

On the Formation of Solid Solution in $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ System

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The formation of solid solution in the $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ system in atmospheres of oxygen, air and argon was examined at a constant temperature of 1000 °C. In oxygen, a small amount of the NaCl-type compound was found to co-exist with the cubic spinel in the composition range $x \leq 0.1$. A single phase of the cubic spinel was found in the range 0.1 to 1.3 and the tetragonal spinel above 1.9. In the range $x = 1.3$ to 1.9 where the cubic and tetragonal spinels co-exist they both have very broadened diffraction line profiles. In air, the identified phases and the changes in their lattice constants with composition were very similar to those in oxygen, except that the NaCl-type compound and the cubic spinel co-existed over a larger range. In argon, the cubic spinel was not observed over any of the composition range and the NaCl-type compound and the tetragonal spinel co-existed in the wide range of 1.1 to 2.3. The experimental results are discussed with regard to the cation distribution in the spinel and also to the relative stability of Co^{3+} - and Mn^{3+} -ions under the low partial pressure of oxygen.

1. Introduction

A number of studies have been made on the spinel-type compounds and their solid solutions containing manganese because of their interesting crystallographic, magnetic and electrical properties. Hausmanite Mn_3O_4 has been found to have a Jahn-Teller type tetragonal distortion of Mn^{3+} -ions in octahedral sites of the spinel structure [1]. Wickham and Croft [2] studied the $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ system using X-ray and magnetic measurements and tried to explain the tetragonal distortion of the solid solution from consideration of its cation distribution. Aoki [3] produced a phase diagram of this system and discussed the relation between the tetragonal distortion and the Mn^{3+} -ion content. His phase diagram [3] agrees well with the diagram published later and covers a wider range of temperature [4]. In order to find the overall tetragonal distortion, the critical content of Mn^{3+} -ions in the octahedral sites was concluded to be about 60% in a number of studies on this system [2,3] and on other Mn^{3+} containing spinels [5, 6].

The elements manganese and cobalt are known to have different oxidation states. In systems containing these elements and oxygen

the stability of the oxides depends strongly on the partial pressure of oxygen [7, 8]. Mn_3O_4 is known to be stable up to a higher temperature than Co_3O_4 under the same oxygen pressure, i.e. Mn^{3+} -ions are more stable than Co^{3+} -ions at high temperatures under the same oxygen pressure. Since the formation of a solid solution between Co_3O_4 and Mn_3O_4 was expected to depend strongly on oxygen pressure, the mixtures of Co_3O_4 and Mn_3O_4 were heated at a constant temperature in various atmospheres and the phases formed were examined by X-ray diffraction techniques.

2. Experimental

The starting material Co_3O_4 was prepared by hydrolysis of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (reagent grade) followed by heating to 800 °C in air. Another starting material Mn_3O_4 was made by decomposition of MnCO_3 (reagent grade) at 1000 °C in air. Both starting materials were confirmed by X-ray diffraction techniques to be a single phase. The powder mixtures of Co_3O_4 and Mn_3O_4 in different proportions, which were compressed into discs 5 mm in diameter and 3 mm thick, at a pressure of 3500 kg/cm², were heated at 1000 °C under a flow of argon,

air or oxygen in a tube furnace. The flow rate of gases was about 6 to 8 cc/sec. After the heat-treatment under oxygen and argon, the samples were furnace cooled. After the heat-treatment in air, the samples were rapidly cooled by removal from the furnace. The heated disc was pulverised in an agate mortar and then its powder pattern was taken using a diffractometer with a scintillation counter and pulse-height analyser. The radiation used was Mo $K\alpha$. The lattice constants were determined from the appropriate diffraction lines, which were recorded at a scanning speed of $1/4^\circ/\text{min}$, by referring to an internal silicon standard. The lattice constant a for the cubic spinel was measured from (511) or (400) lines and for the NaCl-type compound from (220) lines with an accuracy of $\pm 0.003 \text{ \AA}$. For the tetragonal spinel, a was measured from (220) lines and c from (004) lines with an accuracy of $\pm 0.005 \text{ \AA}$. For the tetragonal spinel, in the present work, the value of $\sqrt{2}\cdot a$ is shown as a' for convenience.

3. Results and Discussion

The changes of phases and their lattice constants with composition for the heat-treatments under oxygen, air and argon are shown in figs. 1, 2 and 3, respectively.

