JOURNAL OF SOLID STATE CHEMISTRY **38**, 82–86 (1981)

The System GeO_2–FeO–Fe_2O_3 at 1000°C

E. TAKAYAMA,* N. KIMIZUKA, K. KATO, H. YAMAMURA, AND H. HANEDA

National Institute for Research in Inorganic Materials, Sakuramura, Niiharigun, Ibaraki 305, Japan

Received July 18, 1980; in final form October 24, 1980

The phase diagram of the GeO_2–FeO–Fe_2O_3 system was established. Four new compounds, $Fe_{3.2}Ge_{1.8}O_8$, $Fe_9Ge_5O_{22}$, $Fe_4Ge_2O_9$, and $Fe_{10}Ge_9O_{29}$, were found in the system. The diagram is much more complex than the corresponding one of SiO_2–FeO–Fe_2O_3. The difference between the two systems may be related to the ionic radii of the cations, Ge^{4+} and Si^{4+}.

Introduction

While the system SiO_2–FeO–Fe_2O_3 has been investigated by many workers because of its geological interest, and for the purpose of application to steelmaking (*1*), the related ternary system GeO_2–FeO–Fe_2O_3 has never been studied.

Germanates are usually available as model systems for corresponding silicates under high temperature and high pressure. In the system SiO_2–FeO–Fe_2O_3, only one silicate, Fe_2SiO_4 (olivine-type structure), exists at 1 atm. It is only at high pressure that $FeSiO_3$ becomes stable, and Fe_2SiO_4 takes a spinel-type structure (*2*). In the system GeO_2–FeO, $FeGeO_3$ is stable even at 1 atm, and Fe_2GeO_4 has a spinel-type structure. From studying the corresponding system with GeO_2, some suggestions can be expected at high pressure for the SiO_2–FeO–Fe_2O_3 system, which is very fundamental to geology. Moreover, the comparison of germanates and silicates is one of the most interesting aspects of crystal chemistry.

The purpose of this work is to establish the phase diagram of the system GeO_2–FeO–Fe_2O_3 and to compare it with the corresponding diagram of the SiO_2-containing system.

Experimental

Iron metal (99.99%), GeO_2 (99.99%), and Fe_2O_3 (99.9%) were used as starting materials. Wustite is not appropriate as a starting material, because it has a nonstoichiometric composition, $Fe_{1-x}O$, at 1 atm (*3*).

Prior to use, GeO_2 and Fe_2O_3 were calcined at 1000°C. Iron metal was dried at 100°C for 2 days and then analyzed by thermogravimetry in a reducing atmosphere (CO_2/H_2 = 0.1), at 1000°C. The precise composition of the "iron metal" which we used was $FeO_{0.028}$.

The starting materials were mixed to desired ratios in an agate mortar with ethyl alcohol, then the mixture thus obtained was

---

* To whom all correspondence should be addressed.

0022-4596/81/070082-05$02.00/0

Copyright © 1981 by Academic Press, Inc.
All rights of reproduction in any form reserved.

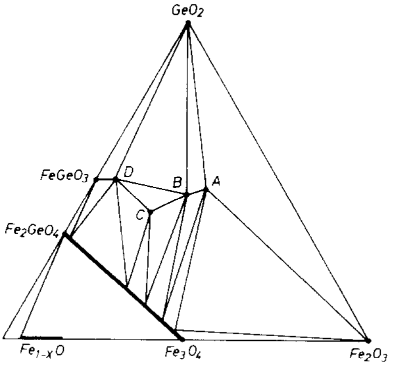

FIG. 1. Phase diagram of the system GeO_2–FeO–Fe_2O_3 at 1000°C. (A: $Fe_{3.2}Ge_{1.8}O_8$; B: $Fe_9Ge_5O_{22}$; C: $Fe_4Ge_2O_9$; D: $Fe_{10}Ge_9O_{29}$.)

dried under a nitrogen atmosphere to prevent further oxidation of the "iron metal." The mixture (about 2 g) was sealed in an evacuated silica tube (8 mm in diameter, about 40 mm in length) and was allowed to react at 1000 ± 2°C in a Pt–40%Rh wire-wound tubular furnace. The temperature of the furnace was measured with a Pt–Pt13%Rh thermocouple which had been calibrated at the gold point. The silica-tube method has been successfully applied to the system MgO–FeO–GeO_2 by Navrotsky and Hughes (*4*), and attack on the silica tubes was reported to be minimal.

Every sample was fired in the furnace until its powder X-ray pattern did not change. It took about 100 hr for the samples to react fully. More than 80 samples were fired and examined.

