JOURNAL OF SOLID STATE CHEMISTRY **44**, 307–317 (1982)

The System BaO–GeO_2 at High Pressures and Temperatures, with Special Reference to High-Pressure Transformations in $BaGeO_3$, $BaGe_2O_5$, and $Ba_2Ge_5O_{12}$

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Received March 10, 1982; in revised form May 11, 1982

Phase relations in the system BaO–GeO_2 were investigated in the pressure range 20–70 kbar in the temperature range 750–1200°C. Several new phases were identified in this system: an atmospheric phase of $BaGe_2O_5$ (monoclinic $BaGe_2O_5$ I), two high-pressure phases of $BaGe_2O_5$ (monoclinic $BaGe_2O_5$ II and tetragonal $BaGe_2O_5$ III), and a high-pressure phase of $Ba_2Ge_5O_{12}$. The phase boundary curve between $BaGe_2O_5$ II and $BaGe_2O_5$ III was preliminarily determined as $P(\text{kbar}) = 7.7 + 0.047T$ (°C). The high-pressure phases of $BaGeO_3$, which were previously reported by Y. Shimizu, Y. Syono, and S. Akimoto (*High Temp.-High Pressures* **2**, 113 (1970)) in the pressure range 15–95 kbar, were interpreted to be not single-phase materials but complicated mixtures of more than two phases in the system BaO–GeO_2. X-Ray powder diffraction data for the new compounds synthesized in this study are given.

Introduction

Comprehensive studies of the phase relations in the system BaO–GeO_2 at high temperatures and at atmospheric pressure have been made mainly by Soviet investigators (*1–4*). A phase diagram of this system has been reported by Grebenshchikov *et al.* (*3*). It has recently been pointed out by H. Takei (private communication), however, that the phase diagram is incompatible with information from the crystal growth of a few phases in the system. Some uncertainties have also been revealed in the indexing of the X-ray powder diffraction data for $BaGeO_3$ in this system (ASTM card, 21-69, 21-70; Takei, private communication). This system appears to be still not fully understood.

Shimizu *et al.* (*5*) studied the stability relations in $BaGeO_3$ at high pressures and high temperatures as a part of a series of investigations on the high-pressure crystal chemistry of $A^{2+}B^{4+}O_3$-type compounds. They reported that the atmospheric-pressure phase of $BaGeO_3$ with the pseudowollastonite structure (low-temperature phase) transformed to a high-pressure phase ("$BaGeO_3$ II") with pseudoorthorhombic symmetry at around 15 kbar and at temperatures ranging from 650 to 1000°C. They also reported that $BaGeO_3$ finally transformed to the perovskite-like structure at around 100 kbar through several other intermediate

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0022-4596/82/120307-11$02.00/0

phases with unknown structure in the pressure range 30–95 kbar.

In the present study, we at first intended to reexamine the high-pressure behavior of $BaGeO_3$ and to obtain single crystals of high-pressure phases of $BaGeO_3$ with the unknown structures. In the course of the reinvestigation, however, we extended our interest to the wide compositional range in the system $BaO-GeO_2$ for a more complete understanding of the stability relations of $BaGeO_3$ at high pressures. This paper reports the synthesis of a new atmospheric-pressure phase and three new high-pressure phases in the system $BaO-GeO_2$. Previous data on the high-pressure stability of $BaGeO_3$ are interpreted on the basis of the present results.

Experimental Procedure

A series of atmospheric-pressure phases of samples with different molecular ratios of $BaO:GeO_2$ (2:1, 1:1, 1:2, 2:5, 1:3, and 1:4) were prepared by mixing intimately $BaCO_3$ and GeO_2 of guaranteed quality in the required compositions and firing at 1350–1400°C for several hours in air (except for a sample of 2:1). Polycrystalline Ba_2GeO_4 sample was prepared at 1200°C in vacuum (10^{-4} Torr). Single crystals of $BaGeO_3$ (high-temperature phase), $BaGe_2O_5$, and $BaGe_4O_9$ were obtained by cooling in platinum crucibles. These crystals were powdered and used as starting materials for the high-pressure experiments. In the case of samples which do not exist as a single phase at atmospheric pressure but decompose into a mixture of compounds with different compositions (for example, $Ba_2Ge_5O_{12}$), powder samples of the sintered mixture were used as starting materials for the high-pressure experiments.

