Phase Equilibria in $Fe–Fe_2O_3–Ln_2O_3$ (Ln = Sm and Er) Systems at 1200 °C

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Phase equilibria in $Fe–Fe_2O_3–Ln_2O_3$ (Ln = Sm and Er) systems were established at 1200 °C. In the $Fe–Fe_2O_3–Sm_2O_3$ system, perovskite, garnet, magnetite, wustite, and metallic iron were stable, while in the $Fe–Fe_2O_3–Er_2O_3$ system, the $ErFe_2O_4$ phase appeared in addition to the other five phases. On the basis of the phase equilibria, the Gibbs free energy for the reaction of $LnFeO_3$, $Ln_3Fe_5O_{12}$, and $ErFe_2O_4$ from Ln_2O_3, metallic iron, and oxygen was determined to be as follows: $SmFeO_3$ -64.1 ± 0.1 kcal, $Sm_3Fe_5O_{12}$ -298.5 ± 0.5 kcal, $ErFe_2O_4$ -100.8 ± 0.1 kcal, $ErFeO_3$ -59.7 ± 0.3 kcal, and $Er_3Fe_5O_{12}$ -286.2 ± 0.7 kcal.

In previous studies, Kimizuka and Katsura,[1] Sugihara *et al.*,[2] and Kimizuka and Katsura[3,4] have established the phase equilibria in $Fe–Fe_2O_3–Ln_2O_3$ systems (Ln = La, Y, Eu, and Yb) at 1200 °C. They have also determined the standard Gibbs free energy for reaction of each ternary double oxide found in these systems from metallic iron, Ln_2O_3, and oxygen. On the basis of these studies, Kimizuka and Katsura[4] have proposed that $Fe–Fe_2O_3–Ln_2O_3$ systems (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) can be classified into four groups with respect to the assemblage of ternary compounds which are in stable co-existence at 1200 °C. According to them, the $Fe–Fe_2O_3–Sm_2O_3$ system may belong to the B-type having two ternary compounds, $SmFeO_3$ and $Sm_3Fe_5O_{12}$, while the $Fe–Fe_2O_3–Er_2O_3$ system is of the C-type having the three stable ternary compounds, $ErFeO_3$, $Er_3Fe_5O_{12}$, and $ErFe_2O_4$. Preceding these studies, Schneider *et al.*[5] had studied the subsolidus binary phase equilibria for the $Fe_2O_3–Sm_2O_3$, and the $Fe_2O_3–Er_2O_3$ systems by the X-ray powder diffraction technique at various temperatures, and found the two rare-earth iron oxides of perovskite and garnet at 1200 °C. The discovers of two new compounds, $LnFe_2O_4$ (Ln = Ho, Er, Tm, and Y) and $Ln_2Fe_3O_7$ (Ln = Yb and Lu) have recently been reported by Kimizuka and Katsura,[3,4] Kimizuka *et al.*,[6,7] Kato *et al.*,[8,9] Tannieres *et al.*,[10] and Evrard *et al.*[11,12]

The objectives of the present study are, firstly, to ascertain the validity of the classification for two systems involving Sm_2O_3 and Er_2O_3 at 1200 °C, after establishing the phase equilibria in these systems, and secondly, to determine the standard Gibbs free energy for reaction of $LnFeO_3$, $LnFe_2O_4$, and $Ln_3Fe_5O_{12}$ compounds at 1200 °C from metallic iron, Ln_2O_3, and oxygen.

Experimental

Analytical grade Fe_2O_3, Sm_2O_3(99.9%), and Er_2O_3-(99.9%) powder were employed as starting materials. Desired ratios of Ln_2O_3/Fe_2O_3 were obtained by mixing thoroughly in an agate mortar with ethyl alcohol. Mixtures thus obtained were treated by the same procedures as those described previously.[2–4]

Mixed gases of CO_2 and H_2 were used to obtain low oxygen partial pressures in the present experiment. The actual oxygen partial pressures of the gas phase was measured by means of a solid electrolytic cell composed of $(ZrO_2)_{0.85}$-$(CaO)_{0.15}$.[13]

Phases in quenched samples were identified by the powder X-ray diffraction method with Mn-filtered Fe$K\alpha$ radiation.