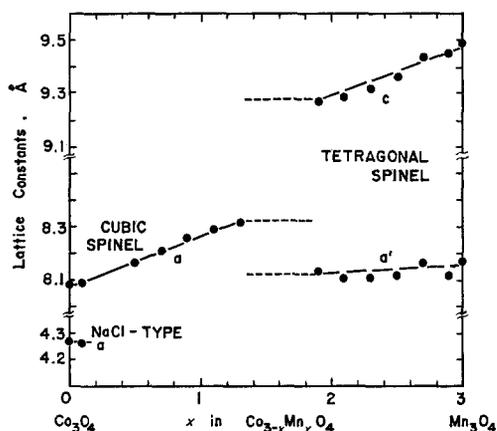


Figure 1 Phases and variation of their lattice constants with composition in oxygen at 1000°C for 48 h.

In oxygen, a small amount of the NaCl-type compound was found in addition to a large amount of cubic spinel in the composition range $x \leq 0.1$. This NaCl-type compound was assumed to be cobaltous oxide CoO from its lattice constant. The solid solubility of Mn^{2+} -ions in CoO was not appreciable from the lattice

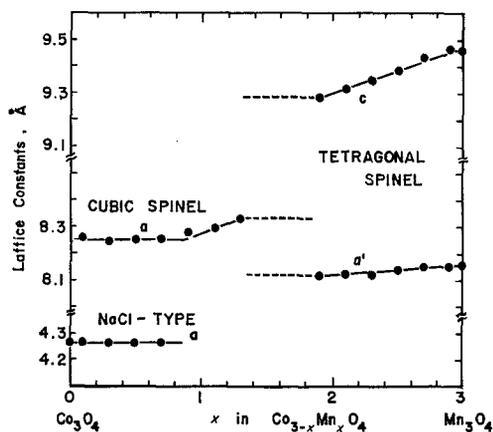


Figure 2 Phases and variation of their lattice constants with composition in air at 1000°C for 48 h.

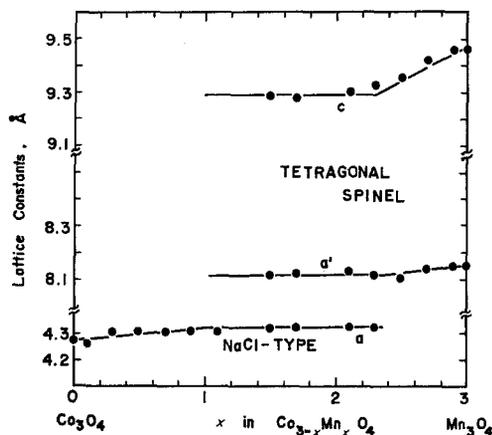


Figure 3 Phases and variation of their lattice constants with composition in argon at 1000°C for 96 h.

constant measurements, although the change of lattice constant of CoO with Mn^{2+} -substitution was very small (a for CoO is 4.2667 \AA , while a for MnO is 4.4448 \AA). In the composition range $0.1 < x < 1.3$ a single phase of the cubic spinel was found. The change of lattice constant with composition could be approximated by a straight line. Between $x = 1.3$ and 1.9 , two phases co-existed, namely the cubic and tetragonal spinels. Above $x = 1.9$, a single phase of the tetragonal spinel was observed, whose lattice constant changed almost linearly with composition.

In air, the phases identified and the changes in their lattice constants with composition were

very similar to those under oxygen. The composition range where the NaCl-type compound co-existed with the cubic spinel, extended however, up to 0.9, being much wider than observed under oxygen.

In argon, the cubic spinel could not be observed over the range of compositions. The NaCl-type compound was detected up to $x = 2.3$, and was obtained as a single phase at $x < 1.1$. From its lattice constant, the substitution of Co^{2+} -ions by Mn^{2+} -ions was assumed. The composition range $x = 1.1$ to 2.3 was a two phase region of the NaCl-type compound and the tetragonal spinel. After 48 h heat treatment, the lattice constant c of the tetragonal spinel showed relatively large scatter. However, it became almost constant after repeating the heat-treatment of 48 h.