High-pressure and high-temperature experiments were chiefly made with the aid of a tetrahedral anvil apparatus. The two runs (Nos. 3 and 4 in Table I) at relatively low pressures (20–30 kbar) were carried out with the aid of a cubic anvil apparatus. In the experiments using the tetrahedral anvil apparatus, tungsten–carbide anvils with 15-mm edge and baked pyrophyllite tetrahedrons with 20-mm edge were used. For the cubic anvil apparatus, a combination of 16-mm-edge anvils with 21-mm-edge cubes was adopted. In the usual runs, powder samples of the starting materials were directly embedded in the tubular graphite furnace which was placed diagonally with the axis of the cylinder between opposite edges of the pyrophyllite tetrahedron, or at the center of the pyrophyllite cube with the axis of the cylinder perpendicular to the opposite faces of the cube. Pressure values were calibrated against press load at room temperature based on the well-established pressure-fixed points of low-Bi (25.5 kbar), low-Ba (55 kbar), and high-Bi (77 kbar).

A conventional quenching technique was used for investigating the phase relations. After pressure was applied to the sample, temperature was brought to the desired value and held there for 20–80 min. The sample was then quenched by turning off the heating power under the working pressure. After releasing the pressure, the phases present in the quenched samples were examined by means of an X-ray powder diffractometer and a petrographic microscope. A considerable amount of loss of BaO component in the starting materials was found in almost all the runs. The use of a platinum heater instead of the graphite heater was partially effective in reducing the BaO loss. The pyrophyllite cubes used for runs 3 and 4 were baked incompletely at 500°C, and this results in production of hydrooxide phases in the products.

Structure analysis was carried out with a precession camera on single crystals obtained in the present study. Single crystals and sections of the quenched samples were also examined by means of an electron microprobe analyzer (XMA). Figure 1 shows

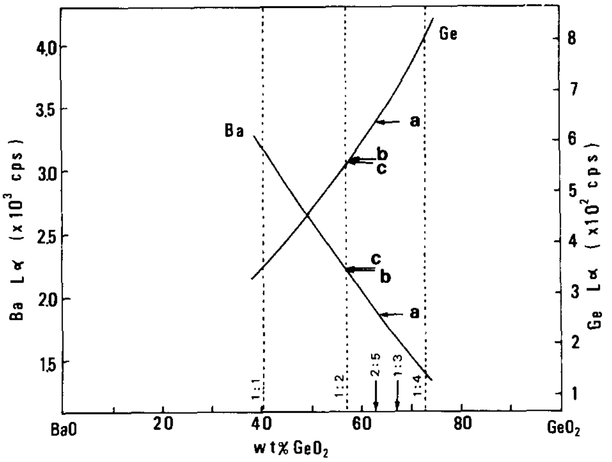

FIG. 1. Procedure for determining the chemical composition of the high-pressure phases in the system BaO–GeO$_2$. Solid curves are the calibration curves obtained on the basis of the three standard samples (BaGeO$_3$, BaGe$_2$O$_5$, and BaGe$_4$O$_9$). a: Single crystal of high-pressure phase of Ba$_2$Ge$_5$O$_{12}$. b: Single crystal of BaGe$_2$O$_5$ II. c: Homogeneous polycrystalline aggregate of BaGe$_2$O$_5$ III.

the procedure for determining the chemical composition of the samples using the microprobe analyzer. Single crystals of atmospheric-pressure phase of BaGeO$_3$ (high-temperature phase), atmospheric-pressure phase of BaGe$_2$O$_5$, and BaGe$_4$O$_9$ were used as standard materials. In Fig. 1, the observed intensities of both Ba-*Lα* and Ge-*Lα* lines are plotted against the chemical compositions (weight percent of GeO$_2$). On the basis of the calibration curves shown in the figure, the chemical composition of the high-pressure phases in the system BaO–GeO$_2$ was determined.