Details of the apparatus and procedures for maintaining constant temperature, methods of thermogravimetry and quenching, the criterion for equilibrium-establishment, and the method of wet chemical analysis are the same as those described in a previous paper.[2–4,14] Lattice constants were determined by the powder X-ray diffraction method with Mn-filtered Fe$K\alpha_1$ radiation and with a slow scanning speed of 0.5° per minute. Instrumental errors were calibrated by measuring the diffraction angles of a standard specimen of silicon.

Results and Discussion

Phase Equilibria. *The $Fe–Fe_2O_3–Sm_2O_3$ System:* Six samples with Sm_2O_3/Fe_2O_3 compositions of 0.25, 0.60, 0.724, 1, 1.222, and 1.5 were prepared. The results of the phase equilibria are illustrated in Fig. 1. The following phases were stable under the experimental conditions: samarium sesquioxide (Sm_2O_3),

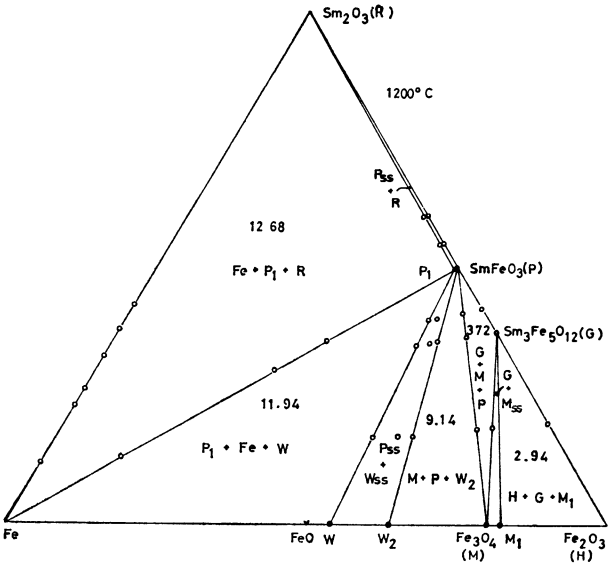

Fig. 1. Phase equilibria in the $Fe–Fe_2O_3–Sm_2O_3$ system at 1200 °C (mol%). Numbers in the figure mean values of $-\log P_{O_2}$ at which three crystalline phases are in equilibrium state. Letters R, P, G, and M represent stoichiometric compositions of Sm_2O_3, $SmFeO_3$, $Sm_3Fe_5O_{12}$, and Fe_3O_4, respectively. M_1 means the endmember of the magnetic solid solution with a chemical composition, $Fe_{2.957}O_4$. P_{ss}, W_{ss}, and M_{ss} mean the solid solution of $SmFeO_3$ from P to P_1, of FeO from W to W_2, and Fe_3O_4 from M to M_1, respectively. The other letters as for in Table 2.

TABLE 1. LATTICE CONSTANTS OF TERNARY OXIDES

Composition	a (Å)	b (Å)	c (Å)	V(Å^3)
$SmFeO_3$				
$SmFeO_{3.000}$	5.398±0.002	5.598±0.002	7.708±0.002	232.9±0.2
$SmFeO_{2.982}$	5.398±0.001	5.591±0.001	7.706±0.001	232.6±0.1
(a)$^{15)}$	5.394	5.592	7.711	
$ErFeO_3$				
$ErFeO_{3.000}$	5.262±0.001	5.584±0.001	7.593±0.001	223.1±0.1
$ErFeO_{2.974}$	5.261±0.001	5.585±0.001	7.592±0.001	223.1±0.1
$Sm_3Fe_5O_{12}$				
$Sm_3Fe_5O_{12.00}$	12.519±0.002			1962.1±0.6
(b)$^{16)}$	12.524			
(c)$^{17)}$	12.529			1967.2
$Er_3Fe_5O_{12}$				
$Er_3Fe_5O_{12.00}$	12.346±0.001			1881.8±0.5
(b)$^{16)}$	12.349			
(d)$^{18)}$	12.347			1882.3
$ErFe_2O_4$ (hexagonal)				
$ErFe_2O_{3.984}$	3.489±0.001		24.929±0.004	262.8±0.2
$ErFe_2O_{3.957}$	3.494±0.001		24.927±0.004	263.6±0.2
$ErFe_2O_{3.904}$	3.500±0.001		24.948±0.005	264.6±0.3

hematite (Fe_2O_3), magnetite (Fe_3O_4), wustite (FeO), metallic iron (γ-Fe), samarium-iron-perovskite ($SmFeO_3$), and samarium-iron-garnet ($Sm_3Fe_5O_{12}$).

