

## Crystallization and Phase Transformation of Sodium Orthoferrites

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Upon heating mixtures of  $\alpha$ - $\text{Fe}_2\text{O}_3$  powder in a sodium hydroxide melt at around  $200^\circ\text{C}$ , unstable  $\beta$ - $\text{NaFeO}_2$  crystallizes in the first reaction stage and transforms spontaneously to stable  $\alpha$ - $\text{NaFeO}_2$ . The process is typical of the Ostwald Step Rule. When  $\gamma$ - $\text{Fe}_2\text{O}_3$  is used as the starting material, instead of  $\alpha$ - $\text{Fe}_2\text{O}_3$ , stable  $\alpha$ - $\text{NaFeO}_2$  always crystallizes out. It was clearly observed that even though the reactions are of the dissolution and recrystallization type, three-dimensional structural relations can be preserved between the reactant and the product crystals. The nucleation mechanism is discussed on the basis of topotaxy.

### Introduction

The low-temperature phase of  $\text{NaFeO}_2$ ,  $\alpha$ - $\text{NaFeO}_2$ , crystallizes with a  $\text{CsCl}_2$ I-type structure ( $D_{3d}^5-R\bar{3}m$ ) (1), and transforms at  $760^\circ\text{C}$  (2) to the high-temperature phase,  $\beta$ - $\text{NaFeO}_2$  ( $C_{2v}^9-Pna2_1$ ) (3). The phase transformation involves the rearrangement of the first coordination of  $\text{O}^{2-}$  around both the  $\text{Na}^+$  and  $\text{Fe}^{3+}$ .

When fine particles ( $\sim 0.2 \mu\text{m}$ ) of  $\alpha$ - $\text{Fe}_2\text{O}_3$  ( $\text{Cr}_2\text{O}_3$ -type structure) are heated in a large volume of  $\text{NaOH} \cdot n\text{H}_2\text{O}$  melt at low temperatures, around  $200^\circ\text{C}$ , the unstable  $\beta$ - $\text{NaFeO}_2$  form crystallizes out as very coarse triangular prisms ( $\sim 0.1 \text{ mm}$  long) in the first stage and then transforms spontaneously to stable  $\alpha$ - $\text{NaFeO}_2$ , which appears as tiny rhombohedra several microns in size. The processes follow the Ostwald Step Rule. The phase transformation from the  $\beta$  to the  $\alpha$  phase obeyed a kinetic equation of the first order with an activation energy of approximately 23 kcal/mole (4). The aim of this paper is to discuss the mechanisms of the reaction which takes

place and is typical of the Ostwald Step Rule.

### Experimental

#### Materials

An analytical reagent grade of very fine-grained  $\alpha$ - $\text{Fe}_2\text{O}_3$  powder ( $0.2 \mu\text{m}$  in mean diameter) was employed.  $\gamma$ - $\text{Fe}_2\text{O}_3$  was obtained by the oxidation of magnetite prepared by the Harber method (5). The particles of the oxide were almost perfect cubes of  $0.2 \mu\text{m}$  mean edge length. Monotropic transformation from the  $\gamma$  form to the  $\alpha$  form was observed above  $350^\circ\text{C}$ .

The sodium hydroxide and sodium carbonate used were analytical reagent grade chemicals.

#### Sample Preparation

Varying amounts of  $\text{NaOH}$  and  $\text{Fe}_2\text{O}_3$  were mixed with a small amount of water. The slurry was placed in a Ag boat which was inserted into the hot zone of a quartz tube through which air free from  $\text{CO}_2$  was gently passed. It is to be noted that the

excess of NaOH added over the stoichiometric composition of  $\text{NaFeO}_2$  played a very important role in the reaction.

