Short communications

Analytic calculation of cation distribution equilibria in the cubic phase of jacobsite-hausmannite system

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Abstract

Cation and cation vacancy distribution equilibria in the cubic phase of jacobsite-hausmannite solid solution system have been calculated by a defect-chemical approach as a function of some equilibrium constants, partial pressure of oxygen P_{O_2} and compositional ratio x in $Mn_xFe_{3-x}O_4$ ($x = 1$ to 3). The concentration of metal vacancy was zero and a considerable amount of Fe^{2+} in the octahedral site, which was equal to Fe^{3+} in the tetrahedral site, appeared in case of appropriate values of equilibrium constants and small values of P_{O_2} . The distribution results in a fairly good agreement with the reported Mössbauer spectroscopic data. In spite of constant metal ratio, the concentration of Fe^{3+} is lessened with increasing P_{O_2} and metal vacancy in the tetrahedral site appeared considerably. These results suggest that the estimation of temperature and P_{O_2} for formation of natural specimen is possible from the observed values of cation distribution, if some thermodynamic values are known.

Introduction

In our previous work (Osawa *et al.* 1992), we constructed the phase diagram of the $MnFe_2O_4$ - Mn_3O_4 system experimentally under low oxygen partial pressures controlled by hematite-magnetite buffer. We indicated also that the true binary system $MnFe_2O_4$ - Mn_3O_4 appears only under low oxygen pressures and that the inconsistency of lattice parameters of synthesized tetragonal phase with a certain Fe/Mn ratio among previous works was due to the excess of Mn^{3+} in the samples. The excess of Mn^{3+} in the phase was explained by oxidation of Mn^{2+} accompanying the site exchange of Fe^{3+} ,

where V denotes metal vacancy and subscripts T and O stand for the tetrahedral and the octahedral sites respectively. The X-ray study of synthetic $MnFe_2O_4$ revealed that the metal

vacancies were exclusively in the octahedral sites (Yamanaka and Nakahira, 1973).

The oxidation of pure tetragonal hausmannite $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$ was indicated by measurement of the lattice parameters (Kikuchi *et al.*, 1994). However, Eqn. (1) does not express the above case, since the oxidation by the above reaction needs Fe^{3+}_o . The oxidation of pure hausmannite creates Mn^{3+} inevitably in the tetrahedral site Mn^{3+}_t as

Since Mn^{3+} prefers the octahedral site according to Jahn-Teller effect, most of Mn^{3+} will occupy the octahedral site by the following exchange reaction, if enough Fe^{3+}_o presents:

Eqn. (1) is derived by combination of Eqns. (2) and (3). Yoo and Tuller (1988) first calculated the cation distributions in the $\text{Fe}_3\text{O}_4\text{-Mn}_3\text{O}_4$ system by applying a defect-chemical approach. They applied the result to the thermoelectric power data of a ferrite $\text{Mn}_{0.863}\text{Fe}_{2.137}\text{O}_4$ and indicated that the amount of Mn^{3+}_t was very small at low temperatures but was expected to increase as temperature increases. However, their calculations were limited within the true binary system and the influence of metal vacancy and Po_2 were ignored.

At high temperatures, Fe^{2+} can be formed by an interatomic reaction as indicated by Lotgering (1964):

which was confirmed by the Mössbauer spectrum study (Yamanaka, 1972). This reaction produces also an excess of Mn^{3+} .

The equilibrium among the above chemical species in relation to Po_2 are described in the present study.