Sm_2O_3 was stable in oxygen partial pressures from one to $10^{-12.8}$ atm at 1200 °C, and appeared to have no significant nonstoichiometry in its composition. The deviation from the stoichiometric composition of $SmFeO_3$ extended up to $SmFeO_{2.982}$ at an oxygen partial pressure of $10^{-12.68}$ atm. The lattice constants of the $SmFeO_3$ solid solution seemed to be constant irrespective of the compositional variation. The data are given in Table 1 together with the data of Geller and Wood.$^{15)}$ This is the same trend as those found for $EuFeO_3$,$^{2)}$ $YFeO_3$,$^{3)}$ and $YbFeO_3$.$^{4)}$ $Sm_3Fe_5O_{12}$ had no compositional variation and remained stoichiometric under the experimental conditions. The lattice constants of $Sm_3Fe_5O_{12}$ were almost identical with those obtained by Bertaut and Forrat$^{16)}$ and Espinosa.$^{17)}$ The data are given in Table 1.

The Fe–Fe_2O_3–Er_2O_3 System: Seven samples with Er_2O_3/Fe_2O_3 compositions of 0.25, 0.429, 0.499, 0.6, 0.739, 1 and 1.222 were prepared. Figure 2 shows the experimental results. The following phases were stable under the experimental conditions: erbium sesquioxide (Er_2O_3), hematite (Fe_2O_3), magnetite (Fe_3O_4), wustite (FeO), metallic iron (γ-Fe), erbium-iron-perovskite ($ErFeO_3$), erbium-iron-garnet ($Er_3Fe_5O_{12}$), and $ErFe_2O_4$.

Er_2O_3 was stable in oxygen partial pressures from one to $10^{-12.0}$ atm, and appeared to have no compositional variation. The deviation from the stoichiometric composition of $ErFeO_3$ extended up to $ErFeO_{2.973}$ at an oxygen partial pressure of $10^{-11.19}$ atm. The lattice constants of the $ErFeO_3$ solid solution seemed to be constant irrespective of the compositional variations. The data are given in Table 1. $Er_3Fe_5O_{12}$ had no compositional variation under the experimental conditions, and its lattice constants were almost identical with those obtained by Bertaut and Forrat$^{16)}$ and Geller *et al.*$^{18)}$ The data are given in Table 1. The $ErFe_2O_4$ phase had a wide composition range from $ErFe_2O_{3.955}$ at an oxygen partial pressure of $10^{-10.00}$ atm to $ErFe_2O_{3.903}$ at an oxygen partial pressure of $10^{-11.96}$ atm. The lattice constants of the $ErFe_2O_4$ solid solution were determined on the basis of the study of the crystal structure by Kato *et al.*,$^{8)}$ and these data are also given in Table 1. As shown in Table 1, the lattice constants of this solid solution increase with decreasing oxygen content.

In conclusion, from the studies of the phase equilibria of two systems, it has become clear that the Fe–Fe_2O_3–Sm_2O_3 system belongs to the B-type having two ternary compounds as presumed by Kimizuka and Katsura,$^{4)}$ and that the Fe–Fe_2O_3–Er_2O_3 system belongs to the C-type having three ternary compounds, $ErFeO_3$, $Er_3Fe_5O_{12}$, and $ErFe_2O_4$.

Calculations of Standard Gibbs Free Energies of Ternary Compounds. On the basis of the phase equilibria, we can determine the standard free energy of reaction of the respective $ErFe_2O_4$, $SmFeO_3$, $Sm_3Fe_5O_{12}$, $ErFeO_3$, and $Er_3Fe_5O_{12}$ compounds, referring to the following equations:

$$Fe + 1/2Sm_2O_3 + 3/4O_2 = SmFeO_3 \tag{1}$$

$$5Fe + 3/2Sm_2O_3 + 15/4O_2 = Sm_3Fe_5O_{12} \tag{2}$$

$$2Fe + 1/2Er_2O_3 + 5/4O_2 = ErFe_2O_4 \tag{3}$$

$$Fe + 1/2Er_2O_3 + 3/4O_2 = ErFeO_3 \tag{4}$$

$$5Fe + 3/2Er_2O_3 + 15/4O_2 = Er_3Fe_5O_{12} \tag{5}$$

The standard Gibbs free energies of reaction (1) and (3) may be calculated directly by adopting each equilibrium oxygen partial pressure corresponding to the equation. Here, the activity of each component of $SmFeO_3$ and $ErFe_2O_4$ in each solid solution was set equal to one, and where the compositions were $SmFeO_{2.982}$ (P_1 in Fig. 1) and $ErFe_2O_{3.903}$ (A in Fig. 2), both were in equilibrium with metallic iron and sesquioxide.