### X-Ray Analysis

The agglomerated samples were powdered and examined in an X-ray diffractometer using  $\text{FeK}\alpha$  radiation. The percentage of the crystalline phases present in each sample was determined by measuring the relative intensities of the two strongest peaks,  $(10\bar{1}4)$  and  $(11\bar{2}0)$  for  $\alpha\text{-Fe}_2\text{O}_3$ ,  $(220)$  and  $(311)$  for  $\gamma\text{-Fe}_2\text{O}_3$ ,  $(111)$  and  $(211)$  for  $\alpha\text{-NaFeO}_2$ , and  $(110)$  and  $(120)$  for  $\beta\text{-NaFeO}_2$ . Prior to these measurements, the standardization curves were determined. Precautions were taken to avoid preferred orientations in the coarse crystals.

### Results and Discussion

Typical curves showing the isothermal changes during the crystallization and phase transformation of sodium orthoferrites are shown in Fig. 1. The starting materials consisted of 0.05 mole of either  $\alpha$  or  $\gamma\text{-Fe}_2\text{O}_3$  and 0.15 mole of NaOH with a small amount of water added.

From observations of the crystallization of the two polymorphs of sodium orthoferrite, a number of conclusions which have an important bearing on the reaction mechanism are apparent. These are summarized as follows:

(1) The solid-liquid-type reactions take place in the presence of liquid phase sodium hydroxide at very low heating temperatures, around  $200^\circ\text{C}$ ;

(2) Starting from the slurry of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{NaOH-H}_2\text{O}$ , unstable  $\beta\text{-NaFeO}_2$  crystals were invariably formed in the first reaction stage. The crystals were very coarse prismatic columns as large as 0.1 mm in length. Crystallization was observed even at temperatures as low as  $120^\circ\text{C}$ ;

(3) After prolonged heating at higher temperatures, above about  $150^\circ\text{C}$ , the unstable

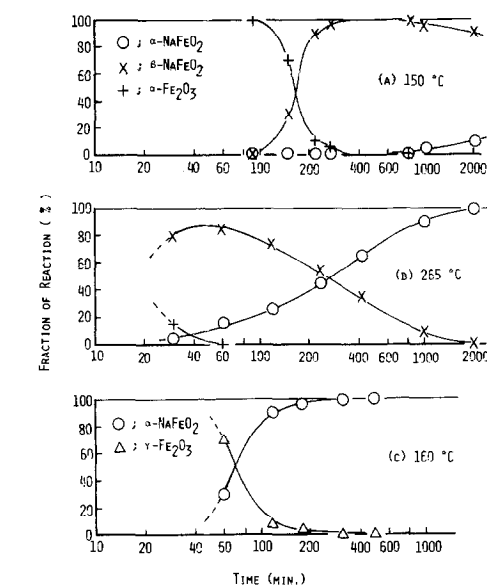


FIG. 1. Representative isotherms for the  $\alpha\text{-Fe}_2\text{O}_3\text{-NaOH} \cdot n\text{H}_2\text{O}$  and  $\gamma\text{-Fe}_2\text{O}_3\text{-NaOH} \cdot n\text{H}_2\text{O}$  systems.

$\beta\text{-NaFeO}_2$  crystals dissolved and stable  $\alpha\text{-NaFeO}_2$  crystals appeared spontaneously in the form of very tiny hexagonal plates or rhombohedra of the order of  $10\ \mu\text{m}$  in size;

(4) The crystallization of the unstable  $\beta\text{-NaFeO}_2$  phase bears out the Ostwald Step Rule that unstable phases are often formed under conditions where another phase should be stable;

(5) A condition required for the spontaneous transformation of the unstable  $\beta\text{-NaFeO}_2$  into the stable  $\alpha\text{-NaFeO}_2$  is the coexistence of liquid phase sodium hydroxide, which may act as a solvent or flux for the sodium orthoferrites. It was confirmed that in the absence of this liquid phase, the unstable  $\beta\text{-NaFeO}_2$  crystals remain unchanged even after heating for 3 weeks at temperatures up to as high as  $700^\circ\text{C}$ ;

