JOURNAL OF SOLID STATE CHEMISTRY **18**, 263–269 (1976)

Phase Equilibria and Thermodynamics of Coexisting Phases in Rare-Earth Element–Iron–Oxygen Systems. II. The Praseodymium–Iron–Oxygen System*

YU. D. TRETYAKOV, V. V. SOROKIN, AND A. P. ERASTOVA

Moscow State University, Chemistry Department, Moscow, U.S.S.R.

Received November 11, 1975

The phase equilibria and the thermodynamics of coexisting phases in the Pr–Fe–O system have been studied using static and dynamic methods for attaining equilibrium with subsequent annealing and identification of the condensed phases by X-ray analysis. Equilibrium phase diagrams have been constructed to define the changes that take place in the Pr–Fe–O system on variation of the partial oxygen pressure, the temperature, and the composition of the initial mixture of oxides. An isothermal cross section at 1300°K and equilibrium diagrams of the type $P_{O_2} = f$(composition) with $T =$ constant, $P_{O_2} = f(1/T)$ with one composition parameter fixed and $T = f$(composition) with $P_{O_2} =$ constant have been constructed. It has been shown in the Pr–Fe–O system that only one ternary compound with perovskite structure, $PrFeO_3$, is formed, and furthermore, it is stable no matter how high the partial oxygen pressure.

Introduction

Information about the equilibrium conditions of formation and the thermodynamics of coexisting phases in ferrite-forming systems of the *R*-Fe-O type (*R* = rare earth element is necessary both for selecting optimal conditions for synthesis and thermal processing of the rare-earth element ferrites and for explaining the nature of their magnetic properties and crystallographic structure. Such information in the literature is contradictory and, at times, completely lacking.

Praseodymium, like the first element in the lanthanide series, cerium, possesses variable valency in oxide phases. Therefore, the character of ferrite-forming reactions in the Pr–Fe–O system is sensitive to temperature and to any change in the chemical potential of oxygen in the equilibrium gaseous phase.

According to reports (*1–3*) the formation of one intermediate phase orthoferrite $PrFeO_3$, is possible in the Pr–Fe–O system; it has a perovskite structure and possesses great thermal stability with respect to oxidation (*4*, *5*). The attempts of (*3–6*) to obtain a ferrogarnet of praseodymium, "$Pr_3Fe_5O_{12}$," were not successful. The Pr^{3+} ion is too large to form a ferrite-garnet structure, but Pr^{3+} can enter into a ferrite-garnet structure to a limited degree, forming a series of solid solutions (*5*, *7*, *8*). A structure of the pyrochlore type also is not realized in the Pr–Fe–O system (*4*).

The goal of the present work is to investigate the phase equilibria and the thermodynamics of coexisting phases in the Pr–Fe–O system, limited to the range Pr_2O_3–PrO_2–Fe_2O_3–Fe, to construct equilibrium diagrams which define the character of phase changes in the system during changes in partial oxygen pressure, temperature, and composition of the initial oxide mixture, and to evaluate the thermal stability of the intermediate product, orthoferrite $PrFeO_3$, with respect to oxidation.

---

* Original manuscript received in Russian. A copy is available on written request to the Editor.

Printed in Great Britain

Experimental

For studying the phase equilibria, static and dynamic methods for attaining equilibrium were used, followed by annealing and identification of the condensed phases by X-ray analysis.

As starting materials for preparation of the specimens to be studied, we used metals and oxides of a high degree of purity. The metallic praseodymium was 99.998%; the praseodymium oxide Pr_6O_{11} contained <0.001% by weight impurity. Praseodymium sesquioxide Pr_2O_3 was formed by reduction under vacuum (10^{-4} atm) at 1000°C for 8 hr. In our work, we used iron carbonyl powder containing <0.002% by weight impurity and iron oxide Fe_2O_3 which was obtained by thermal decomposition of Mohr's salt (amount of any impurity was <0.002% by weight) at a temperature of 800°C for 5 hr in air. The completeness of decomposition of the sulfates was checked by reaction with $BaCl_2$.

