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The System GeO_2–ZnO–Fe_2O_3 at 1000°C

In previous work (*1–3*), we studied phase relations of the systems GeO_2–FeO–Fe_2O_3 and GeO_2–MnO–Mn_2O_3. In the former system, some new compounds were found and the phase diagram is quite different from the corresponding silicate system, SiO_2–FeO–Fe_2O_3. On the contrary, the phase diagram of the latter system is geometrically identical with that of SiO_2–MnO–Mn_2O_3. This paper reports the phase relations of the system GeO_2–ZnO–Fe_2O_3. Owing to the spherical electronic configuration and tendency of covalent bond formation (*4*), Zn^{2+} and Ge^{4+} prefer tetrahedral sites to octahedral sites. ZnO and Zn_2GeO_4 take, consistent with this feature of cations, wurtzite and phenacite structures, respectively. It is only at high pressures that rock salt and spinel structures become stable (*5, 6*). In addition, Fe^{3+} also has a spherical electronic configuration, and tends to occupy, though not so strongly as Zn^{2+} and Ge^{4+}, tetrahedral sites (*7*). The present system is characteristic in this respect, compared with the systems GeO_2–FeO–Fe_2O_3 and GeO_2–MnO–Mn_2O_3 in which Mn^{3+} and Fe^{2+} are anisotropic and have octahedral site preference energies (*7, 8*).

GeO_2(99.99%), Fe_2O_3(99.9%), and ZnO (reagent grade) were used as starting materials. After being calcined at 1000°C, these materials were mixed to desired ratios in an agate mortar with ethyl alcohol. The mixture thus obtained (about 2 g) was dried and placed in a platinum crucible. The sample was allowed to react at 1000 ± 2°C in a Pt60%–Rh40% wire-wound tubular furnace. Every sample was fired until its powder X-ray pattern did not change. It took about 120 hr to react fully, except for the syntheses of spinel solid solutions, $Zn_{1+x}Fe_{2-2x}Ge_xO_4$. They were obtained from the reaction between $ZnFe_2O_4$ and Zn_2GeO_4 which had been previously synthesized. Since the reaction rate between two compounds is small compared with that between GeO_2, Fe_2O_3, and ZnO, it took about 3 weeks until the lattice constant of the spinel solid solution did not change any more. The identification of the compounds and the determination of lattice constants were carried out by means of the powder X-ray method using Fe*Kα* radiation. About 40 kinds of samples were fired and examined.

The phase diagram obtained in the present work is shown in Fig. 1. There exists a new ternary germanate between GeO_2 and $ZnFe_2O_4$. This compound is dark brown and nonmagnetic at room temperature. It is thought in the present stage that the composition of the compound is $Zn_5Fe_{10}Ge_8O_{36}$. The powder X-ray data are shown in Table I. Recently, we found new germanates, $Fe_{15}Ge_8O_{36}$ and $Co_5Fe_{10}Ge_8O_{36}$, which are isostructural with each other, and determined their crystal structure (*2, 9*).

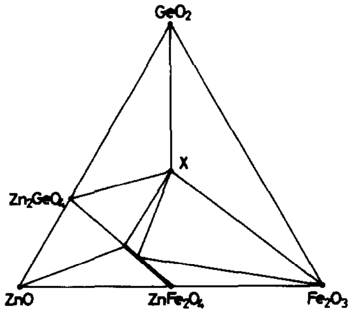

FIG. 1. The phase diagram of the system GeO_2–ZnO–Fe_2O_3 at 1000°C. *X*: $Zn_5Fe_{10}Ge_8O_{36}$.

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TABLE I

POWDER X-RAY DATA FOR $Zn_5Fe_{10}Ge_8O_{36}$

d (Å)	I (%)	d (Å)	I (%)
9.81	1	2.494	100
7.01	6	2.479	30
5.70	6	2.459	7
4.89	10	2.453	4
4.56	5	2.388	14
4.06	6	2.378	18
4.02	13	2.350	37
3.89	17	2.334	14
3.54	24	2.315	24
3.50	41	2.286	21
3.48	46	2.104	18
3.41	8	2.083	45
3.38	13	2.054	17
3.36	9	1.962	10
3.32	48	1.921	10
3.30	65	1.915	12
3.28	20	1.647	17
3.14	12	1.618	13
2.993	90	1.596	10
2.964	55	1.591	20
2.917	26	1.573	24
2.888	17	1.559	8
2.846	48	1.546	6
2.825	26	1.507	6
2.773	60	1.503	12
2.724	18	1.493	29
2.691	10	1.486	17
2.646	10	1.483	44
2.638	60	1.465	27
2.607	34	1.460	28
2.549	100	1.457	42
2.518	74	1.445	29