TABLE I

IONIC RADII (Å); AFTER SHANNON AND PREWITT (*5*)

Ion	C. N. 4	C. N. 6
Fe^{2+}	0.63	0.77
Fe^{3+}	0.49	0.645
Ge^{4+}	0.40	0.54
Si^{4+}	0.26	0.40

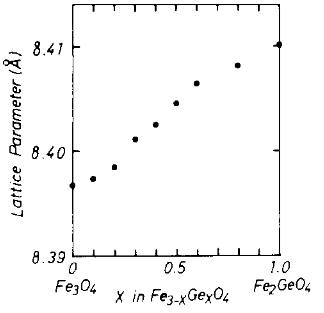

FIG. 2. The relation between the lattice parameter and x in $Fe_{3-x}Ge_xO_4$.

The identification of phases and the determination of lattice parameters were carried out by means of powder X-ray data collected on a diffractometer (Japan Electron Optics Laboratory, Model Dx-GO-S) using FeKα radiation.

Thermogravimetric methods under controlled oxygen fugacity are usually used for oxide systems which contain variable-valence elements. Unfortunately, such methods cannot be applied to the present system because of the rather vigorous vaporization of GeO_2 under high temperature and low oxygen fugacity.

Results and Discussion

The phase diagram obtained in the present work is shown in Fig. 1. Four new compounds, $Fe_{3.2}Ge_{1.8}O_8$, $Fe_9Ge_5O_{22}$, $Fe_4Ge_2O_9$, and $Fe_{10}Ge_9O_{29}$, were found in the system. The diagram is, therefore, much more complex than the corresponding one with SiO_2. What causes the great differences between the two systems? One of the possible answers to this question can

TABLE II

CATION DISTRIBUTION FOR $Fe_3Ge_2O_8$ AND $Fe_{3.2}Ge_{1.8}O_8$

C. N.	$Fe_3Ge_2O_8$	$Fe_{3.2}Ge_{1.8}O_8$
4	$2Ge^{4+}$	$1.8Ge^{4+} + 0.2Fe^{3+}$
6	$2Fe^{3+} + Fe^{2+}$	$2.2Fe^{3+} + 0.8Fe^{2+}$

TABLE III

POWDER X-RAY DATA FOR $Fe_{3.2}Ge_{1.8}O_8$

$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
$0\ 1\ 1$	5.85	5.827	5
$1\ 0\ \bar{2}$	4.59	4.588	5
$2\ 1\ \bar{1}$	3.79	3.783	15
$2\ 0\ 0$	3.76	3.754	40
$0\ 2\ 1$	3.71	3.712	5
$1\ 2\ \bar{1}$	3.65	3.650	20
$2\ 1\ \bar{2}$	3.44	3.439	60
$1\ 2\ \bar{2}$	3.08	3.086	35
$1\ 0\ 2$	3.04	3.035	10
$2\ 2\ \bar{1}$	2.976	2.975	5
$0\ 2\ 2$	2.916	2.913	75
$1\ 1\ \bar{3}$	2.866	2.863	65
$1\ 1\ 2$	2.855	2.852	85
$3\ 0\ \bar{2}$	2.793	2.791	55
$2\ 1\ 1$	2.764	2.763	5
$3\ 1\ \bar{2}$	2.645	2.647	70
$1\ 3\ \bar{1}$	2.610	2.609	100
$3\ 1\ \bar{3}$	2.410	2.409	25
$3\ 1\ 0$	2.399	2.397	30
$1\ 3\ \bar{2}$	2.376	2.378	30
$2\ 0\ 2$	2.280	2.280	10
$1\ 0\ \bar{4}$	2.250	2.248	10
$2\ 3\ \bar{2}$	2.237	2.238	25
$2\ 1\ \bar{4}$	2.212	2.212	20
$1\ 1\ \bar{4}$	2.171	2.170	10
$1\ 1\ 3$	2.164	2.164	20
$3\ 2\ 0$	2.147	2.146	15
$4\ 0\ \bar{2}$	2.123	2.123	15
$0\ 4\ 0$	2.086	2.085	10
$0\ 0\ 4$	2.036	2.036	15
$1\ 4\ \bar{1}$	2.010	2.010	20
$2\ 2\ 2$	2.000	2.001	10
$4\ 2\ \bar{1}$	1.840	1.840	20
$2\ 4\ \bar{2}$	1.826	1.825	15
$1\ 1\ \bar{5}$	1.734	1.734	10
$1\ 1\ 4$	1.729	1.729	20
$4\ 2\ \bar{4}$	1.719	1.719	15
$4\ 2\ 0$	1.712	1.712	15
$5\ 1\ \bar{2}$	1.654	1.654	20
$1\ 5\ 1$	1.567	1.567	30
$0\ 5\ 2$	1.544	1.544	10
$2\ 5\ 0$	1.525	1.524	15
$4\ 4\ \bar{2}$	1.487	1.487	45
$4\ 0\ \bar{6}$	1.474	1.474	20
$1\ 5\ \bar{3}$	1.463	1.463	30
$0\ 4\ 4$	1.457	1.457	50