In order to calculate the standard Gibbs free energy of reaction (2), it is necessary to calculate the standard Gibbs free energy of the following reaction (6):

$$3SmFeO_3 + 2/3Fe_3O_4 + 1/6O_2 = Sm_3Fe_5O_{12} \qquad (6)$$

This may be readily calculated on the basis of the experimental results illustrated in Fig. 1. The activity of the $SmFeO_3$ component in stoichiometric composition which was in equilibrium with both stoichiometric Fe_3O_4 and $Sm_3Fe_5O_{12}$ was calculated by means of the Gibbs-Duhem equation. The relationship between $-1/2 \log P_{O_2}$ and N_O/N_{SmFeO_3}, the fraction ratio of oxygen to $SmFeO_3$, indicating the deviation from stoichiometry, was substantially linear from the present experimental results, and the activity was calculated to be 1.125. A detailed calculation method has been described in the paper of Kimizuka and Katsura.[4] Since the standard Gibbs free energy of formation of Fe_3O_4 referred to the Eq. 7.

$$3Fe + 2O_2 = Fe_3O_4 \qquad (7)$$

has been determined by Darken and Gurry,[19] the standard Gibbs free energy of $Sm_3Fe_5O_{12}$ referred to Eq. 2 may be determined by adding together $3\Delta G°(1)$, $\Delta G°(6)$, and $2/3\Delta G°(7)$.

In order to calculate the standard Gibbs free energy referred to Eq. 4, we have to invoke the following reaction (8):

$$1/4Er_2O_3 + 1/2ErFe_2O_4 + 1/8O_2 = ErFeO_3. \qquad (8)$$

The standard Gibbs free energy of reaction (8) may be readily calculated on the basis of the experimental results shown in Fig. 2. Here, the activity of the $ErFeO_3$ component with composition $ErFeO_{2.973}$ (P_3 in Fig. 2) was set equal to one. The activity of the $ErFe_2O_4$ component in the $ErFe_2O_4$ solid solution from $ErFe_2O_{3.903}$ to $ErFe_2O_{3\ 995}$ is calculated by means of the Gibbs-Duhem equation, and the relationship between $-1/2 \log P_{O_2}$ and $N_O/N_{ErFe_2O_4}$ was substantially linear from the experimental results. After determining the activity of $ErFe_2O_4$ with a composition of $ErFe_2O_{3.942}$ (A_1 in Fig. 2), we may determine the standard Gibbs free energy referred to Eq. 4 by adding together $1/2\ \Delta G°(3)$ and $\Delta G°(8)$.

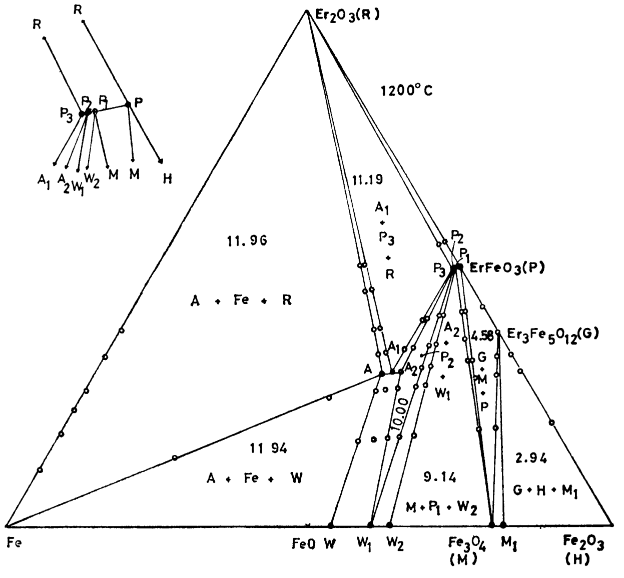

Fig. 2. Phase equilibria in the Fe–Fe_2O_3–Er_2O_3 system at 1200 °C (mol %). Numbers in the figure mean values of $-\log P_{O_2}$ at which three crystalline phases are in equilibrium state. Letters R, P, G, amd M represent stoichiometric compositions of Er_2O_3, $ErFeO_3$, $Er_3Fe_5O_{12}$, and Fe_3O_4, respectively. M_1 means the endmember of the magnetite solid solution with a chemical composition, $Fe_{2.957}O_4$. The other letters as for in Table 2.

