fig. 2a as functions of temperature and composition in argon and in air, respectively. The two-phase regions are shown by open marks and the region for the single phase of spinel solid solution by filled marks. The changes of lattice constants of spinel solid solution with composition are shown in Fig. 1b at 1120°C in argon and in Fig. 2b at 1300°C in air, as typical examples. For tetragonal spinels, the value of $(a'^2c_0)^{1/3}$ is also shown in each figure.

The lattice constants of all spinel solid solutions which appeared in the single phase in argon fell on the relations shown in Fig. 1b at 1120°C. The linear change of a_0 (and $(a'^2c_0)^{1/3}$ for tetragonal spinel) with composition in argon coincided with that reported by Nogués and Poix (8).

The spinels with $x = 0.0-0.4$ obtained at 1300°C were annealed at 1050°C for 190 hr. The decomposition of the single phase of spinel solid solutions with $x = 0.0-0.2$ into SnO_2 and the solid solutions with low concentration of Sn^{4+} was observed.

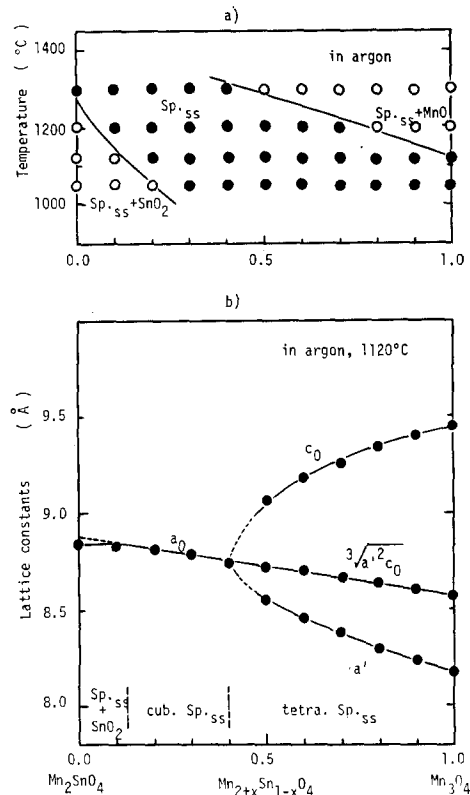
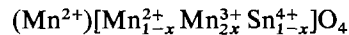


FIG. 1. Phase relation and change of lattice constants in the Mn_2SnO_4 - Mn_3O_4 system in argon.

Discussion

The region of the spinel solid solution was strongly influenced by the stability of the valence of manganese ions in a given atmosphere and probably by the existence of Sn^{4+} ions in the octahedral sites of the spinel structure, as will be explained below. Nogués and Poix (8) showed the cation distribution



for the solid solution $Mn_{2+x}Sn_{1-x}O_4$. This cation distribution suggests that, in order to incorporate Sn^{4+} ions into the spinel structure, the Mn^{3+} and Mn^{2+} ions must coexist on the octahedral sites in the ratio determined by x . Therefore, we may explain the present results in different atmospheres by the balance between the stability of manganese ions, which is determined by the atmosphere where the solid solutions are in equilibrium, and the