(6) Replacing  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$  fine powders were heated with  $\text{NaOH} \cdot n\text{H}_2\text{O}$  melts at various temperatures. The only phase produced was the stable  $\alpha\text{-NaFeO}_2$  phase, the  $\beta$ -phase never being formed (Fig. 1c). The  $\alpha\text{-NaFeO}_2$  crystals were tiny rhom-

boheda with an average size of 10  $\mu\text{m}$ ;

(7) The solid-liquid-type reactions in the formation of  $\alpha$ - and  $\beta$ - $\text{NaFeO}_2$ , and the phase change from  $\beta$  to  $\alpha$  phase, are typical of dissolution and crystallization reactions.

Prior to discussing the solid-liquid-type reactions, it would seem worthwhile to analyze the solid state formation of sodium orthoferrites, which may give some strong clues to the problems. The results of this analysis are summarized as follows:

(1) If, instead of sodium hydroxide, sodium carbonate is mixed with the ferric oxides, the reaction proceeds by solid-solid-type reactions, and the formation of sodium orthoferrites is observed on heating samples to temperatures as high as above 600°C;

(2) From mixtures of  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{CO}_3$ , the unstable  $\beta$ - $\text{NaFeO}_2$  invariably formed. The Ostwald Step Rule is also observed;

(3) In the dry condition, the unstable  $\beta$ - $\text{NaFeO}_2$ , once formed, did not transform to  $\alpha$ - $\text{NaFeO}_2$ ;

(4) If fluxes are added, such as 0.87  $\text{PbO}$ –0.13  $\text{B}_2\text{O}_3$  or a eutectic  $\text{NaCl}$ – $\text{Na}_2\text{CO}_3$  mixture, in the ratio 1:0.5 by weight, the phase transformation from the unstable  $\beta$  to the stable  $\alpha$  phase was clearly observed at around 700°C (4). The most effective flux was liquid phase sodium hydroxide;

(5) On heating mixtures of  $\gamma$ - $\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{CO}_3$ , the stable  $\alpha$ - $\text{NaFeO}_2$  phase was formed at temperature above 600°C. It is to be noted, however, that in the course of the reaction  $\gamma$ - $\text{Fe}_2\text{O}_3$  is stabilized by  $\text{Na}^+$  against monotropic transformation to  $\alpha$ - $\text{Fe}_2\text{O}_3$ . This stabilization occurs by the filling of the vacancies distributed in the octahedral sites of the spinal structure with  $\text{Na}^+$  by the substitution reaction ( $\frac{2}{3}\Delta + \frac{1}{3}\text{Fe}^{3+} \rightarrow \text{Na}^+$ , where  $\Delta$  denotes the vacancies);

(6) Thus, by solid state reactions,  $\alpha$ - $\text{Fe}_2\text{O}_3$  is converted to  $\beta$ - $\text{NaFeO}_2$ , and  $\gamma$ - $\text{Fe}_2\text{O}_3$  is converted to  $\alpha$ - $\text{NaFeO}_2$ . The close

structural relations between the reactants and the reaction products can be seen with regard to their oxygen frameworks. As is shown in Fig. 2a–d, stacking of oxygen ion layers of the oxides is conveniently represented as -A-B-A-B- for both  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\beta$ - $\text{NaFeO}_2$ , and as -A-B-C-A-B-C- for both  $\gamma$ - $\text{Fe}_2\text{O}_3$  and  $\alpha$ - $\text{NaFeO}_2$ ;