For research on phase equilibria in the Pr–Fe–O system corresponding to specific ratios of Pr:Fe:O, preparations were made in the following manner. Measured portions of powders $Pr + Pr_6O_{11} + Fe_2O_3 + Fe$ or of $Pr_6O_{11} + Fe_2O_3 + Fe$ were homogenized in an agate mortar under a layer of ether for 3 hr, pressed into tablets (diameter, 9 mm; pressing pressure, 2 t/cm^2), and sealed into ampoules evacuated to 10^{-3} mm mercury. Double quartz ampoules, with a tantalum chip getter in the space between, were used for the firings. Heating was carried out at a temperature of 1300°K for 48 hr, after which the specimens were sharply quenched by immersing the ampoules in water.

The single-phase praseodymium orthoferrite $PrFeO_3$ was obtained by roasting the $Pr_2O_3 + Fe_2O_3$ mixture for 10 hr at a temperature of 1350°C with an intermediate grinding. The product of the heating, according to X-ray analysis data, had the structure of a single-phase perovskite.

X-ray analysis of the condensed phases was done with FeK_α radiation. Photographic filming was done in a high-resolution camera of diameter 143.25 mm with FeK_α radiation.

Basic Results and Discussion

Using data in the literature on the behavior of binary systems of Pr–O (*9*, *10*) and Fe–O (*11*), and also data on the thermodynamic properties of $PrFeO_3$ (*12*), we examined possible means of triangulating the phase triangle and then tested them by heating mixtures of condensed phases corresponding to strictly determined ratios of Pr:Fe:O in sealed, previously evacuated quartz ampoules. The compositions studied and their phase make-up after attaining equilibrium at 1300°K and sharp quenching are presented in Table I. An isothermal cross section of the phase diagram of the system constructed on the basis of these data is shown in Fig. 1. Here the compositions studied are denoted by Arabic numerals and the coexisting phases of the

TABLE I

COMPOSITIONS OF THE Pr–Fe–O SYSTEM

	Overall composition			
N	Pr	Fe	O	Phase composition (data from X-ray analysis)
1	0.250	0.250	0.500	$Pr_2O_3 + PrFeO_3 + Fe$
2	0.300	0.090	0.610	Pr_2O_3 + "$PrO_{1.6}$" + $PrFeO_3$
3	0.180	0.210	0.610	"$PrO_{1.6}$" + $Fe_2O_3 + PrFeO_3$
4	0.060	0.360	0.580	$PrFeO_3 + Fe_2O_3 + Fe_3O_4$
5	0.070	0.400	0.530	$PrFeO_3 + Fe_3O_4 + Fe_{1-x}O$
6	0.120	0.420	0.460	$PrFeO_3 + Fe_{1-x}O + Fe$
7	0.030	0.375	0.595	$PrFeO_3 + Fe_2O_3 + Fe_3O_4$

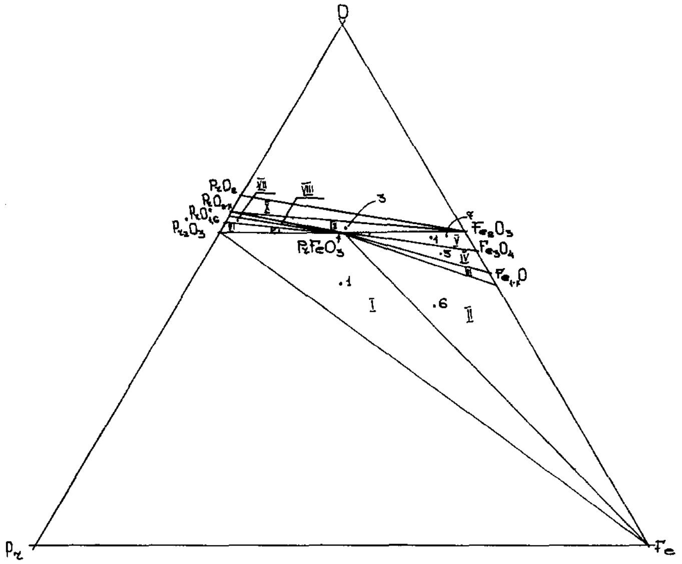


FIG. 1. Isothermal cross section of the phase diagram of the Pr–Fe–O system at 1300°K.