To determine the standard Gibbs free energy referred to Eq. 5, it is necessary to calculate the standard Gibbs free energy of the following reaction (9):

$$3ErFeO_3 + 2/3Fe_3O_4 + 1/6O_2 = Er_3Fe_5O_{12} \qquad (9)$$

The procedure for determining the standard Gibbs free energy of reaction (9) is the same as that for reaction (6). Adding together $2/3\ \Delta G°(7)$, $3\Delta G°(4)$, and $\Delta G°(9)$, we obtain the value of $\Delta G°(5)$. The calculated activity data are summarized in Table 2, and the standard Gibbs free energies of reactions (1) to (9) are given in Table 3.

Table 2. Composition and activity in solid solutions

Component	Composition	Symbol	$-\log P_{O_2}$	$\log a_i$
FeO	$FeO_{1.049}$	W	11.94	0
	$FeO_{1.125}$	W_1	10.00	−0.0805
	$FeO_{1.166}$	W_2	9.14	−0.150
$SmFeO_3$	$SmFeO_{2.982}$	P_1	12.68	0
	$SmFeO_{3.000}$	P	9.14	0.0512
			0.68	0.0512
$Sm_3Fe_5O_{12}$	$Sm_3Fe_5O_{12.00}$	G	3.72	0
$ErFe_2O_4$[a)]	$ErFe_2O_{3.903}$	A	11.96	0
	$ErFe_2O_{3.942}$	A_1	11.19	0.0350
	$ErFe_2O_{3.995}$	A_2	10.00	0.0478
$ErFeO_3$[b)]	$ErFeO_{2.973}$	P_3	11.19	0
	$ErFeO_{2.977}$	P_2	10.00	0.0213
	$ErFeO_{2.980}$	P_1	9.14	0.0240
	$ErFeO_{3.000}$	P	3.64	0.0509
$Er_3Fe_5O_{12}$	$Er_3Fe_5O_{12.00}$	G	4.58	0

a) The relationship between the composition and $\log P_{O_2}$ is, $N_O/N_{ErFe_2O_4} = 0.04494 \log P_{O_2} + 0.4447$. b) The relationship between the composition and $\log P_{O_2}$ is, $N_O/N_{ErFeO_3} = 0.03571 \log P_{O_2} + 0.0130$.

Table 3. The summary of the standard gibbs free energy values

	Reactions	$-\Delta G°$(kcal)
(1)	$Fe + 1/2Sm_2O_3 + 3/4O_2 = SmFeO_3$	64.1±0.1
(2)	$5Fe + 3/2Sm_2O_3 + 15/4O_2 = Sm_3Fe_5O_{12}$	298.5±0.5
(3)	$2Fe + 1/2Er_2O_3 + 5/4O_2 = ErFe_2O_4$	100.8±0.1
(4)	$Fe + 1/2Er_2O_3 + 3/4O_2 = ErFeO_3$	59.7±0.3
(5)	$5Fe + 3/2Er_2O_3 + 15/4O_2 = Er_3Fe_5O_{12}$	286.2±0.7
(6)	$3SmFeO_3 + 2/3Fe_3O_4 + 1/6O_2 = Sm_3Fe_5O_{12}$	3.2±0.2
(7)	$3Fe + 2O_2 = Fe_3O_4$	154.5±0.3
(8)	$1/4Er_2O_3 + 1/2ErFe_2O_4 + 1/8O_2 = Er_2FeO_3$	9.3±0.2
(9)	$3ErFeO_3 + 2/3Fe_3O_4 + 1/6O_2 = Er_3Fe_5O_{12}$	4.1±0.3

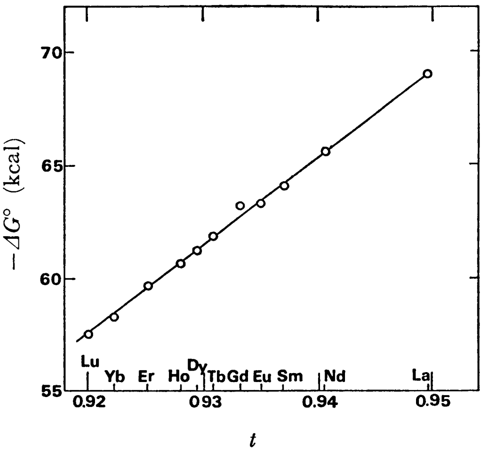

Fig. 3. The relationship between ΔG° and the tolerance factor t.