The data shown in Table I can not be, however, assigned by reference to the lattice constants of $Fe_{15}Ge_8O_{36}$ and $Co_5Fe_{10}Ge_8O_{36}$. It seems that $Zn_5Fe_{10}Ge_8O_{36}$ is not isostructural with them. Single-crystal synthesis of this germanate is in progress for the purpose of structural analysis.

The solubility limit of Zn_2GeO_4 in $ZnFe_2O_4$ (normal spinel structure) is 0.368 as mole fraction of Zn_2GeO_4, while $ZnFe_2O_4$ is slightly soluble in Zn_2GeO_4 (phenacite structure). The lattice constants of spinel solid solutions are shown in Fig. 2, related to mole fraction of Zn_2GeO_4. Along the solution line, the following cation substitution must occur:

$$2Fe^{3+} \rightarrow Ge^{4+} + Zn^{2+}.$$

Similar substitution was found between Fe^{3+}, Fe^{2+}, and Ge^{4+} in the system GeO_2–FeO–Fe_2O_3 (*1*), and between Mn^{3+}, Mn^{2+}, and Ge^{4+} in the system GeO_2–MnO–Mn_2O_3 (*3*). These solid solutions follow Vegard's law. The lattice constant of pure Zn_2GeO_4 spinel is estimated by extrapolation to be 8.365 Å. On the other hand, 8.350 Å was reported for a lattice constant of cubic spinel, Zn_2GeO_4, synthesized at high pressure (*6*). The difference between the two values is significant. As a possible explanation for this fact one can think about cation distribution in the cubic spinel synthesized at high pressure and in the spinel solid solutions of the present system. Zn_2GeO_4 spinel at high pressure is regarded as an inverse spinel, $Zn[ZnGe]O_4$ (*10*). It is suggested from the fact described above that in the spinel solid solutions of the present system Ge^{4+} occupies the tetrahedral site, i.e., the cation distribution of the solid solutions is $(Ge,Zn)[(Zn,Fe)_2]O_4$. If this is true, the estimated value (8.365 Å) corresponds to the lattice constant of normal spinel, $Ge[Zn_2]O_4$.

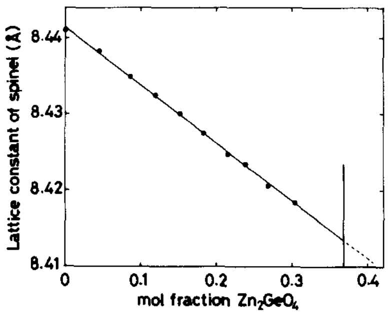

FIG. 2. Lattice constants of spinel solid solutions $Zn_{1+x}Fe_{2-2x}Ge_xO_4$.

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References

1. E. Takayama, N. Kimizuka, K. Kato, H. Yamamura, and H. Haneda, *J. Solid State Chem.* **38**, 82 (1981).
2. E. Takayama, N. Kimizuka, K. Kato, and A. Yamamoto, in preparation.
3. E. Takayama, *J. Solid State Chem.* **39**, 133 (1981).
4. R. C. Evans, "An Introduction to Crystal Chemistry," Cambridge Univ. Press, London/New York (1964).
5. C. H. Bates, W. B. White, and R. Roy, *Science* **137**, 993 (1962).
6. Y. Syono, S. Akimoto, and Y. Matsui, *J. Solid State Chem.* **3**, 369 (1971).
7. A. Navrotsky and O. J. Kleppa, *J. Inorg. Nucl. Chem.* **29**, 2701 (1967).
8. D. S. McClure, *J. Phys. Chem. Solids* **3**, 311 (1957).
9. K. Kato, E. Takayama, N. Kimizuka, H. Haneda, and H. Yamamura, to be published.
10. A. Navrotsky, *J. Solid State Chem.* **6**, 42 (1973).

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