

Powder X-Ray Study on Iron-Germanium Pyroxenes

In the process of establishing the phase diagram of the $\text{GeO}_2\text{-FeO-Fe}_2\text{O}_3$ system at 1000°C (1), we prepared FeGeO_3 and obtained its powder X-ray pattern. In the same work, we found a new ternary compound whose composition is very close to FeGeO_3 and was reported as $\text{Fe}_{10}\text{Ge}_9\text{O}_{29}$.

FeGeO_3 has a clinopyroxene structure and its lattice constants were first reported as $a = 9.56 \text{ \AA}$, $b = 9.16 \text{ \AA}$, $c = 5.21 \text{ \AA}$, and $\beta = 102.5^\circ$ by Royen and Forwerg with d values (2) and later as $a = 9.74 \text{ \AA}$, $b = 9.12 \text{ \AA}$, $c = 5.19 \text{ \AA}$, and $\beta = 102.4^\circ$ by Grebenshchikov *et al.* without d values (3). The d values obtained by us are, however, quite different from those of Royen and Forwerg. The present work was undertaken in order to clarify the reasons for this discrepancy and the relation between FeGeO_3 and the compound having composition close to FeGeO_3 . (Hereafter, this compound will be referred to as compound D, according to the notation in the previous paper.)

The methods of preparation of the powder samples and the measurement of powder X-ray patterns were described previously (1). For FeGeO_3 , needle-like single crystals were also obtained on continued heating of powder material in a silica tube, for a period of 2 weeks at 1000°C . The Weissenberg photographs were taken for this single crystal.

The powder X-ray data for FeGeO_3 could be indexed as shown in Table I based on the Weissenberg photographs. The compound has a monoclinic lattice as reported earlier (2), and the lattice constants were calculated to be $a = 9.793(2) \text{ \AA}$, $b = 9.145(1) \text{ \AA}$, $c = 5.195(1) \text{ \AA}$, and $\beta = 101.85(2)^\circ$.

On the other hand, the d values for

compound D can also be indexed on an assumption of an orthorhombic lattice, as shown in Table II. The lattice constants are $a = 18.913(2) \text{ \AA}$, $b = 9.106(1) \text{ \AA}$, and $c = 5.428(1) \text{ \AA}$. The powder X-ray pattern of compound D resembles that of germanium-containing orthopyroxene such as MnGeO_3 (4), or CoGeO_3 (5). The lattice constants resemble each other as well. On the basis of

TABLE I
POWDER X-RAY DATA FOR $\text{Fe}_{1.07}\text{Ge}_{0.93}\text{O}_3$

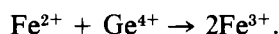
hkl	d_{obs} (\AA)	d_{calc} (\AA)	I_{obs}
0 2 0	4.58	4.573	5
1 1 $\bar{1}$	4.34	4.340	5
0 2 1	3.40	3.400	25
2 2 0	3.31	3.308	35
3 1 0	3.02	3.016	80
2 2 $\bar{1}$	2.973	2.972	55
3 1 $\bar{1}$	2.849	2.847	25
2 2 1	2.610	2.609	55
1 3 $\bar{1}$	2.593	2.593	100
0 0 2	2.541	2.542	30
4 0 0	2.397	2.396	10
0 4 0	2.287	2.286	5
1 1 2	2.269	2.268	5
3 1 2	2.161	2.161	30
3 3 $\bar{1}$	2.138	2.137	5
4 2 $\bar{1}$	2.099	2.099	5
0 4 1	2.086	2.085	10
2 4 0	2.064	2.064	10
2 4 $\bar{1}$	1.975	1.974	5
2 2 2	1.890	1.891	5
5 1 0	1.876	1.876	10
2 4 1	1.856	1.856	15
5 3 $\bar{1}$	1.630	1.630	25
3 5 0	1.587	1.587	30
0 6 0	1.524	1.524	15
1 3 $\bar{3}$	1.505	1.505	20
6 0 $\bar{2}$	1.498	1.498	15
3 5 1	1.473	1.473	35
3 5 $\bar{2}$	1.413	1.413	10

TABLE II
POWDER X-RAY DATA FOR $\text{Fe}_{1.07}\text{Ge}_{0.93}\text{O}_3$
(COMPOUND D)

