

## Substitution of Manganese Ions for Iron Ions in Dicalcium Ferrite

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Substitution of manganese ions in  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$  was studied by x-ray diffraction analysis, magnetic and Mössbauer effect measurements. The maximum amount of manganese ions in  $2\text{CaO}\cdot\text{Mn}_x\text{Fe}_{2-x}\text{O}_3$  was determined to be about 0.5 in  $x$  by x-ray diffraction and microstructure analyses. Néel temperature of  $2\text{CaO}\cdot\text{Mn}_x\text{Fe}_{2-x}\text{O}_3$  ( $0 \leq x \leq 0.5$ ) decreased with increase of  $x$ . Lattice parameters of  $2\text{CaO}\cdot\text{Mn}_x\text{Fe}_{2-x}\text{O}_3$  varied depending on the temperature, from which it was quenched, over the range  $500^\circ$  to  $800^\circ\text{C}$ . This phenomenon was explained on the basis of difference in the ion distribution in crystal lattice determined by Mössbauer effect measurement.

### INTRODUCTION

Dicalcium ferrite  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$  has the orthorhombic structure, belonging to the space group  $\text{Pcmn}_{2n}^{16}$ , with lattice parameters:  $a=5.64\text{\AA}$ ,  $b=14.68\text{\AA}$ ,  $c=5.39\text{\AA}$ .<sup>1)</sup> The iron ions occupy two different sites in the crystal lattice of  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ . One site has a tetrahedron environment, while the other an octahedron environment. It was reported that the trivalent ions, such as  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$  and  $\text{Sc}^{3+}$ , were substituted for iron ions on the two lattice sites to a certain degree and the distribution of substituent ions on the two lattice sites were determined by means of the Mössbauer effect.<sup>2)</sup>

In the course of an investigation on the phase equilibria in calcium oxide-manganese zinc ferrite<sup>3)</sup> it was found that divalent zinc ions could not replace the iron ions in  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$  and the iron ions in  $2\text{CaO}\cdot(\text{Mn}_2\text{O}_3)_{1/6}(\text{Fe}_2\text{O}_3)_{5/6}$  were replaced by zinc ions when zinc ions were less than manganese ions. For this phenomenon an explanation was given as follows. Since the electrical neutrality in  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$  is maintained, the divalent zinc ions can not replace the trivalent iron ions. When the manganese and zinc ions are substituted for the iron ions in  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ , the condition for the electrical neutrality requires the presence of  $\text{Mn}^{4+}$  in the resulting compound where the zinc ions are divalent and the iron ions trivalent.

A clear explanation has not yet been made concerning the replacement, the valency state and the distribution of manganese ions in  $2\text{CaO}\cdot\text{Mn}_x\text{Fe}_{2-x}\text{O}_3$ . The purpose of the present investigation is to elucidate these problems.

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## EXPERIMENTALS AND RESULTS

## 1. Preparation of Sample.

Commercial chemicals of highest purity were used as starting materials.  $\text{CaCO}_3$ ,  $\text{MnCO}_3$  and  $\alpha\text{-FeOOH}$  were mixed in stainless steel mills with a methanol medium and dried. The mixtures were compacted and calcined at  $1000^\circ\text{C}$  for 1 hr. The calcined compacts were then crushed in an agate mortar. The powder was pressed at 1 ton per sq. cm, heated at  $1400^\circ\text{C}$  for 25 hr and further at  $1000^\circ\text{C}$  for 1 hr and then quenched to room temperature in air. The sintered specimens thus obtained were ground to fine powder for x-ray analysis, magnetic and Mössbauer effect measurement.