Pr–Fe–O system in the range Pr_2O_3–PrO_2–Fe_2O_3–Fe are denoted by Roman numerals. The regions of coexisting phases are presented in Table II. One must keep in mind that the portion of the diagram above the Pr_2O_3–Fe_2O_3 line has not been determined in a well-defined manner for the following reasons. (1) The phase composition of annealed specimens does not reflect the equilibrium composition for praseodymium oxides. In particular, we did not succeed in preventing ordering of defects in the nonstoichiometric fluorite phase of PrO_{2-x} with formation of ordered structures (*9*, *10*, *13*). (2) For several of the phase regions, for example, PrO_{2-x} when $x > 0.28$, the equilibrium oxygen pressure at 1300°K in the range $PrFeO_3$–Fe_2O_3–PrO_x far exceeds 1 atm.

TABLE II

COEXISTING PHASES IN THE Pr–Fe–O SYSTEM AT 1300°K

Region	Phase composition
I	$Pr_2O_3 + PrFeO_3 + Fe$
II	$PrFeO_3 + Fe_{1-x}O + Fe$
III	$PrFeO_3 + Fe_{1-x}O$
IV	$PrFeO_3 + Fe_3O_4 + Fe_{1-x}O$
V	$PrFeO_3 + Fe_2O_3 + Fe_3O_4$
VI	Pr_2O_3 + "$PrO_{1.6}$" + $PrFeO_3$
VII	"$PrO_{1.6}$" + $PrFeO_3$
VIII	"$PrO_{1.6}$" + $PrFeO_3 + PrO_{2-x}$
IX	$PrO_{2-x} + Fe_2O_3 + PrFeO_3$
X	$PrO_{2-x} + PrO_2 + Fe_2O_3$

In order to evaluate the character of phase changes during the change in partial oxygen pressure, it was necessary to construct an equilibrium diagram of P_{O_2} vs f (composition) with T = constant. The equilibrium isothermal diagram $\log P_{O_2} = f\ (\xi_{Pr})$, where $\xi = n_{Pr}/(n_{Pr} + n_{Fe})$, is presented in Fig. 2. Figure 2a also shows the isothermal diagram $\xi_O = f\ (\xi_{Pr})$, where $\xi_O = n_O/(n_{Fe} + n_{Pr})$. In constructing the diagram of $\log P_{O_2} = f\ (\xi_{Pr})$ Kaul's data were used (*12*, *16*) for the equilibrium oxygen pressure over the orthoferrite and its reduction products.

The partial pressure of oxygen corresponding to the equilibrium composition of the reaction

$$PrFeO_3 \rightarrow \tfrac{1}{2}Pr_2O_3 + Fe + \tfrac{3}{4}O_2 \qquad (1)$$

is expressed by the equation

$$\log P_{O_2} = 9.21 - (32\,485/T) \quad (1123\text{–}1473°\text{K.}) \qquad (2)$$

