

Phase Equilibria in the System Calcium Oxide-Manganese Zinc Ferrite

Yoshichika BANDO, Takeshi KATO, Yasunori IKEDA and TOSHIO TAKADA*

Received September 16, 1968

The phase diagram for the system $\text{CaO-Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at temperatures ranging from 1150°C to 1350°C in air was determined using the quenching technique and the thermal analysis. The 3:1 compound of $3\text{CaO}\cdot\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_{4.5}$ (or $2\text{CaO}\cdot\text{Mn}_{1/3}\text{Zn}_{1/3}\text{Fe}_{4/3}\text{O}_3$) was detected in this system. This compound was confirmed to have the orthorhombic lattice of $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ type by x-ray diffraction examination and the Mössbauer effect measurement. Between $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and the 3:1 compound was one eutectic at 1277°C with the composition of 62.0 mol% CaO. The solid solution limit of the 3:1 compound in the ferrite was determined to be 12.2 mol% CaO at 1277°C.

I. INTRODUCTION

It has been known that electrical resistivity of ferrites extremely increases with the addition of minor amounts of $\text{CaO}^{1)}$ or CaO and $\text{SiO}_2^{2)}$. The reason for the increase with addition of CaO and SiO_2 has been studied in details. It was suggested from measurements of frequency dependence of resistivity that a ferrite containing 1/10 of 1% (by weight) CaO and SiO_2 would have an inhomogeneous dielectric structure which consists of electrically conducting grains and insulating layers separating the grains. This structure was confirmed by radioautography and other techniques; CaO and SiO_2 were highly localized at the grain boundaries to form insulating layers. The substance existing at grain boundaries was considered to have a composition of $(\text{Ca}_{1-x}\text{Si}_x\text{O}_3)_{1-y}$ (ferrite) $_y$. A possible explanation of the formation of this substance is that a liquid phase containing CaO and SiO_2 may have been formed at the grain boundaries at the sintering temperature. To check this assumption, informations are necessary on phase diagrams of a ternary system of $\text{CaO-SiO}_2\text{-Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and binary systems of $\text{CaO-Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ or $\text{SiO}_2\text{-Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. The present work deals with the phase diagram of the system $\text{CaO-Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$.

II. EXPERIMENTAL

1. Sample Preparation

Specimens of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ were prepared from MnCO_3 (99.99 wt%), ZnO (99.995 wt%), and highly pure $\alpha\text{-FeOOH}$ (with maximum content of 0.002 wt% SiO_2 and 0.005 wt% CaO). These raw materials were mixed in the mol ratio 1:1:4, and calcined at 1000°C for 2 hr in air. Calcination was followed by pulverization. This powder was pressed at 2 ton per sq. cm, heated at 1200°C for 2 hr and then quenched in water. The ferrite sample thus obtained was then ground to fine powder for the use of equilibrium study.

* 坂東尚周, 加藤 毅, 池田靖訓, 高田利夫: Laboratory of Solid State Chemistry. Institute for Chemical Research, Kyoto University, Uji, Kyoto.

2. Determination of Phase Diagram

The phase diagram of $\text{CaO-Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was determined using the quenching technique and the thermal analysis. Mixtures of various compositions in this system were lightly tamped into the 3 mm capsules, which were formed by winding of 0.2 mm platinum wire. The mixtures were kept at various temperatures for 6 hr~10 hr in air to obtained equilibrium state and then quenched in water. Phases present in the samples were identified by microscopy and x-ray diffraction using Fe-K α radiation. The temperature of heating was limited in this experiment to the range from 1150°C to 1350°C in consideration of noticeable loss in zinc above 1400°C and precipitation of $\alpha\text{-Fe}_2\text{O}_3$ below 1100°C. The liquidus and eutectic were determined by the thermal analysis with a Pt-Pt10Rh thermocouple and a pure platinum capsule. Samples were heated at 1350°C for 1 hr and then the furnace was cooled at the rate of 15°C/min. The Mössbauer effect was measured by "TMC set" consisting of Gammascop 102, Drive Unit 306 and Transducer 305.