## 2. X-ray Analysis

X-ray examinations were made using a Nippondenshi diffractometer with an iron target. Qualitative identification was made by scanning from 10 to 85 degrees two theta. X-ray patterns of  $2\text{CaO}\cdot\text{Mn}_x\text{Fe}_{2-x}\text{O}_3$  ( $x < 0.5$ ) were closely resemble to that of  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ , showing these specimens to be a single phase. However, diffraction peaks of  $\text{CaMnO}_3$  phase containing iron ions were observed for the specimens with the compositions of  $x > 0.7$ . The lattice parameters of the series of  $2\text{CaO}\cdot\text{Mn}_x$

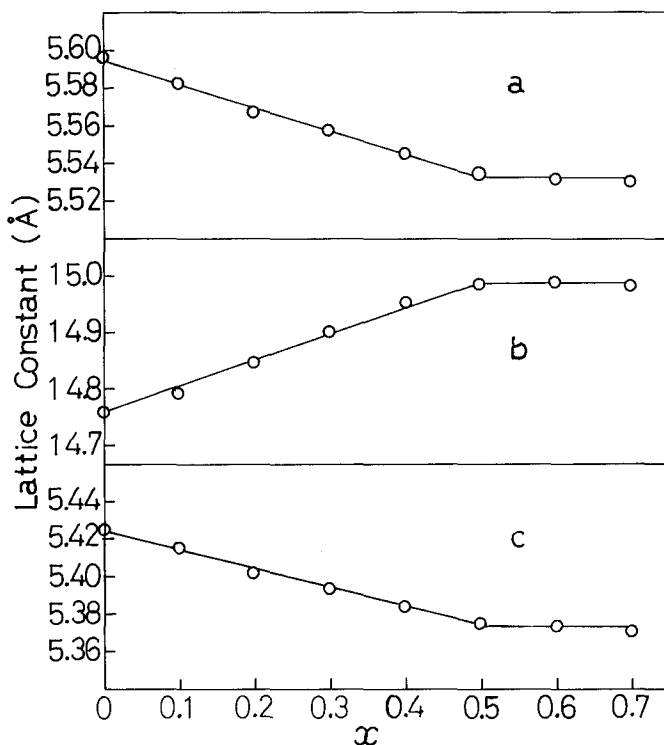


Fig. 1. Variation of lattice constants with  $x$  in  $2\text{CaO}\cdot\text{Mn}_x\text{Fe}_{2-x}\text{O}_3$ .

$\text{Fe}_{2-x}\text{O}_3$  were calculated using the (200), (080) and (202) diffractions for the specimens which were annealed at  $1000^\circ\text{C}$  for 3 hr and quenched to room temperature in air. The results are shown in Fig. 1. It can be seen that the manganese substitution for iron ion in  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$  leads to contraction of lattice parameter  $a$  and  $c$  and expansion of  $b$ . A change in slope is found at  $x=0.5$ . It can be considered that the maximum amount of manganese ions which enter the  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$  lattice structure is nearly equal to  $x=0.5$ .

### 3. Microscopic Examination

Polished sections of the sintered specimens were examined with an Olympus PEM microscope after etched with an aqueous solution of 25% HCl. Microstructures of the specimens are shown in Fig. 2. In the specimens  $x < 0.5$  only a single phase precipitated whereas in those  $x > 0.5$  a second phase co-precipitated. The latter phase seems to be  $\text{CaMnO}_3$  considering from the x-ray data.

### 4. Magnetic Measurement

Magnetic susceptibility was measured with a Shimadzu torsion magnetometer in the range from room temperature to  $873^\circ\text{K}$ . The dicalcium ferrite and the substi-