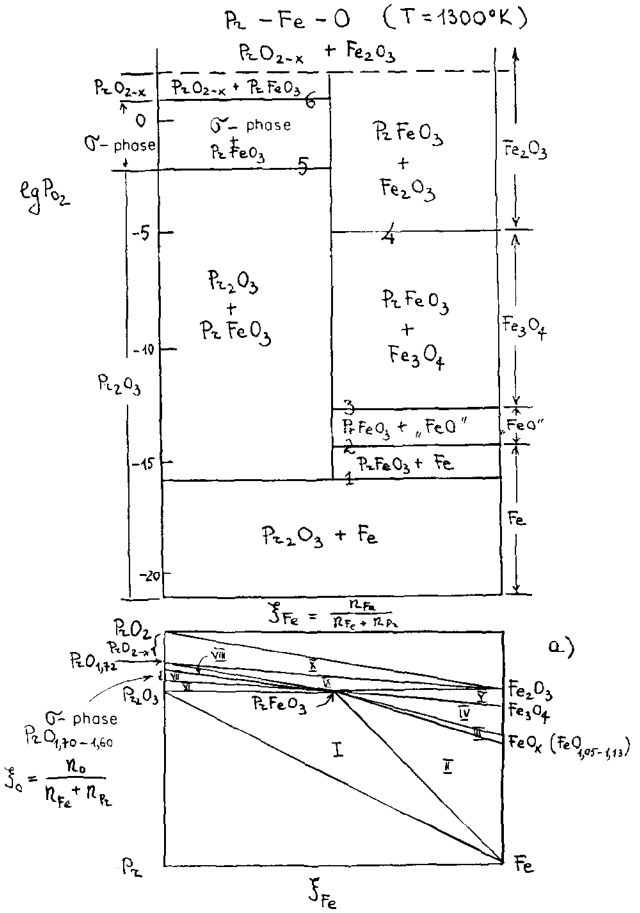


Fig. 2. Equilibrium diagrams of log $P_{O_2} = f(\xi_{Fe})$ and (a) $\xi_O = f(\xi_{Fe})$ of the Pr-F-O system at 1300°K.

In order to evaluate the relative stability of $PrFeO_3$ with respect to oxidation, i.e., to find the partial oxygen pressure for the mixture $PrFeO_3 + Fe_2O_3 + PrO_{1.72}$ (area I in Fig. 1), we did the following calculation: The equilibrium of orthoferrite with its oxidation product can be expressed by the equation

$$Pr_2O_3 \text{ (in the orthoferrite)} + 0.22O_2 = 2\,PrO_{1.72}. \quad (3)$$

It is apparent that the standard free-energy change of reaction (3) is

$$\Delta G^\circ_{(3)} = -RT \ln K_p = -RT \ln \frac{a^2_{PrO_{1.72}}}{a_{Pr_2O_3} P^{0.22}_{O_2}} \quad (4)$$

where $a_{Pr_2O_3}$ = the activity of Pr_2O_3 in the orthoferrite, $a_{PrO_{1.72}}$ = the activity of $PrO_{1.72}$ in the fluorite phase, and P_{O_2} = the equilibrium pressure of oxygen over the coexisting condensed phases $PrFeO_3 + PrO_{1.72} + Fe_2O_3$.

Considering that $PrO_{1.72}$ exists in a pure form, i.e., $a_{PrO_{1.72}} = 1$, we find from Eq. (4)

$$\log P_{O_2} = \frac{\Delta G^\circ_{(3)} - 4.575\,T \log a_{Pr_2O_3}}{(4.575)(0.22)(T)}. \quad (5)$$

Consequently, for calculating P_{O_2} it is necessary to evaluate $\Delta G^\circ_{(3)}$ and $a_{Pr_2O_3}$ (in the praseodymium orthoferrite which is in equilibrium with Fe_2O_3 and $PrO_{1.72}$). The former can be done using Marion's data (*14*) on the equilibrium pressure of oxygen over the condensed phases of the binary Pr-O system. It is apparent that for the reaction

$$PrO_{1.5} + 0.11O_2 = PrO_{1.7} \quad (6)$$

the change in free energy can be presented as the sum of changes in free energy for the reactions of successive oxidation

$$PrO_{1.5} \rightarrow PrO_{1.6};\ PrO_{1.6} \rightarrow PrO_{1.70};$$
$$PrO_{1.70} \rightarrow PrO_{1.72};$$

i.e.,

$$\Delta G^{\circ}_{(6)} = \Delta G^{\circ}_{(PrO_{1.5}\rightarrow PrO_{1.6}} + \Delta G^{\circ}_{(PrO_{1.6}\rightarrow PrO_{1.70})} + \Delta G^{\circ}_{(PrO_{1.70}\rightarrow PrO_{1.72})}$$
$$= 0.650 - 0.193 + 0.106 = -0.737 \text{ kcal.}$$

$$\Delta G^{\circ}_{(3)} = 2\ \Delta G^{\circ}_{(6)} = -1.474 \text{ kcal at } 1300^{\circ}\text{K.}$$