(7)  $\alpha$ - $\text{Fe}_2\text{O}_3$  has the rhombohedral  $\text{Cr}_2\text{O}_3$ -type structure, while  $\beta$ - $\text{NaFeO}_2$  has the orthorhombic structure. The structural examination suggests that the -A-B-A-B- type (001) planes of oxygens in  $\beta$ - $\text{NaFeO}_2$  are oriented parallel to the hexagonally close-packed (001)<sub>hex</sub> planes of oxygens in  $\alpha$ - $\text{Fe}_2\text{O}_3$ . Also, the [110]<sub>hex</sub> direction in  $\alpha$ - $\text{Fe}_2\text{O}_3$  becomes the [010] direction in  $\beta$ - $\text{NaFeO}_2$ .  $\gamma$ - $\text{Fe}_2\text{O}_3$  has the cubic spinel-like structure, while  $\alpha$ - $\text{NaFeO}_2$  has the rhombohedral  $\text{CsCl}_2$ I-type structure. The face-centered close-packed (111) planes of oxygens in  $\gamma$ - $\text{Fe}_2\text{O}_3$  are retained parallel to the -A-B-C-A-B-C- type (001)<sub>hex</sub> planes of oxygens in  $\alpha$ - $\text{NaFeO}_2$ . Also, the [110] direction in  $\gamma$ - $\text{Fe}_2\text{O}_3$  becomes the [010]<sub>hex</sub> direction in  $\alpha$ - $\text{NaFeO}_2$ . The crystal data for the compounds and orientation relationships between the reactant and the product crystals are given in Table I. The dimensional relationships are also given in Fig. 2;

(8) Although the oxygen frameworks are approximately kept unchanged,  $\text{Fe}^{3+}$  in  $\alpha$ - $\text{Fe}_2\text{O}_3$  migrates from octahedral to tetrahedral interstices while  $\text{Na}^+$  is placed into tetrahedral interstices during the formation of  $\beta$ - $\text{NaFeO}_2$ , and  $\text{Fe}^{3+}$  distributed in octahedral and tetrahedral interstices in  $\gamma$ - $\text{Fe}_2\text{O}_3$  is redistributed in only octahedral interstices while  $\text{Na}^+$  is placed in octahedral interstices during the formation of  $\alpha$ - $\text{NaFeO}_2$ . Thus, the main feature of the reactions is the maintenance of the arrangement of oxygen ions of the oxide crystals;

(9) In many solid state reactions in oxides and mixed oxides, cations migrate while the oxygen packing remains approximately unchanged. The term topotaxy has been used

TABLE I  
CRYSTAL DATA FOR  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\beta$ -NaFeO<sub>2</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, AND  $\alpha$ -NaFeO<sub>2</sub>, AND ORIENTATION RELATIONSHIPS BETWEEN  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> AND  $\beta$ -NaFeO<sub>2</sub>, AND  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> AND  $\alpha$ -NaFeO<sub>2</sub>

	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	$\beta$ -NaFeO <sub>2</sub>	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	$\alpha$ -NaFeO <sub>2</sub>
Space group	$D_{3d}^6(D\bar{3}c)$	$C_{2v}^8(Pna2_1)$		$R\bar{3}_d(R\bar{3}m)$
Type	Cr <sub>2</sub> O <sub>3</sub>		Spinel-like	CsCl <sub>2</sub> I
Lattice parameter	Rhombohedral $a = 5.4135 \text{ \AA}$ $\alpha = 55^\circ 17'$ Hexagonal $a = 5.035 \text{ \AA}$ $c = 13.72 \text{ \AA}$	$a = 5.672 \text{ \AA}$ $b = 7.316 \text{ \AA}$ $c = 5.377 \text{ \AA}$	$a = 8.33 \text{ \AA}$	Rhombohedral $a = 5.39 \text{ \AA}$ $\alpha = 31^\circ 20'$ Hexagonal $a = 3.019 \text{ \AA}$ $c = 15.934 \text{ \AA}$
Oxygen layer stackings	-A-B-A-B-	-A-B-A-B-	-A-B-C-A-B-C	-A-B-C-A-B-C-
Cation sites	Fe <sup>3+</sup> ; octa	Fe <sup>3+</sup> ; tetra Na <sup>+</sup> ; tetra	$\frac{3}{4}$ Fe <sup>3+</sup> ; octa $\frac{1}{4}$ Fe <sup>3+</sup> ; tetra $\frac{1}{2}$ Δ; octa	Fe <sup>3+</sup> ; octa Na <sup>+</sup> ; octa
Orientation relationship	$[001]_{\text{hex}}$ $[\bar{1}10]_{\text{hex}}$ $(001)_{\text{hex}}$	       $[001]$ $[010]$ $(001)$	$[111]$ $[\bar{1}10]$ $(111)$	       $[001]_{\text{hex}}$ $[010]_{\text{hex}}$ $(001)_{\text{hex}}$

to describe such reactions. The formation of sodium orthoferrites by solid state reactions can be interpreted in terms of topotaxy;