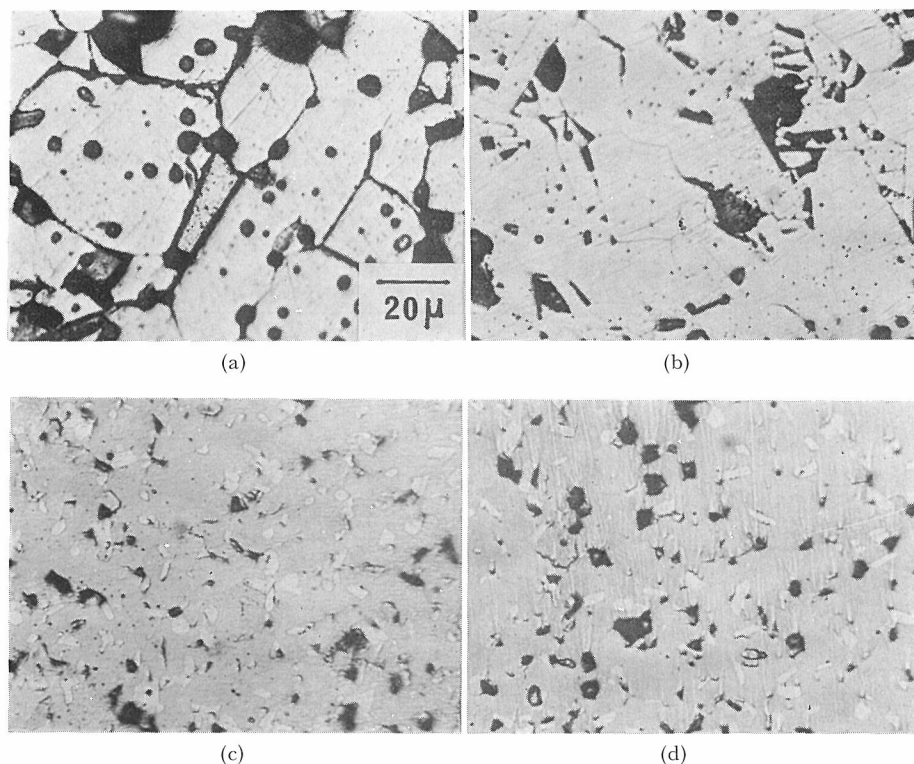


Fig. 2. Microstructures of  $2\text{CaO}\cdot\text{Mn}_x\text{Fe}_{2-x}\text{O}_3$  quenched from  $1300^\circ\text{C}$ .