<i>h k l</i>	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
0 2 0	4.55	4.553	10
1 2 1	3.43	3.430	25
4 1 1	3.32	3.320	10
2 2 1	3.27	3.273	100
3 2 1	3.05	3.052	45
6 1 0	2.978	2.979	95
5 1 1	2.937	2.937	15
4 2 1	2.807	2.807	40
1 3 1	2.623	2.624	25
2 0 2	2.608	2.609	30
5 2 1	2.564	2.564	35
2 3 1	2.551	2.551	20
3 0 2	2.492	2.493	15
3 1 2	2.403	2.404	15
6 2 1	2.339	2.339	10
0 4 0	2.276	2.276	5
5 0 2	2.205	2.205	5
5 1 2	2.144	2.143	5
8 1 1	2.109	2.109	5
1 4 1	2.087	2.086	10
4 4 0	2.050	2.051	20
6 3 1	2.028	2.028	5
8 2 1	1.958	1.957	5
9 1 1	1.917	1.916	5
10 1 0	1.853	1.852	5
6 2 2	1.875	1.874	5
5 4 1	1.835	1.836	5
7 2 2	1.765	1.765	10
8 1 2	1.750	1.749	10
2 4 2	1.716	1.715	5
0 2 5	1.682	1.681	10
1 2 3	1.676	1.675	10
10 2 1	1.662	1.663	10
9 3 1	1.647	1.646	10
6 5 0	1.577	1.577	10
1 3 3	1.549	1.549	15
10 3 1	1.539	1.539	15
0 6 0	1.518	1.518	25
11 3 1	1.442	1.442	15

these data, it seems reasonable to assume that compound D has an orthopyroxene-type structure. According to this, the composition of compound D may not be $\text{Fe}_{10}\text{Ge}_9\text{O}_{29}$, but $\text{Fe}_{1+x}\text{Ge}_{1-x}\text{O}_3$, which can be derived from the following cation substi-

tution relative to FeGeO_3 :



Based on the above discussion, reinvestigation was performed to determine the value of x and this resulted in $x = 0.07$. However, since only the powder X-ray method was used for this purpose, the value is a very rough one and the homogeneity range of composition could not be decided. One might conclude that a clinopyroxene to orthopyroxene transition occurs by the above substitution in FeGeO_3 .

As described previously, a serious discrepancy is present among two sets of d values for FeGeO_3 reported by us and by Royen and Forweg. They reported that the single phase of FeGeO_3 was not obtained, but only a mixture with Fe_2GeO_4 . Actually, they assigned a rather strong diffraction peak, which must be assigned to the reflection from the (002) plane in our indexing, to Fe_2GeO_4 as a second phase. However, a corresponding peak is present in the other germanium-containing clinopyroxenes such as CoGeO_3 (5) and MgGeO_3 (6). Moreover, no other peaks of Fe_2GeO_4 were found in the pattern obtained by us. Their d values were not indexed by themselves but by the NBS (ASTM card No. 16-505), according to the lattice constants reported by them. The indexing does not seem reasonable because of large differences between d_{obs} and d_{calc} . It seems that the sample examined by them might be a mixture with orthopyroxene (compound D) as a second phase, not with Fe_2GeO_4 . Since the compositions of two compounds, FeGeO_3 and $\text{Fe}_{1.07}\text{Ge}_{0.93}\text{O}_3$, are very close to each other, the product is strongly affected by small deviation from the exact mixing ratio of starting materials, such as oxidation of the iron metal used as a starting material.

Acknowledgment

The authors are indebted to Dr. K. Kato, National

Institute for Research in Inorganic Materials, for his continuous encouragement and helpful suggestions.

References

1. E. TAKAYAMA, N. KIMIZUKA, K. KATO, H. YAMAMURA, AND H. HANEDA, *J. Solid State Chem.* **38**, 82 (1981).
2. P. ROYEN AND W. FORWERT, *Z. Anorg. Allg. Chem.* **326**, 113 (1963).
3. R. G. GREBENSHCHIKOV, V. V. MOTSAKOV, AND O. G. CHIGAREVA, *Russ. J. Inorg. Chem.* **21**, 1368 (1976). [Translated from *Zh. Neorg. Khim.* **21**, 2488 (1976).]
4. A. TAUBER, J. A. KOHN, C. G. WHINFREY, AND W. D. BABBAGE, *Amer. Miner.* **48**, 555 (1963).
5. A. TAUBER AND J. A. KOHN, *Amer. Miner.* **50**, 13 (1965).
6. C. R. ROBBINS AND E. M. LEVIN, *Amer. J. Sci.* **257**, 63 (1959).

EIJI TAKAYAMA*
NOBORU KIMIZUKA

*National Institute for Research in Inorganic Materials
Sakura-mura, Niihari-gun
Ibaraki-ken 305, Japan*

Received April 27, 1981

* To whom all correspondence should be addressed.