It is well known that Mn^{3+} -ions occupy octahedral sites preferentially, and Mn^{2+} and Co^{2+} -ions occupy the tetrahedral sites in the spinel structure [9, 10]. Therefore, it is reasonable to assume that at first the Mn^{2+} -ions in the tetrahedral sites are substituted preferentially with Co^{2+} -ions and then Mn^{3+} -ions in the octahedral site are substituted with Co^{3+} -ions [2, 3, 11]. According to this assumption, the cubic and tetragonal spinels, which co-exist in the range $x = 1.3$ to 1.9 in air and oxygen, have cation distributions of $(\text{Co}^{2+}) [\text{Co}_{0.7}^{3+} \text{Mn}_{1.3}^{3+}] \text{O}_4$ and $(\text{Co}^{2+}) [\text{Co}_{0.1}^{3+} \text{Mn}_{1.9}^{3+}] \text{O}_4$ respectively. Below 1.3, the cubic spinel exists in a stable form. This result suggests that the formed spinel is cubic when less than 65% of the octahedral sites for spinel structure are occupied by Mn^{3+} -ions. This agrees well with the critical content of Mn^{3+} -ions for the tetragonal distortion in the spinel [2, 3, 6]. Boucher *et al* [12] measured the cation distribution in the cubic spinel with $x = 0.6$ to 1.2 from neutron diffraction and magnetic measurements, and confirmed the cation distribution of $(\text{Co}^{2+}) [\text{Co}^{3+}_{2-x} \text{Mn}_x^{3+}] \text{O}_4$ in the composition range examined. However, the tetragonal spinel having the largest Co-ion content of about 37 mol % is the one where almost all octahedral sites are still occupied by Mn^{3+} -ions. According to the phase diagram published [3, 4], the maximum Co-ion content in the tetragonal spinel at 1000°C is around 10% (using the present expression $x = 2.7$). According to Irani *et al* [13], the spinel CoMn_2O_4 ($x = 2.0$) is cubic between 900 and 1250°C. However, this structure is known to be very difficult to quench [6].

In the present work, the sample with $x = 1.7$ was heated at 1000°C for 48 h in air and then quenched into ice. The phases identified in this sample were the tetragonal and cubic spinels. Any appreciable change in powder pattern, even sharpening of the diffraction profile, was hardly detectable between quenched and slowly-cooled samples.

In the composition range $x = 1.3$ to 1.9, diffraction line profiles for both cubic and tetragonal spinels were so broad that only the existence of both phases could be identified from the comparison with the patterns for a single phase, as shown in fig. 4, and the lattice constants could not be measured. No appreciable sharpening of the profiles could be observed even by repeating the heat treatment, giving a total heating time of 96 h and by quenching into ice.

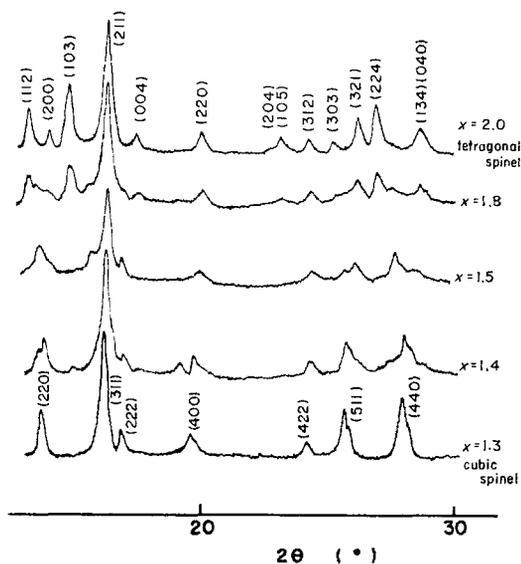


Figure 4 Powder patterns of the samples with different x -values heat-treated in air at 1000°C for 48 h.

In argon, the cubic spinel was not formed, and two phases, namely the tetragonal spinel and the NaCl-type compound, co-existed over a relatively wide range of composition ($1.1 < x < 2.3$). In order to form the cubic spinel with the composition of $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$, Co^{3+} -ions are required, as discussed above. Under low partial pressures of oxygen, however, Co^{3+} -ions are no longer stable and all Co-ions in the system have the oxidation state of +2. Mn^{3+} -ions also tend to reduce to Mn^{2+} but not so notice-

ably as Co^{3+} -ions. Therefore, some of the Mn^{3+} -ions remain stable and form the tetragonal spinel. The tetragonal spinel which has the largest Co^{2+} -ion content is expressed as $(\text{Co}_{0.7}^{2+} \text{Mn}_{0.3}^{2+}) [\text{Mn}_2^{3+}] \text{O}_4$. The remaining Co^{2+} - and Mn^{2+} -ions form the NaCl-type compound. The cubic spinel with $x = 1.3$ which was prepared at 1000°C in air was re-heated to 1000°C in argon and was found to have decomposed to the NaCl-type compound and the tetragonal spinel with almost the same lattice constants as shown in fig. 3. The same results as in fig. 3 were obtained by using CoO as a starting material and heating in argon for 96 h.

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