Results and Discussion

All the results of the high-pressure and high-temperature experiments are summarized in Table I.

Ba$_2$GeO$_4$

This phase is known to have the K$_2$SO$_4$-type structure at atmospheric pressure. No phase transformation was observed on the run at 60 kbar and 1100°C (No. 2 in Table I). The fact that Ba$_2$GeO$_4$ with the K$_2$SO$_4$-type structure appeared as a decomposition product in the runs of BaGeO$_3$ also supports its stability up to 60 kbar.

BaGeO$_3$

As has already been well established, BaGeO$_3$ has two phases at atmospheric pressure; a low-temperature phase (the pseudowollastonite structure) with hexagonal ring structure (*4*, *6*) and a high-temperature phase with orthorhombic chain structure (*6*, *7*). In a previous paper, Shimizu *et al.* (*5*) reported a synthesis of a high-pressure phase of BaGeO$_3$ ("BaGeO$_3$ II") at around 15 kbar using the low-temperature phase of BaGeO$_3$ I (atmospheric phase) as starting material. Since they were unsuccessful in preparing single crystals of "BaGeO$_3$ II," its X-ray diffraction pattern was tentatively indexed using the indices of the SrGeO$_3$ II-type structure with pseudoorthorhombic symmetry by the analogy of the high-pressure behavior between Sr compounds and Ba compounds.

In the present study, high-pressure phase relations of the BaGeO$_3$ composition were reexamined with particular interest in synthesizing single crystals of "BaGeO$_3$ II" and other high-pressure phases reported by

Shimizu *et al.* (*5*). Careful analyses of the quench products, however, revealed that no single-phase material was quenchable for the $BaGeO_3$ composition in the pressure range 20–60 kbar. Our X-ray powder diffraction data for the overall quench product of $BaGeO_3$ at 20 kbar (No. 3 in Table I) were found to be just identical with those reported for "$BaGeO_3$ II" (in a stricter sense, those for "$BaGeO_3$ II" + $Ba(OH)_2$), and further the diffraction data were completely interpreted as a mixture composed of BaO_2, a high-pressure phase of $BaGe_2O_5$ ($BaGe_2O_5$ II), and a high-pressure phase of $Ba_2Ge_5O_{12}$.

As shown in Table I (Nos. 3, 4), in the runs using a graphite heater at 20–30 kbar and at 750–930°C, the high-temperature phase of $BaGeO_3$ completely decomposed and some GeO_2-rich compounds in the $BaO-GeO_2$ system were identified as decomposition products. As will be mentioned later, when we use a graphite furnace for the high-pressure experiments of the present system, the lower the pressure is, the lower the temperature at which change in bulk chemical composition to the GeO_2-rich side begins to take place. At 20–30 kbar, such a change in chemical composition undoubtedly proceeds extensively in the temperature range 650–1000°C. Therefore, it is very unlikely that the run product at about 15 kbar in the previous work (*5*) preserves the initial composition isochemical to $BaGeO_3$.

No successful results were obtained in synthesizing the single-phase materials for $BaGeO_3$ in the pressure range 30–60 kbar. It was revealed that $BaGeO_3$ in this pressure range decomposes principally into a mixture of two phases: a high-pressure phase of $BaGe_2O_5$ plus Ba_2GeO_4 with the K_2SO_4-type structure. The high-pressure phase of $Ba_2Ge_5O_{12}$ is also identified as a secondary phase in the outer part of the sample close to the graphite heater. This may be caused by the shift of the bulk chemical composition to the GeO_2-rich side in the present sample assembly. As will be mentioned later, there are two high-pressure phases in $BaGe_2O_5$ (designated $BaGe_2O_5$ II and $BaGe_2O_5$ III) depending on pressure and temperature. This produced a complicated result in the run at 60 kbar and 1100°C with a graphite heater (No. 5 in Table I). Actually, we could pick out a few single crystals of both $BaGe_2O_5$ II and the high-pressure phase of $Ba_2Ge_5O_{12}$ from the aggregate of $BaGe_2O_5$ III and Ba_2GeO_4. As will be shown later, the pressure–temperature condition of run 5 was just on the phase boundary curve between $BaGe_2O_5$ II and $BaGe_2O_5$ III (see Fig. 2). Since Shimizu *et al.* (*5*) used a graphite heater in their high-pressure and high-temperature experiments, several intermediate-pressure phases of $BaGeO_3$ reported by them may be a complicated mixture of Ba_2GeO_4, $BaGe_2O_5$ II and III, and/or the high-pressure phase of $Ba_2Ge_5O_{12}$.