be found by noting the ionic radii of the two cations, Si^{4+} and Ge^{4+}. As shown in Table I, the ionic radius of Si^{4+} is much less than that of the other cations. In contrast, Ge^{4+} has an ionic radius similar to that of Fe^{3+} or Fe^{2+}. Particularly, the ionic radius of Ge^{4+} [IV] is very close to that of Fe^{3+} [IV]. (The number in brackets denotes the coordination number.) It seems that this character of Ge^{4+} causes the discrepancy between the GeO_2-containing and the SiO_2-containing systems.

Spinel Solid Solution

Since, as described in the previous section, Fe_2SiO_4 has an olivine-type structure, spinel solid solutions between Fe_3O_4 and Fe_2SiO_4 do not, of course, exist. In contrast to this, Fe_2GeO_4 has a normal spinel-type structure (*6*) and forms a continuous series of spinel solid solutions with Fe_3O_4 which has an inverse spinel-type structure.

The following cation substitution must occur along the solution line:

$$Ge^{4+}[IV] + Fe^{2+}[VI] \rightarrow Fe^{3+}[IV] + Fe^{3+}[VI].$$

The similarity of ionic radii of three cations, particularly of Ge^{4+}[IV] and Fe^{3+}[IV], permits this substitution. The ionic radius of Si^{4+}[IV] is so small that the corresponding substitution is impossible.

Figure 2 shows the relation between the lattice parameters and the compositions of the spinel solid solutions. The lattice parameter increases with x in $Fe_{3-x}Ge_xO_4$. It is to be noted that the corresponding silicate spinel, Fe_2SiO_4, which is stable at high pressure, has a very small lattice parameter of 8.235 Å (*7*).

Compound $Fe_{3.2}Ge_{1.8}O_8$

In the previous paper (*8*), we reported the crystal structure of this compound as determined on the assumption that it has a stoichiometric composition of $Fe_3Ge_2O_8$. The basic feature of the structure consists of cubic close packing of oxygen ions with the cations occupying the fourfold and the sixfold coordination sites, as shown in Table II. There exist Ge_2O_7 groups similar to the Si_2O_7 groups found in the modified spinel structure (*9*). Moreover, there are oxygen ions which do not satisfy the electrostatic valence rule of Pauling (*10*).

It was found, meanwhile, that the composition of this compound is not exactly $Fe_3Ge_2O_8$, but is nearly equal to $Fe_{3.2}Ge_{1.8}O_8$; a detectable homogeneity range is not present. This fact has already been suggested in the previous paper (*8*). Despite the correction to the composition, the basic feature of the structure does not seem to need any correction. It is important to note that the ratio of numbers of total cations to oxygen ions remains 5:8 in the corrected composition. The new composition can be derived from $Fe_3Ge_2O_8$ by the cation substitution described in the previous section. According to this, the cat-

TABLE IV

POWDER X-RAY DATA FOR $Fe_4Ge_2O_9$

$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
0 0 4	4.69	4.677	5
1 0 5	3.28	3.281	20
2 0 2	3.21	3.209	5
1 2 1	3.02	3.015	15
2 0 4	2.759	2.759	100
1 1 6	2.619	2.620	5
2 2 0	2.417	2.416	10
0 0 8	2.339	2.338	5
2 0 6	2.302	2.303	10
3 0 3	2.141	2.139	5
1 2 7	2.012	2.012	5
1 2 9	1.719	1.719	10
4 0 0	1.708	1.708	10
2 3 5	1.690	1.690	5
4 0 2	1.680	1.680	25
2 3 7	1.547	1.546	5
3 0 9	1.536	1.535	5
1 1 12	1.483	1.484	5
2 4 4	1.452	1.452	5
2 0 12	1.418	1.418	5