(10) It can reasonably be concluded that the Ostwald Step Rule observed in the solid state reactions may be attributed to topotaxial control of the formation of the sodium orthoferrites from the two types of ferric oxides.

The experimental results shown in Fig. 1 emphasize that  $\beta$ -NaFeO<sub>2</sub> crystallized exclusively from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -NaFeO<sub>2</sub> crystallized exclusively from  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, from the results of the reactions in the liquid phase sodium hydroxide. This suggests that even though the dissolution and crystallization mechanism proceeds in the solid-liquid reactions, the solid reactant may control the structure of the solid product in such a way that the main features of the oxygen framework of the solid reactant are preserved in the structure of the solid prod-

uct. The mechanism of dissolution and crystallization appears to comprise three steps; dissolution of crystals, heterogeneous formation of nuclei and subsequent growth of the nuclei. In order to preserve the oxygen framework common to both the solid reactant and the product, the nucleation mechanism must involve three-dimensional preservation of the oxygen framework, and may be governed not by an epitaxial but by a topotaxial control over the proper sites on the solid reactant. During the dissolution of Fe<sub>2</sub>O<sub>3</sub> crystals in NaOH-*n*H<sub>2</sub>O melts at relatively low temperatures, the bond breaking should occur not homogeneously but heterogeneously around various defects which are distributed randomly in real crystals. There may thus be a chance of producing very tiny crystal blocks. The oxygen framework of the blocks would be preserved approximately unchanged during the rearrangement of Fe<sup>3+</sup> in the blocks and the diffusion

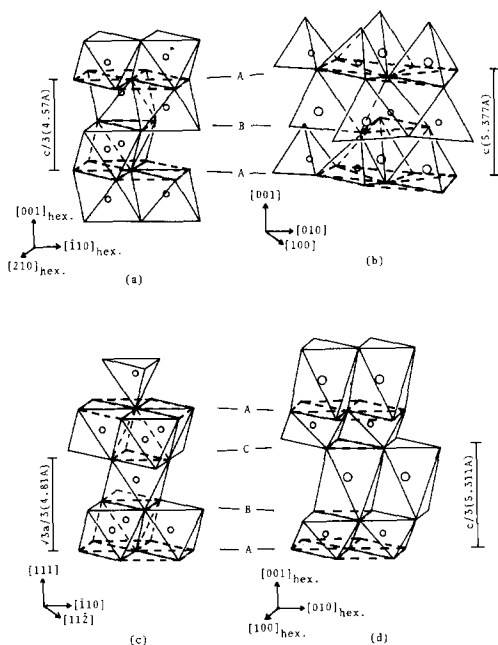


FIG. 2. Schematic diagrams showing structural relations between  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\beta$ - $\text{NaFeO}_2$ , and  $\gamma$ - $\text{Fe}_2\text{O}_3$  and  $\alpha$ - $\text{NaFeO}_2$ . (a) Part of  $\alpha$ - $\text{Fe}_2\text{O}_3$ ; (b)  $\beta$ - $\text{NaFeO}_2$ ; (c) part of  $\gamma$ - $\text{Fe}_2\text{O}_3$  along the body-diagonal direction; (d) part of  $\alpha$ - $\text{NaFeO}_2$ . The O atoms are placed on the corner of the polyhedra. Large and small circles are Na and Fe, respectively.

of  $\text{Na}^+$  into them because oxygen ions are relatively immobile compared with the smaller cations, especially at lower temperatures. Thus, such blocks may act as a precursor phase which is available for the nucleation of the new phases which are structurally related to the mother crystal phases. The Ostwald Step Rule observed in the crystallization of sodium orthoferrites in the solid-liquid reactions may be interpreted in terms of topotaxy.