III. RESULTS AND DISCUSSION

1. Phase Diagram

The equilibrium diagram of the system is presented in Fig. 1. A 3:1 compound ($3\text{CaO} \cdot \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_{4-1.5x}$) was detected in this study. X-ray powder pattern of this compound showed a close resemblance to that of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (see Table 1). According to the x-ray studies made by Bertaut *et al*⁽³⁾, dicalcium ferrite $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ has the orthorhombic structure with the lattice parameters: $a=5.64$, $b=14.68$ and $c=5.39$ Å. From comparison with x-ray patterns of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, it was found that the 3:1 compound have the orthorhombic structure with the calculated lattice parameters: $a=5.54$, $b=14.80$ and $c=5.33$ Å.

Solid solution limit of the 3:1 compound in the manganese zinc ferrite was

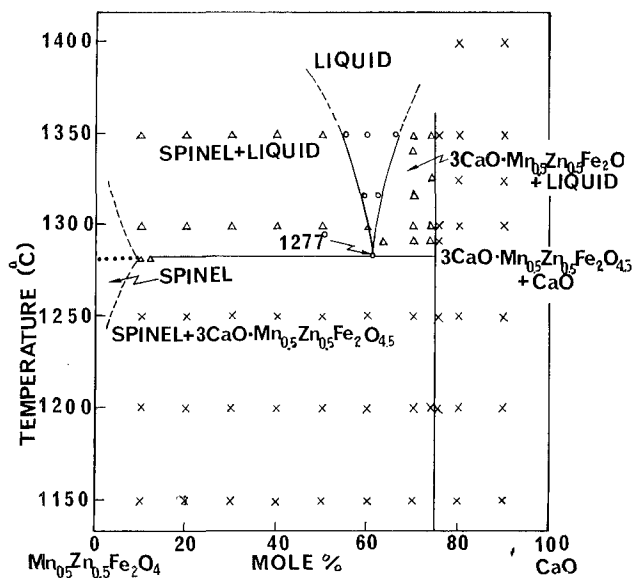


Fig. 1. The phase diagram of $\text{CaO-Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (Condensed phases in equilibrium with air).

Phase Equilibria in Calcium Oxide-Manganese Zinc Ferrite

Table 1. X-ray diffraction data for $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ ³⁾ and $3\text{CaO}\cdot\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_{4+x}$

hkl	$2\text{CaO}\cdot\text{Fe}_2\text{O}_3$		$3\text{CaO}\cdot\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_{4+x}$	
	d (Å)	I/I ₀	d (Å)	I/I ₀
020	7.36	40	7.42	20
110	5.23	10	5.19	10
101	3.88	20	3.86	20
130, 040	3.68	40	3.69	30
131	3.05	20		
200	2.78	70	2.78	45
002	2.71	60	2.69	50
141	2.67	100	2.68	100
150	2.60	20	2.61	25
221, 151	2.35	10		
240	2.22	10		
132, 042	2.18	30	2.17	10
161	2.07	50	2.08	20
202	1.94	70	1.93	40
251	1.90	10		
222	1.88	20		
080	1.84	40	1.85	45
330	1.74	30	1.73	5
181, 072	1.66	10	1.66	5
133	1.62	20		
341	1.59	40	1.58	20
143	1.55	40	1.55	10
280	1.54	10		
082	1.52	20	1.52	10

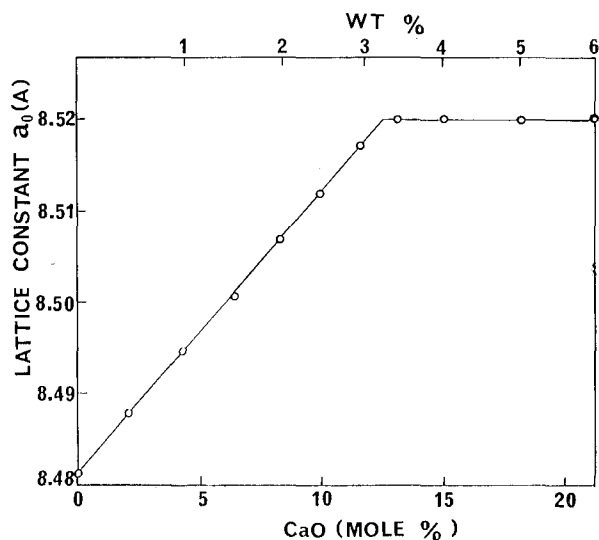


Fig. 2. Lattice constant in the system $\text{CaO-Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Specimens were heated at 1277°C.