(a)  $x=0$ , (b)  $x=0.4$ , (c)  $x=0.55$ , (d)  $x=0.6$

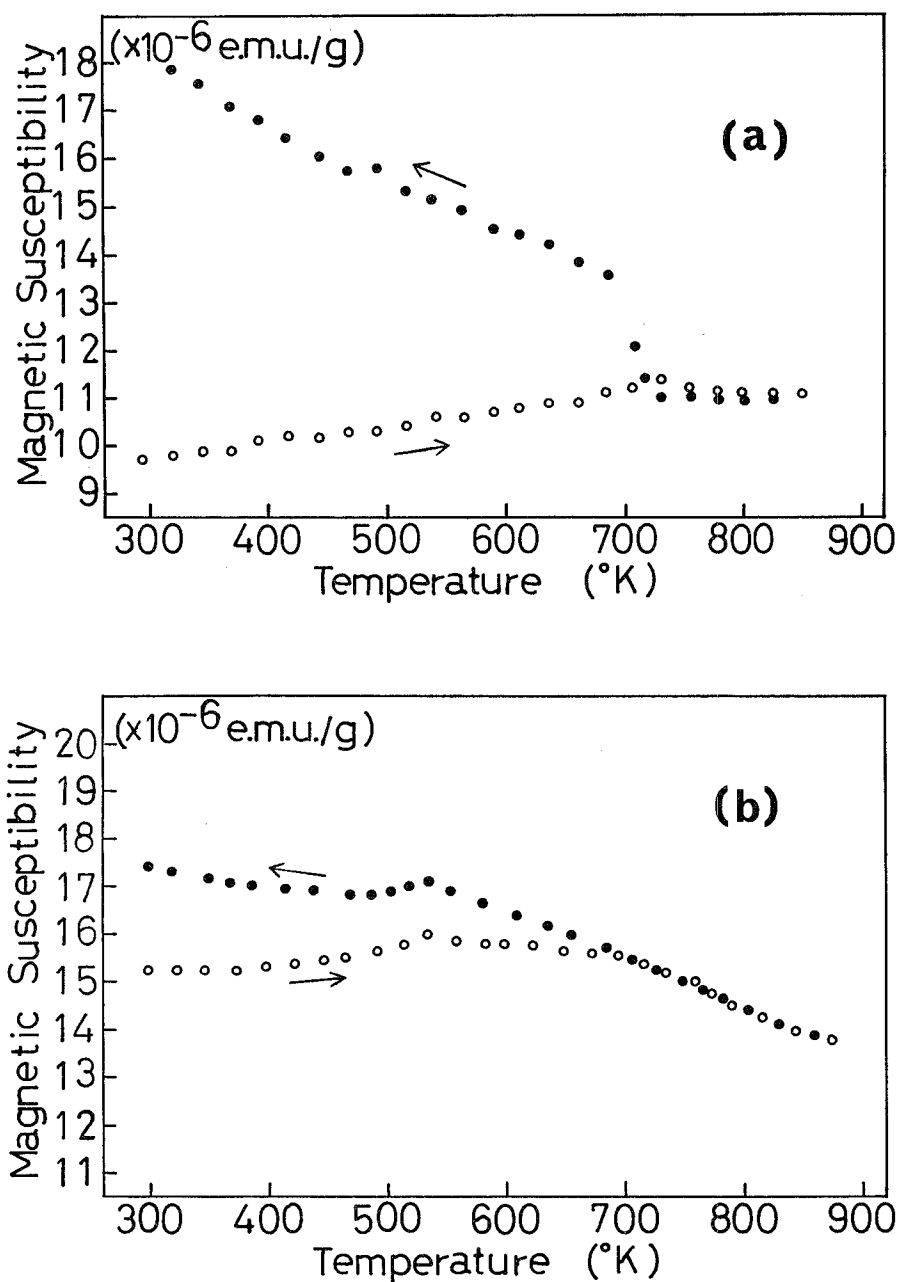


Fig. 3. Temperature dependence of magnetic susceptibilities.

(a)  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ , (b)  $2\text{CaO}\cdot\text{Mn}_{0.3}\text{Fe}_{1.7}\text{O}_3$

tuted compounds were antiferromagnetic and had a spontaneous magnetic moment below Néel temperature when the specimens were cooled down from above Néel temperature in magnetic field (Fig. 3.) As shown in Table 1, Néel temperature

Table 1. Néel Temperatures for  $2\text{CaO}\cdot\text{Mn}_x\text{Fe}_{2-x}\text{O}_3$ 

x	Néel temperature (°K)
0	730
0.1	628
0.2	593
0.3	539

decreased with increase of an amount of manganese ions in the solid solution. This phenomenon can be considered to be caused by the replacement of the iron ions in the crystal lattice of  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$  with the manganese ions.

#### 5. Variation of Lattice Parameters of Mn Substituted Dicalcium Ferrite with Heat Treatment.

The powders of  $2\text{CaO}\cdot\text{Mn}_{0.3}\text{Fe}_{1.7}\text{O}_3$  were heated previously at  $1000^\circ\text{C}$  for 1 hr, slowly cooled to desired temperatures above  $500^\circ\text{C}$ , kept at the temperatures for 1