Formulation

Equilibrium constants K_1 , K_2 and K_3 for Eqns. (2), (3) and (4) are given as

$$K_1 = \frac{[\text{Mn}^{3+}_\text{t}]^{9/4} [\text{V}_\text{o}]^{3/4} [\text{O}^{2-}]}{[\text{Mn}^{2+}_\text{t}]^2 [\text{Mn}^{3+}_\text{o}]^{1/4} \text{Po}_2^{1/2}} \quad (5).$$

$$K_2 = \frac{[\text{Fe}^{3+}_\text{t}] [\text{Mn}^{3+}_\text{o}]}{[\text{Fe}^{3+}_\text{o}] [\text{Mn}^{3+}_\text{t}]} \quad (6).$$

$$K_3 = \frac{[\text{Fe}^{3+}_o][\text{Fe}^{3+}_T][\text{Mn}^{3+}_o]}{[\text{Fe}^{3+}_o]^2[\text{Mn}^{2+}_T]} \quad (7).$$

It is assumed that these constants are independent of x in $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ and the chemical species described are in the cubic phase. The purpose of the following formulation is to express the concentration of eight chemical species, $[\text{Mn}^{2+}_T]$, $[\text{Mn}^{3+}_T]$, $[\text{Mn}^{3+}_o]$, $[\text{Fe}^{2+}_o]$, $[\text{Fe}^{3+}_o]$, $[\text{Fe}^{3+}_T]$, $[\text{V}_o]$ and $[\text{O}^{2-}]$, as a function of K_1 , K_2 , K_3 , Po_2 and x of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$. The other species Fe^{2+}_T , Mn^{2+}_o and V_T are not considered since the concentration of these species must be very small as suggested by many authors (e. g. Yamanaka and Nakahira, 1973).

In addition to Eqns. from (5) to (7), five independent relations are required for calculation of the concentrations. Let us set that the total of concentrations is the number of atoms per formula:

$$[\text{Mn}^{2+}_T] + [\text{Mn}^{3+}_T] + [\text{Mn}^{3+}_o] + [\text{Fe}^{2+}_o] + [\text{Fe}^{3+}_o] + [\text{Fe}^{3+}_T] + [\text{V}_o] + [\text{O}^{2-}] = 7 \quad (8).$$

For the site balance:

$$[\text{O}^{2-}] = 4 \quad (9),$$

$$[\text{Mn}^{2+}_T] + [\text{Mn}^{3+}_T] + [\text{Fe}^{3+}_T] = 1 \quad (10).$$

For the charge balance:

$$2[\text{Mn}^{2+}_T] + 3[\text{Mn}^{3+}_T] + 3[\text{Mn}^{3+}_o] + 2[\text{Fe}^{2+}_o] + 3[\text{Fe}^{3+}_o] + 3[\text{Fe}^{3+}_T] = 2[\text{O}^{2-}] \quad (11).$$

For a given ratio of Fe/Mn ($= \alpha$) which is equal to $(3-x)/x$ of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$:

$$[\text{Fe}^{2+}_o] + [\text{Fe}^{3+}_o] + [\text{Fe}^{3+}_T] = \alpha [\text{Mn}^{2+}_T] + \alpha [\text{Mn}^{3+}_o] + \alpha [\text{Mn}^{3+}_T] \quad (12).$$

After several steps, from Eqns. (6) to (12), the following five concentrations have been described by using K_2 , K_3 , $[\text{Mn}^{2+}_T]$ and $[\text{Mn}^{3+}_T]$ only:

$$[\text{Mn}^{3+}_o] = \frac{-(2\alpha + 1)K_3[\text{Mn}^{2+}_T]^2 + 7K_3[\text{Mn}^{2+}_T] + 8K_2[\text{Mn}^{3+}_T]}{(2\alpha + 3)K_3[\text{Mn}^{2+}_T] + 3(\alpha + 1)K_2[\text{Mn}^{3+}_T]} - \frac{\{(3\alpha + 2)K_2 + (2\alpha + 2)K_3\}[\text{Mn}^{2+}_T][\text{Mn}^{3+}_T] + 3(\alpha + 1)K_2[\text{Mn}^{3+}_T]^2}{(2\alpha + 3)K_3[\text{Mn}^{2+}_T] + 3(\alpha + 1)K_2[\text{Mn}^{3+}_T]} \quad (13).$$