determined by measuring the lattice constant of the ferrite. The ferrite has a spinel structure, and the lattice constant of the pure ferrite was determined to be 8.4812 Å with (731) and (553) lines using Fe-K α_1 and Fe-K α_2 radiations. The lattice constant of the series of spinel-the 3:1 compound, all equilibrated at 1277°C for 12 hr, was plotted against composition in Fig. 2. The horizontal line gives the maximum change in the lattice constant observed in a two-phase mixture, suggesting that solid solution of the 3:1 compound in spinel extends to approximately 12.2 mol% CaO at 1277°C.

The eutectic between the ferrite and the 3:1 compound was located at 1277°C with a composition containing 62.0 mol% CaO. This temperature was obtained by thermal analysis of samples containing 60.0, 62.0 and 64.0 mol% CaO. The photomicrograph for the composition containing 62.0 mol% CaO (Fig. 3) is essentially

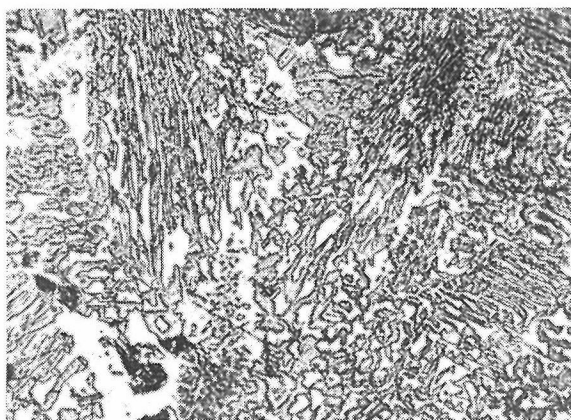


Fig. 3. Microstructure of sample of composition 62.0 mol% CaO (Etched $\times 400$)

all eutectic and is the basis for positioning the eutectic at this composition. The liquidus line was determined by the quenching technique and thermal analysis below 1350°C as shown in Fig. 1. The solid solubility of the ferrite or CaO in the 3:1 compound was not observed both by x-ray diffraction and in microstructure.

2. The 3:1 Compound

The 3:1 compound was determined to have the $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ -type structure. The space group of $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ was classified as Pcmn (D_{2h}^{16}). Bertaut *et al.*⁽³⁾ suggested that the iron ion should be found on two different sites in the crystal lattice of $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$. One of the sites has a tetrahedron environment, the other an octahedron environment. The replacement of the iron ions on the two lattice sites by the manganese and zinc ions was analysed by x-ray diffraction and the Mössbauer technique. In $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ the replacement of the iron ions by the manganese ions caused a change in the lattice parameter. The formula for this system is $2\text{CaO}\cdot(\text{Mn}_2\text{O}_3)_x\cdot(\text{Fe}_2\text{O}_3)_{1-x}$. For $0 < x < 0.25$ homogeneous crystals could be obtained by calcination of mixture of CaCO_3 , MnCO_3 and $\alpha\text{-Fe}_2\text{O}_3$. The zinc ions could be observed not to replace the iron ions in $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ by x-ray diffraction examination; there existed three phases of CaO, ZnO and $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ in the composition of $2\text{CaO}\cdot x\text{ZnO}\cdot(1-x/2)\text{Fe}_2\text{O}_3$ ($x = 0.05 \sim 0.2$). However, the iron ions in $2\text{CaO}\cdot(\text{Mn}_2\text{O}_3)_{1/6}\cdot(\text{Fe}_2\text{O}_3)_{5/6}$ were replaced by the zinc ions when the zinc ions were less than the manganese ions.