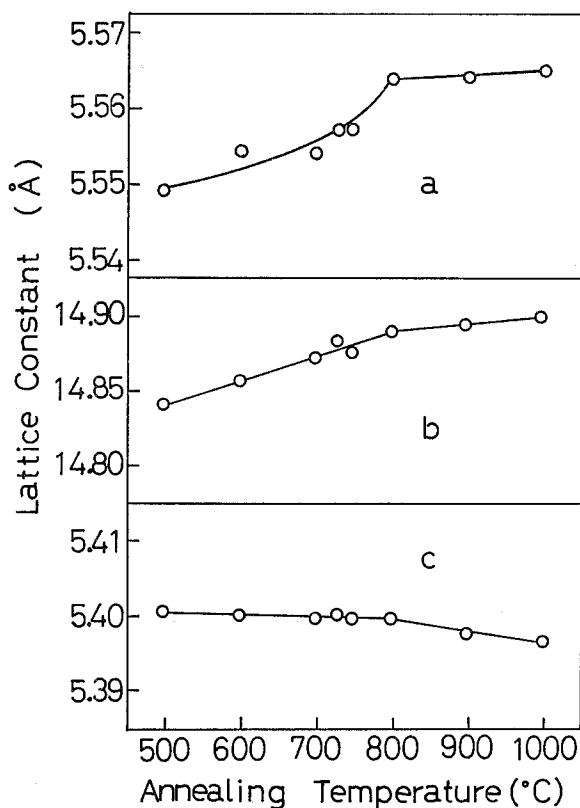


Fig. 4. Variation of lattice constants of  $2\text{CaO}\cdot\text{Mn}_{0.3}\text{Fe}_{1.7}\text{O}_3$  with annealing temperature.