$$[\text{Fe}^{3+}_o] = -(2\alpha + 1)[\text{Mn}^{2+}_T] - 2(\alpha + 1)[\text{Mn}^{3+}_T] - (2\alpha + 3)[\text{Mn}^{3+}_o] + 7 \quad (14),$$

$$[\text{Fe}^{2+}_o] = (3\alpha + 2)[\text{Mn}^{2+}_T] + 3(\alpha + 1)[\text{Mn}^{3+}_T] + 3(\alpha + 1)[\text{Mn}^{3+}_o] - 8 \quad (15),$$

$$[\text{Fe}^{3+}_T] = 1 - [\text{Mn}^{2+}_T] - [\text{Mn}^{3+}_T] \quad (16),$$

$$[\text{V}_o] = 2 - [\text{Mn}^{3+}_o] - [\text{Fe}^{3+}_o] - [\text{Fe}^{2+}_o] \quad (17).$$

Substitutions of Eqns. (13)-(17) to Eqn. (5) and to Eqn. (6) yield, two equations, which entirely consist of parameters, $[\text{Mn}^{2+}_T]$, $[\text{Mn}^{3+}_T]$, K_1 , K_2 , K_3 , Po_2 , and α . Hence,

$[\text{Mn}^{2+}_\text{T}]$ and $[\text{Mn}^{3+}_\text{T}]$ are calculated for a given set of parameters K_1 , K_2 , K_3 , P_{O_2} , and α . Newton-Raphson method was used for the computation.

Result of calculation

Since the thermodynamic values for reactions shown by Eqns. (5) to (7) are not known, values K_1 , K_2 and K_3 were tentatively chosen. Fig. 1 shows the concentrations of ion as a function of x in $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ for a set of values, $K_1=0.01$, $K_2=1000$, $K_3=0.004$ and $P_{\text{O}_2}=10^{-12}$. The large value for K_2 is to reduce the amount of Mn^{3+}_T . It indicates that the concentration of vacancy is nearly zero and a considerable amount of $[\text{Fe}^{2+}_\text{O}]$, which is equal to $[\text{Fe}^{3+}_\text{T}]$, is involved in the formula. The values of $[\text{Mn}^{3+}_\text{T}]$ are less than 10^{-4} throughout the system. The values of $[\text{Fe}^{3+}_\text{O}]$ and $[\text{Fe}^{2+}_\text{O}]$ measured by Mössbauer spectra

FIG. 1. Calculated cation distribution in the cubic phase of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ as a function of x by the data set ($K_1=0.01$, $K_2=1000$, $K_3=0.004$ and $P_{\text{O}_2}=10^{-12}$). The open squares and the filled squares are the measured data for $[\text{Fe}^{3+}_\text{O}]$ and $[\text{Fe}^{2+}_\text{O}]$ respectively by Yamanaka (1972).

collected from a work of Yamanaka (1972) are plotted with open squares and filled squares respectively. The data agree well with the calculated curves. In Fig. 2, the equilibrium constants are the same as in Fig. 1 but a higher oxygen pressure ($P_{O_2}=0.2$). It indicates that Fe^{2+}_O is diminished and a considerable amount of vacancy appeared. The values of $[Mn^{3+}_T]$ are less than 10^{-4} and increased slightly with the increase of x .

The coincidence between the observed values and calculated values shown in Fig. 1 does not mean that the observed values reflect the unique condition of temperature and P_{O_2} . Even so, the present study indicates that the estimation of temperature and P_{O_2} for formation of natural specimen is possible from the observed values of cation distribution if some thermodynamic values for K_1 , K_2 and K_3 are known.

FIG.2. Calculated cation and cation vacancy distribution in the cubic phase of $Mn_xFe_{3-x}O_4$ as a function of x by the data set ($K_1=0.01$, $K_2=1000$, $K_3=0.004$ and $P_{O_2}=0.2$).

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