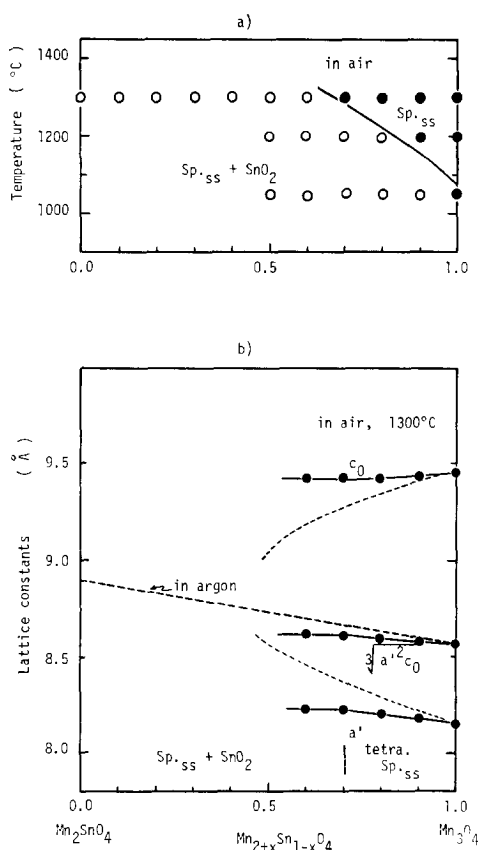


FIG. 2. Phase relation and change of lattice constants in the $\text{Mn}_2\text{SnO}_4\text{-Mn}_3\text{O}_4$ system in air.

effect of existence of Sn^{4+} ions in the octahedral sites.

At low temperatures below 1120°C in argon, Mn^{3+} ions are so stable that the spinel solid solutions are obtained in rather wide ranges of composition at the side of Mn_3O_4 . In order to obtain the spinel at the compositions near $x = 0$, large amounts of manganese ions ($1 - x$) must be in the state of +2. Therefore, it may be said that Sn^{4+} ions in octahedral sites cannot regulate the amount of manganese ions to +2 state enough by overcoming the stability of Mn^{3+} ions. Only at high temperatures, above 1300°C in argon, Mn^{2+} ions became stable and Mn^{3+} unstable. Therefore, the spinel single phase with the $x = 0$ composition can be obtained. Its lattice constant is 8.88 \AA , which is the same as the reported value (8) and the extrapolated value

in Fig. 1b. On the side of Mn_2SnO_4 there is a rather wide range of solid solutions up to $x = 0.4$. The results at 1300°C suggest that Sn^{4+} ions in octahedral sites overcome the stability of Mn^{2+} ions and make manganese ions up to the amount of $0.8 (=2x)$ to the +3 state. At 1200°C in argon, the imperfect balance of these two effects was observed at $x \geq 0.8$. At this region the spinel solid solutions had the lattice constants changing with x , but we could not obtain the single phase. The coexisting manganese oxides were MnO and Mn_3O_4 . This result may be explained as follows: At this temperature, the stability of Mn^{2+} ions is not so high that the valence of manganese ions incorporated into octahedral sites of spinel were regulated by Sn^{4+} ions, as observed at low temperatures. The coexistence of MnO and Mn_3O_4 in the sample after cooling agrees with a low stability of Mn^{2+} ions at this temperature.

At $x = 0$, the single phase of spinel was not obtained below 1200°C . The lattice constant is always smaller than 8.88 \AA , suggesting the existence of Mn^{3+} ions. Gilileo and Mitchel (6) obtained the spinel with the lattice constant of 8.84 \AA in nitrogen atmosphere and concluded the existence of Mn^{3+} ions from the measurement of magnetic susceptibility. A similar phenomenon was found on the cobalt-tin spinel in oxygen at 1200°C , which was explained by the existence of the small amount of Co^{3+} ion (11).

In air, high oxygen partial pressure, much higher than in argon, shifts the stability of Mn^{2+} ions toward higher temperatures. Therefore, the spinel single phase is obtained only in the limited region near Mn_3O_4 . At 1050°C , no incorporation of Sn^{4+} ions into a spinel structure was observed. This is because Mn^{3+} ions are so stable that any manganese ions in the octahedral sites cannot be reduced to the +2 state in order to compensate the charges of Sn^{4+} ions. All of the spinel solid solutions formed at 1120 and 1300°C were tetragonal and the changes of the lattice constants with a composition of x were different from those observed in argon, as shown in Fig. 2b. No second phase was detected even by using a high-power X-ray source. Larger tetragonality of solid solutions

in air suggests the existence of larger amounts of Mn^{3+} ions. We do not know why the lattice constants are different in the spinels prepared in argon and in air. We might assume the cation vacancies in the spinel structure are due to the evaporation of Sn ions or the incorporation of excess oxygen atoms.

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