As for $a_{Pr_2O_3}$, it can be estimated, knowing from Kaul's data (*12*, *16*) that for the reaction

$$\tfrac{1}{2}Pr_2O_3 + \tfrac{1}{2}Fe_2O_3 = PrFeO_3 \qquad (7)$$

$\Delta G^{\circ}_{(7)} = -13.23 + 0.28 \times 10^{-3}\,T = -12.87$ kcal/mole at 1300°K. Thus since $\Delta G^{\circ}_{(7)} = -RT \ln K_p = -RT \ln (a^{-1/2}_{Fe_2O_3}\ a^{-1/2}_{Pr_2O_3})$ then $\log (a_{Fe_2O_3}\ a_{Pr_2O_3}) = 2\Delta G^{\circ}_{(7)}/4.575\quad T = -(12\,870)\quad (2)/(4.575)\,(1300) = -4.328$. In the orthoferrite formed in equilibrium with hematite, $a_{Fe_2O_3} = 1$, and consequently, $\log a_{Fe_2O_3} = -4.328$ (at 1300°K). Setting this value equal to the magnitude of $\Delta G^{\circ}_{(3)} = -1.474$ kcal in Eq. (5), we find

$$\log P_{O_2} = \frac{-1.474 + 25\,740}{1307} = 18.57.$$

In spite of the approximate nature of this calculation, it can be confirmed that praseodymium orthoferrite is stable at any value, no matter how high, of the partial oxygen pressure, i.e., the interaction with Fe_2O_3 makes Pr^{3+} extremely stable.

A review of the equilibrium isothermal diagrams of $\log P_{O_2} = f\,(\xi_{Pr})$ and $\xi_O = f\,(\xi_{Fe})$ of the Pr–Fe–O system presented in Fig. 2 and the summary of the fixed points of the diagram presented in Table III indicate that at low oxygen pressure a mixture of Pr_2O_3 and metallic iron is in equilibrium. The praseodymium orthoferrite is formed spontaneously from Pr_2O_3 + Fe when $-\log P_{O_2} \leqslant 15.8$. For compositions with $\xi_{Pr} > 0.5$, ferroperovskite coexists with Pr_2O_3 up to a partial oxygen pressure corresponding to $-\log P_{O_2} \leqslant 2.2$, where the σ-phase is formed in place of sesquioxide; at $\log P_{O_2} \geqslant 0.86$ ferroperovskite coexists with the fluorite phase PrO_{2-x}. For compositions with $\xi_{Pr} < 0.5$, praseodymium ferroperovskite, formed when $\log P_{O_2} = -15.8$, coexists consecutively with metallic iron, wustite, magnetite, and hematite as the partial oxygen pressure increases. The borderline of disintegration of ferroperovskite into $PrO_{2-x} + Fe_2O_3$ corresponds to a very high pressure of P_{O_2}.

TABLE III

Summary of the Fixed Points of the Pr–Fe–O Diagram (Fig. 2)

Point	Equation $P_{O_2} = A - B/T$		$-\log p_{O_2}$ at 1300°K	Source
	A	B		
1	9.21	32 485	15.8	(*12*, *16*)
2	6.78	27 600	14.45	(*10*, *11*)
3	11.06	31 090	12.8	(*10*, *11*)
4	14.90	25 900	5.0	(*10*, *11*)
5	11.20	17 390	2.2	(*14*)
6	12.48	15 100	–0.86	Our calculations

Comparison of Fig. 2 with the analogous diagram of the Ce–Fe–O system (*17*) indicates that along with general similarity, there are principal differences in the behavior of both systems related to stability of the orthoferrite phase. Thus, whereas in the Pr–Fe–O system the orthoferrite is formed directly from Pr_2O_3 + Fe, in the Ce–Fe–O system consecutive transformations $(Ce_2O_3 + Fe) \rightarrow (CeO_{1.70} + Fe) \rightarrow (CeO_{2-x} + Fe)$ with rise in partial oxygen pressure occur en route to formation of cerium orthoferrite. The second basic difference in the behavior of these systems consists of the fact that the orthoferrite in the Ce–Fe–O system cannot coexist with magnetite and wustite (as is observed in the Pr–Fe–O system) but forms a triangle of coexisting phases $CeFeO_3$–CeO_2–Fe_3O_4.