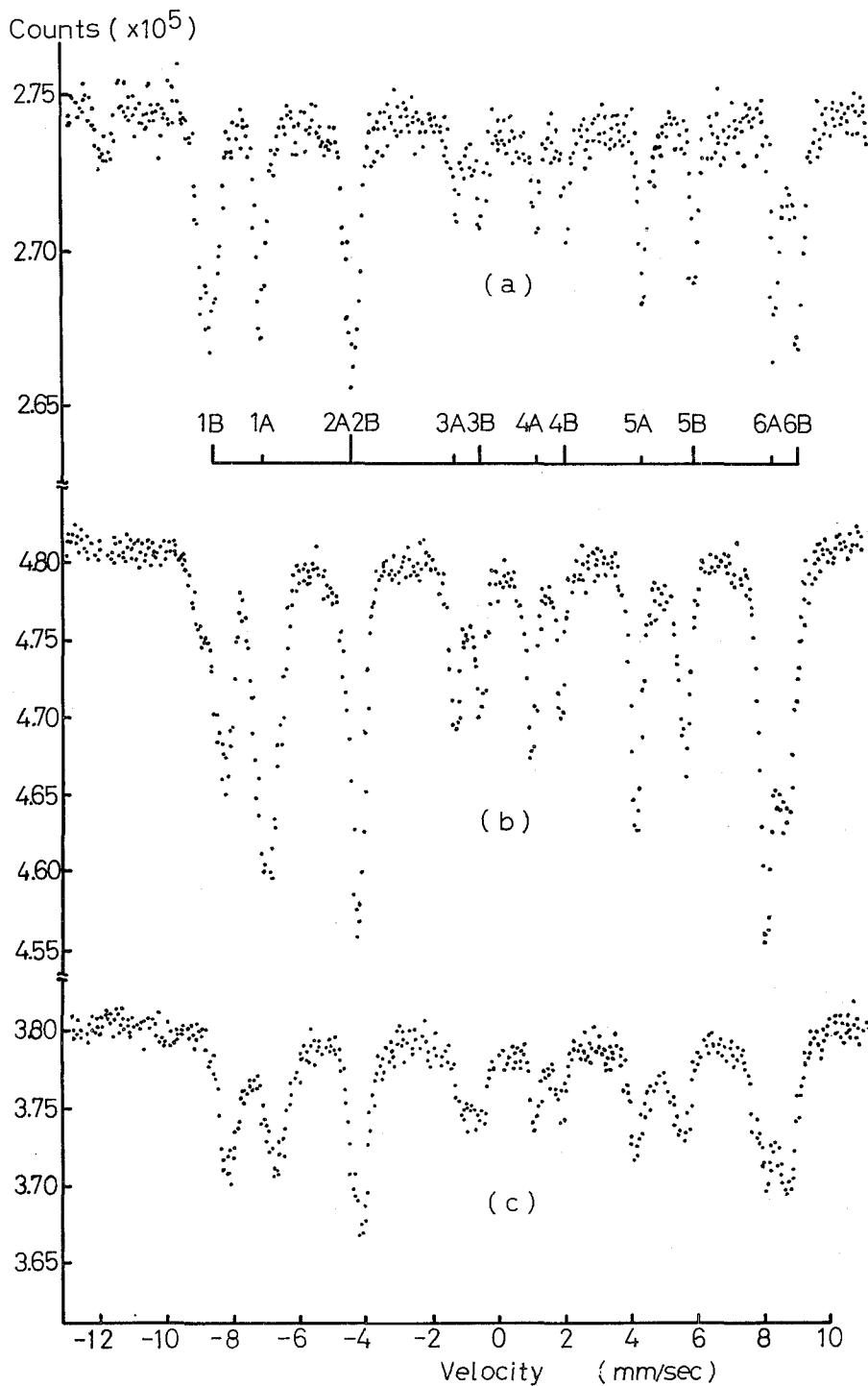


Fig. 5. Mössbauer spectra of (a)  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ , (b)  $2\text{CaO}\cdot\text{Mn}_{0.3}\text{Fe}_{1.7}\text{O}_3$  quenched from  $1200^\circ\text{C}$  and (c)  $2\text{CaO}\cdot\text{Nn}_{0.3}\text{Fe}_{1.7}\text{O}_3$  annealed at  $500^\circ\text{C}$  for 20 hr.

to 25 hr in air to obtain equilibrium state, and quenched in water. Variation of lattice parameters of the specimens with annealing temperature is shown in Fig. 4. When the annealing temperature was above 800°C, there was little variation in lattice parameters. In the range lower than 800°C, however, the lattice parameters *a* and *b* decreased and *c* increased with decreasing annealing temperature. The similar feature was observed for the other specimens having a different amount of manganese ions.

The variation of lattice parameters is considered to be caused by the alternation of the valency state and the ion distribution of the manganese ions. This was confirmed by the following Mössbauer effect measurement.

## 6. Mössbauer Effect Measurement

Mössbauer effect measurements at liquid nitrogen temperature were carried out using an apparatus consisting of Erlon's driving unit and Nothern Scientific Co's 1000 channel pulse height analyzer. Calibration of the velocity scale was made using pure Fe and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as standard absorbers. Figure 5(a) shows the Mössbauer spectra of 2CaO·Fe<sub>2</sub>O<sub>3</sub>. The spectrum consists of two six line spectra of equal intensity (the larger internal field corresponding to the octahedral sites). The two spectra are well-separated and the magnetic splitting is different. The spectrum of 2CaO·Mn<sub>0.3</sub>Fe<sub>1.7</sub>O<sub>3</sub> heated at 1200°C is shown in Fig. 5(b). This figure indicates a similar splitting to that presented in Fig. 5(a). However, the intensities of two spectra representing the two sites are very different and the intensity ratio is 0.7. Therefore, it is clear that all of the manganese ions locate at the octahedral sites. Figure 5(c) shows the spectrum of the specimens annealed at 500°C for 24 hr. The spectrum consists of two six line spectra of equal intensity. In this case, manganese ions locate equally at octahedral and tetrahedral sites. This fact shows that the variation of lattice constants with the quenching temperature is mainly caused by that of ion distribution. This variation would lead the crystal toward a more ordered and more stable form at higher temperature.

It may be necessary to consider change of valency of manganese ions with heat treatment. However, the valency of manganese ions could not be directly confirmed by means of chemical analysis and chemical shift measurement of fluorescent x-ray. The details of the valency state will be published elsewhere in the near future.

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