TABLE V

POWDER X-RAY DATA FOR $Fe_9Ge_5O_{22}$ AND $Fe_{10}Ge_9O_{29}$

$Fe_9Ge_5O_{22}$		$Fe_{10}Ge_9O_{29}$	
d_{obs} (Å)	I_{obs}	d_{obs} (Å)	I_{obs}
5.75	5	4.55	10
5.23	5	3.43	25
4.42	5	3.32	10
4.24	10	3.27	100
3.90	15	3.10	5
3.66	25	3.05	45
3.46	10	2.978	95
3.34	55	2.937	15
3.29	30	2.807	40
3.20	35	2.623	25
3.16	25	2.608	30
3.11	10	2.564	35
3.01	100	2.551	20
2.992	25	2.492	15
2.927	20	2.403	15
2.903	10	2.339	10
2.871	45	2.276	5
2.847	15	2.205	5
2.836	25	2.144	5
2.664	35	2.109	5
2.642	25	2.087	10
2.597	25	2.050	20
2.554	30	2.028	5
2.544	95	1.958	5
2.518	40	1.917	5
2.506	20	1.853	5
2.399	20	1.875	5
2.373	10	1.835	5
2.364	20	1.765	10
2.325	30	1.750	10
2.301	10	1.716	5
2.253	15	1.682	10
2.105	10	1.676	10
2.093	25	1.662	10
2.069	25	1.647	10
1.914	10	1.577	10
1.898	10	1.549	15
1.716	10	1.539	15
1.596	20	1.518	25
1.587	10	1.442	15
1.584	20		
1.564	20		
1.499	25		
1.490	35		
1.478	25		
1.475	40		
1.468	25		
1.453	25		

ions may be distributed as shown in Table II for the corrected composition.

The cation substitution mentioned above may decrease the Ge–Ge repulsion within a Ge_2O_7 group, which seems to be otherwise very strong, and can also decrease instability caused by the violation of electrostatic valence rule. This is a possible reason why the real composition deviates from the stoichiometric one.

The compound was also studied by means of Mössbauer spectroscopy on a spectrometer (Elscient Co.) operated in constant-acceleration mode. The source was ^{57}Co dispersed in copper. The spectrum obtained at room temperature consists of two doublets, which were identified with Fe^{3+}[VI] and Fe^{2+}[VI] with quadrupole splitting, by least-squares curve fitting. The intensity ratio of Fe^{3+}[VI]/Fe^{2+}[VI] was found to be 2.44, on the assumption that recoilless fractions of Fe^{3+} and Fe^{2+} are equal to each other. The value is in rough agreement with 2.75 expected from the cation distribution shown in Table II. The difference of the two values may be attributed to the fact that the assumption mentioned above is not satisfied exactly. No peaks were detected corresponding to Fe^{3+}[IV]; this is probably due to their very weak intensities.

The powder X-ray data were indexed as shown in Table III. The compound is monoclinic and the lattice parameters, calculated by least-squares method, are a = 8.490(1) Å, b = 8.340(1) Å, c = 9.209(1) Å, and β = 117.83(1)°.

Compounds $Fe_9Ge_5O_{22}$, $Fe_4Ge_2O_9$, and $Fe_{10}Ge_9O_{29}$

Unfortunately, since structural data have not been obtained for these compounds, detailed discussion is impossible at the present stage. Only for $Fe_4Ge_2O_9$, the powder X-ray data could be indexed as shown in Table IV, on the assumption of a tetragonal lattice. The lattice parameters are a = 6.832(1) Å, and c = 18.705(2) Å. The powder X-ray data for the other compounds are shown in Table V.

Acknowledgment

The authors are indebted to Professor T. Katsura, Tokyo Institute of Technology; and Mr. Y. Matsui, National Institute for Research in Inorganic Materials, for their continuous encouragement and helpful suggestions.

References

1. A. Muan and E. F. Osborn, "Phase Equilibria among Oxides in Steelmaking," p. 53, Addison–Wesley, Reading, Mass. (1965).
2. A. Navrotsky, *in* "Progress in Solid State Chemistry" (J. O. McCaldin and G. Somorjai, Eds.), Vol. 11, p. 203, Pergamon, Elmsford, N.Y. (1976).
3. L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.* **67**, 1398 (1945).
4. A. Navrotsky and L. Hughes, Jr., *J. Solid State Chem.* **16**, 185 (1976).
5. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B* **25**, 925 (1969).
6. F. Hartmann-Boutron and P. Imbert, *J. Appl. Phys.* **39**, 775 (1968).
7. A. E. Ringwood, *Geochim. Cosmochim. Acta* **15**, 18 (1958).
8. K. Kato, E. Takayama, and N. Kimizuka, *Naturwissenschaften* **66**, 616 (1979).
9. N. Morimoto, M. Tokonami, and K. Koto, *Amer. Miner.* **57**, 62 (1972).
10. L. Pauling, "The Nature of the Chemical Bond," 3rd ed., p. 547, Cornell Univ. Press, New York, (1960).