Fig. 3 shows the equilibrium diagram of $\log P_{O_2} = f\,(1/T)$ for various ratios of Pr:Fe, i.e., for various values of ξ_{Pr}. This diagram gives an impression of the character of phase

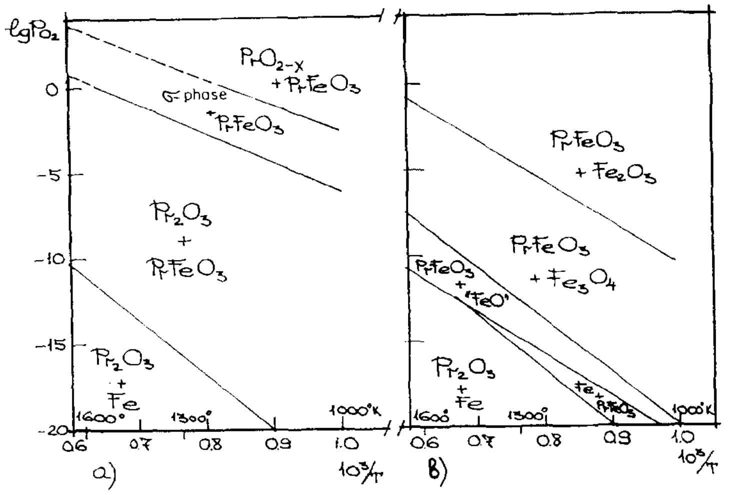
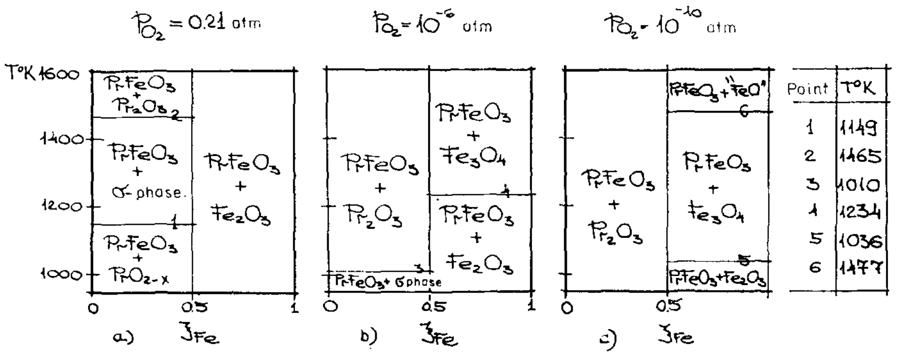


FIG. 3. State diagram of $P_{O_2} = f(1/T)$ for the equilibrium mixture of condensed phases in the Pr–Fe–O system for (a) $\xi_{Pr} < 0.5$ and (b) $\xi_{Pr} > 0.5$.



Point	T°K
1	1149
2	1465
3	1010
4	1234
5	1036
6	1477

FIG. 4. State diagram of the Pr–Fe–O on coordinates $T = f(\xi_{Fe})$ with P_{O_2} = constant for three values of the partial oxygen pressure: (a) 0.21 atm; (b) 10^{-6} atm; and (c) 10^{-10} atm.

changes occurring in the Pr–Fe–O system on change of partial oxygen pressure and temperature at a fixed composition parameter. It is apparent that the zone of stability of single-phase ferroperovskite is rather broad and, at high enough partial oxygen pressure, the stability of ferroperovskite is not very sensitive to temperature change. This property of the system is also reflected in the equilibrium state diagram constructed on the coordinates $T = f(\xi_{Fe})$ for $P_{O_2} = 0.21$, 10^{-6}, and 10^{-10} atm and introduced in Fig. 4 with indication of the temperatures of the phase changes.