According to Carr and Fyfe, the overall reaction mechanism for the Ostwald Step Rule observed in the crystallization of amorphous silica is governed by a series of epitaxial controls (6). In epitaxy, which is a surface phenomenon, three-dimensional structural relationships are not necessarily preserved between the substrate crystals and the growing crystals.

An alternative interpretation of the Ostwald Step Rule is that there is a tendency for the crystallization to occur first of the phase which has the least surface energy with respect to the reactant. Thus, crystallization of the phase which has the highest molar volume with respect to the reactant is preferred, since surface energy is inversely related to molar volume (7, 8). The molar volumes at room temperature for the various phases under consideration are shown in Table II. Closing the above interpretation, and inspecting Table II, the unstable  $\beta$ - $\text{NaFeO}_2$  phase would be expected to crystallize out with both  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\gamma$ - $\text{Fe}_2\text{O}_3$ , and this is not the case.

The other interpretation of the Ostwald Step Rule is that there is a tendency for reactions to occur in which there is a minimum entropy change, rather than reactions which yield the most thermodynamically stable phase (9). Unfortunately, no data have been found in the literature to confirm or refute this.

Few data on the mechanisms of the reconstructive phase transformation by the dissolution and recrystallization process are available. It is noteworthy that the measured activation energy of about 23 kcal/mole seems significantly small compared with the value observed for the reconstructive solid-solid transformation of orthorhombic to hexagonal  $\text{Na}_2\text{BeF}_4$ , where the value appeared to be 160 kcal/mole (10). Bond breaking may be associated with a high activation energy, pre-

TABLE II  
MOLAR VOLUME OF THE  
COMPOUNDS (AT RT)

Compound	Volume ( $\text{cm}^3/\text{mole}$ )
$\alpha$ - $\text{Fe}_2\text{O}_3$	30.3
$\gamma$ - $\text{Fe}_2\text{O}_3$	32.5
$\alpha$ - $\text{NaFeO}_2$	25.3
$\beta$ - $\text{NaFeO}_2$	32.7

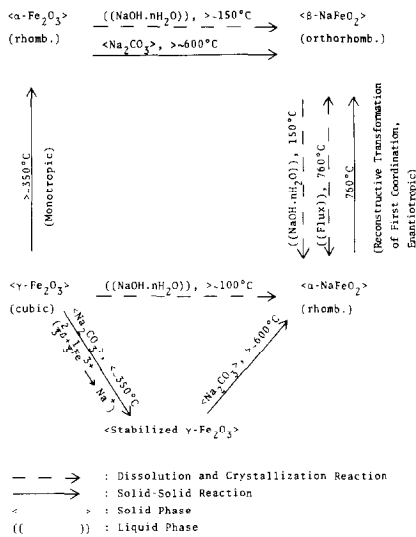


FIG. 3. Reaction paths in the formation of sodium orthoferrites.

sumably approximately equal to the heat of evaporation. In the present case, the liquid phase of NaOH-nH<sub>2</sub>O melts acts not only as a solvent of the oxides but also as a source of a high concentration of OH<sup>-</sup>, so accelerating the bond breaking of the oxides by replacing O<sup>2-</sup> by 2OH<sup>-</sup>. This may be the reason for the low activation energy observed. The dissolution of iron oxides and the formation of sodium orthoferrites at relatively low temperatures, as low as

150°C, in the presence of liquid phase sodium hydroxide may be interpreted in the same manner. Together with hydrothermal solution, the acceleration of the polymorphic transformation of anatase into rutile was discussed by Matthew (8).

The reaction paths in the formation of sodium orthoferrites are summarized in Fig. 3.

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