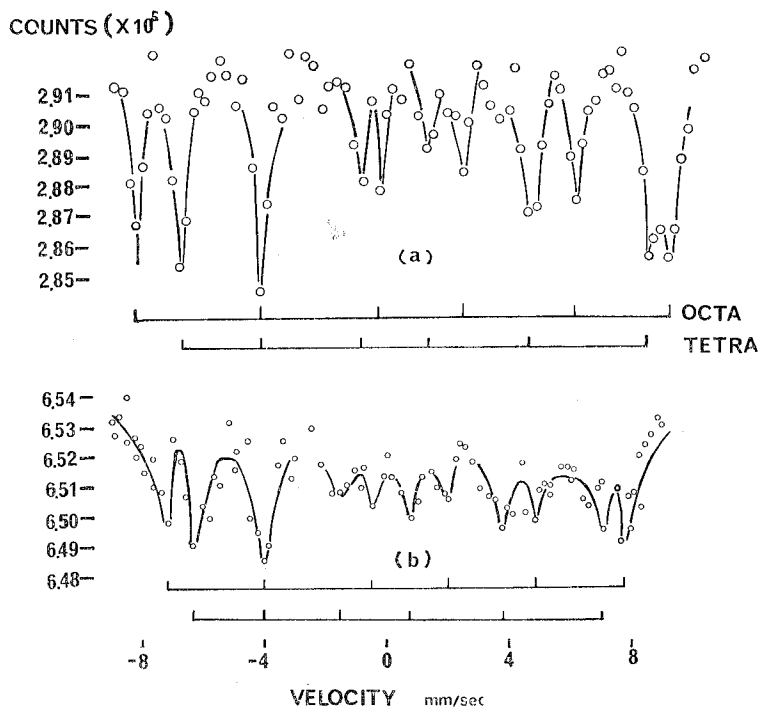


Fig. 4. Mössbauer spectra at the liquid nitrogen temperature:
 (a) $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (b) $3\text{CaO} \cdot \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_{4.5}$

The hyperfine structure of the 14.4 KeV nuclear resonance line of Fe^{57} in $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ at the liquid nitrogen temperature is shown in Fig. 4a. It has been reported that the spectrum with the smaller magnetic splitting is caused by Fe^{57} ions on the tetrahedron sites and another spectrum on the octahedron sites⁴). The hyperfine spectrum of Fe^{57} on the 3:1 compound at the liquid nitrogen temperature is shown in Fig. 4b. The intensities of the two spectra representing the two lattice sites are also equal. This spectrum reconfirmed that the 3:1 compound had $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ -type structure. The hyperfine fields at the tetrahedron and octahedron sites of the 3:1 compound are both smaller than those of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$. The values of isomer shift of Fe^{57} ions on the tetrahedron and octahedron sites are almost equal to those of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ respectively. The same values of the isomer shift indicate that all iron ions are present as trivalency. As the manganese and zinc ions are assumed to replace the iron ions in $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, electrical neutrality requires the presence of Mn^{4+} in the 3:1 compound, where the zinc ion is divalent and the iron ion trivalent. Therefore, the composition of the 3:1 compound was considered to be $3\text{CaO} \cdot \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_{4.5}$ or $2\text{CaO} \cdot \text{Mn}_{1/3}\text{Zn}_{1/3}\text{Fe}_{4/3}\text{O}_3$. The diagram in this experiment is not truly binary, because cation is present in different oxidation state in the various composition ratios. The investigation on replacement of the iron ions by various metallic ions in $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ will be reported elsewhere in the future.

IV. CONCLUSION

The following conclusions may be drawn from the present investigation:

- (1) The existence of the compound $3\text{CaO} \cdot \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_{4.5}$ was confirmed from investigation of phase diagram in the system $\text{CaO}-\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. The compound has $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ -type structure, with $a=5.54$, $b=14.80$ and $c=5.33$ Å.
- (2) The eutectic between the ferrite and the compound is located at 1277°C with a composition containing 62.0 mol% CaO.
- (3) The solid solution limit of $3\text{CaO} \cdot \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_{4.5}$ in the ferrite is 12.2 mol% CaO at 1277°C .

REFERENCES

- (1) C. Guillaud, M. Paulus and R. Vantier, *Compt. Rend.*, **4**, 2712 (1956).
- (2) T. Akashi, *Trans. Japan Inst. Metals*, **2**, 171 (1961).
T. Akashi, *J. Appl. Phys. Japan*, **30**, 928 (1961).
T. Akashi, *Funtai Oyobi Funmatsuyakin*, **8**, 101 and 195 (1961).
- (3) E. F. Bertaut, P. Blum and A. Sagrieres, *Acta cryst.*, **12**, 149 (1959).
- (4) F. Pobell and F. Wittmann, *Phys. Letters*, **19**, 175 (1965).