In conclusion, it should be noted that we have also attempted to clarify the possibility of forming the compound $PrFe_{12}O_{19}$, which is analogous to that observed in the La–Fe–O system (*15*) and which has the structure of magnetoplumbite. It turned out that under any thermal treatment in the temperature range 1000–1400°C and pressure range P_{O_2} from 10^{-3} atm to 1 atm the mixture of oxides of total composition "$PrFe_{12}O_{19}$" is triphase and consists of ferroperovskite, magnetite, and hematite. At the same time, it has been established that the only ternary compound formed in the Pr–Fe–O system is orthoferrite $PrFeO_3$.

Conclusions

Phase equilibria and the thermodynamics of coexisting phases in the Pr–Fe–O system have been studied. Equilibrium phase diagrams have been constructed to show the character of changes taking place in the Pr–Fe–O system on change of partial oxygen pressure, temperature, and composition of the initial mixture of oxides: log $P_{O_2} = f\ (\xi_{Fe})$ and $\xi_O = f\ (\xi_{Fe})$ at 1300°K, $P_{O_2} = f(1/T)$ with fixed composition parameter, and $T = f\ (\xi_{Fe})$, $P_{O_2} = \text{constant}$. It has been shown that in the Pr–Fe–O system only one ternary compound, orthoferrite $PrFeO_3$, which is stable at any value of P_{O_2}, is formed.

Acknowledgments

The authors express their appreciation to Dr. A. R. Kaul for his help in carrying out the present work and for fruitful discussions of the results.

References

1. N. A. Toropov, V. N. Barzakovskii, I. A. Bondar, and Yu. P. Udalov, "State Diagrams of the Silicate Systems," Vol. 2, Leningrad (1970).
2. S. G. Schneider, R. S. Roth, and J. L. Waring, *J. Res. Nat. Bur. Stand.* **65A**, 345 (1961).
3. J. Beretka, *Aust. J. Appl. Sci.* **15**, 1 (1964).
4. V. V. Sorokin, Yu. D. Tretyakov, and O. S. Zaitsev, "Proceedings of the First All-Union Conference on Metal Oxides," p. 164, Kiev (1974).
5. Yu. D. Tretyakov and V. V. Sorokin, "Proceedings of the 11th Rare Earth Research Conference," Michigan (1974).
6. F. Bertaut and F. Forrat, *Compt. Rend.* **244**, 96 (1957).
7. B. V. Mill, *in* "Magnetic and Crystalline Studies of Ferrites" (K. P. Belov and Yu. D. Tretyakov, Ed.), Moscow (1971).
8. G. P. Espinosa, *J. Chem. Phys.* **37**, 234 (1962).
9. B. G. Hyde, D. J. M. Bevan, L. Eyring, *Phil. Trans. Roy. Soc., London, Ser. A.* **259**, 583 (1966).
10. Yu. D. Tretyakov, "The Chemistry of Nonstoichiometric Oxides," Moscow University Press, Moscow (1974).
11. Yu. D. Tretyakov, "The Thermodynamics of Ferrites," Chemistry Press, Leningrad (1967).
12. A. R. Kaul and Yu. D. Tretyakov, "Proceedings of the Fourth All-Union Conference on the High Temperature Chemistry of Silicates and Oxides," p. 95, Leningrad (1974).
13. D. Burnham and L. Eyring, *J. Phys. Chem.* **72**, 4415 (1968).
14. Y. Wilbert, A. Duquesnoy, and E. Marion, *Compt. Rend.* **C264**, 316 (1967).
15. V. L. Moruzzi and M. W. Shafer, *J. Amer. Ceram. Soc.* **43**, 367 (1960).
16. Yu. D. Tretyakov and A. R. Kaul, *J. Solid State Chem.*, in press.
17. Yu. D. Tretyakov, V. V. Sorokin, A. R. Kaul, and A. P. Erastova, *J. Solid State Chem.*, **18**, 253 (1976).