The Relationship Between the Value of ΔG° of Lanthanoid-Iron-Perovskite and the Tolerance Factor. Katsura *et al.*[20] and Kimizuka and Katsura[4] have pointed out that the standard Gibbs free energy of reactions of lanthanoid-iron-perovskite from metallic iron, lanthanoid sesquioxide, and oxygen may change proportionally with the tolerance factor defined by Goldschmidt.[21] The tolerance factor t is defined as $\gamma_A + \gamma_O = t\sqrt{2}(\gamma_B + \gamma_O)$, where γ_A, γ_B, and γ_O are the ionic radii of the A-atom, B-atom, and O-atom of the perovskite, ABO_3, respectively.

The same rule holds also for $ErFeO_3$, $HoFeO_3$,[22] and $LuFeO_3$[23] as seen in Fig. 3. The deviation from the general trend in $GdFeO_3$ is estimated to be about 400—500 cal, and is significant in considering the range of the experimental errors. A more detailed discussion will be published in the near future after the completion of the study of all the lanthanoid-iron-perovskite members.

References

1) N. Kimizuka and T. Katsura, *Bull. Chem. Soc. Jpn.*, **47**, 1801 (1974).
2) T. Sugihara, N. Kimizuka, and T. Katsura, *Bull. Chem. Soc. Jpn.*, **48**, 1806 (1975).
3) N. Kimizuka and T. Katsura, *J. Solid State Chem.*, **13**, 176 (1975).
4) N. Kimizuka and T. Katsura, *J. Solid State Chem.*, **15**, 151 (1975).
5) S. J. Schneider, R. S. Roth, and J. L. Waring, *J. Res. NBS*, **64A**, 345 (1960).
6) N. Kimizuka, A. Takenaka, Y. Sasada, and T. Katsura, *Solid State Commun.*, **15**, 1321 (1974).
7) N. Kimizuka, A. Takenaka, Y. Sasada, and T. Katsura, *Solid State Commun.*, **15**, 1199 (1974).
8) K. Kato, I. Kawada, N. Kimizuka, and T. Katsura, *Z. Krist.*, **141**, 314 (1975).
9) K. Kato, I. Kawada, N. Kimizuka, I. Shindo, and T. Katsura, *Z. Krist.*, in press (Die Kristallstruktur von $Yb_2Fe_3O_7$).
10) N. Tannieres, O. Evrard, and J. Aubry, *C. R. Acad. Sci. Paris*, **278**, 241 (1974).
11) O. Evrard, B. Malaman, F. Jeannot, N. Tannieres, and J. Aubry, *C. R. Acad. Sci. Paris*, **278**, 413 (1974).
12) O. Evrard, B. Malaman, N. Tannieres, F. Jeannot, and J. Aubry *C. R. Acad. Sci. Paris*, **279**, 1021 (1974).
13) T. Katsura and H. Hasegawa, *Bull. Chem. Soc. Jpn.*, **40**, 561 (1967).
14) I. Iwasaki, T. Katsura, M. Yoshida, and T. Tarutani, *Bunseki Kagaku*, **6**, 211 (1957).
15) S. Geller and E. A. Wood, *Acta Crystallogr.*, **9**, 563 (1956).
16) F. Bertaut and F. Forrat, *C. R. Acad. Sci. Paris*, **244**, 96 (1957).
17) G. P. Espinosa, *J. Chem. Phys.*, **37**, 2344 (1962).
18) S. Geller, H. J. Williams, and R. C. Sherwood, *Phys. Rev.*, **123**, 1962 (1961).
19) L. S. Darken and R. W. Gurry, *J. Am. Chem. Soc.*, **67**, 1398 (1945), **68**, 798 (1946).
20) T. Kastura, K. Kitayama, T. Sugihara, and N. Kimizuka, *Bull. Chem. Soc. Jpn.*, **48**, 1809 (1975).
21) V. M. Goldschmidt, T. Barth, G. Lunde, and W. H. Zachariasen, Pt. VIII Skrifter Norske Videnskaps-Akad. Oslo, I. Mat. Naturv. K I, No. 2 (1926).
22) T. Sekine and T. Katsura, unpublished data.
23) T. Sekine and T. Katsura, *J. Solid State Chem.*, **17** (1976), in press.