$BaGe_2O_5$

In the system $BaO-GeO_2$, Ba_3GeO_5, Ba_2GeO_4, $BaGeO_3$, $BaGe_4O_9$, and $BaGe_{19}O_{39}$ have been reported to exist at atmospheric pressure (*3*). In this work, the synthesis of Ba_2GeO_4, $BaGeO_3$, and $BaGe_4O_9$ as single-phase samples was confirmed. Prior to the work by Grebenshchikov *et al.* (*3*), Koelmans and Verhagen (*8*) reported a synthesis of $BaGe_2O_5$ (sintered powder) and gave X-ray powder diffraction data for that sample. No further detailed crystal data have been given and there remained some doubts that the $BaGe_2O_5$ phase reported by them might be a metastable phase or not a single phase. It was found in the present study that $BaGe_2O_5$ actually exists as a single phase ($BaGe_2O_5$ I) at atmospheric pressure in the system $BaO-GeO_2$, and a single crystal of this phase was used as a standard sample for XMA analysis. However, the X-ray powder diffraction patterns of the present $BaGe_2O_5$ I are completely different

TABLE I

RESULTS OF THE HIGH-PRESSURE AND HIGH-TEMPERATURE EXPERIMENTS ON THE SYSTEM BaO–GeO$_2$

	Starting material						Phases present	
Run No.	Bulk composition	Phase	Heater	Pressure (kbar)	Temperature (°C)	Time (min)	Center	Outer shell
1	Ba_2GeO_4	$BaCO_3 + GeO_2$	G	60	1100	30	$BaCO_3 + GeO_2$(Tet)	
2	Ba_2GeO_4	Ba_2GeO_4	G	60	1100	30	Ba_2GeO_4	
3[a]	$BaGeO_3$	$BaGeO_3$	G	20–25	930	60	$Ba(OH)_2 + BaO_2 + BaGe_2O_5$ II + $Ba_2Ge_5O_{12}$	
4[a]	$BaGeO_3$	$BaGeO_3$	G	30	750	60	$Ba(OH)_2 + Ba_2GeO_4 + BaGe_2O_5$ II + $Ba_2Ge_5O_{12}$ + $Ba_3Ge_9O_{21} \cdot H_2O$ (*12*) + GeO_2	
5	$BaGeO_3$	$BaGeO_3$	G	60	1100	30	$Ba_2GeO_4 + BaGe_2O_5$ II + $BaGe_2O_5$ III + $Ba_2Ge_5O_{12}$	
6	$BaGe_2O_5$	$BaGe_2O_5$	G	40	750	80	$BaGe_2O_5$ II	$Ba_2Ge_5O_{12}$
7	$BaGe_2O_5$	$BaGe_2O_5$	Pt	40	850	60	$BaGe_2O_5$ II	$Ba_2Ge_5O_{12}$
8	$BaGe_2O_5$	$BaGe_2O_5$	G	60	1100	30	$BaGe_2O_5$ III	$Ba_2Ge_5O_{12}$
9[b]	$BaGe_2O_5$	$BaGe_2O_5$	G	60	1100	30	$BaGe_2O_5$ III	$Ba_2Ge_5O_{12}$
10	$BaGe_2O_5$	$BaGe_2O_5$	G	60	750	30	$BaGe_2O_5$ III	
11	$BaGe_2O_5$	$BaGe_2O_5$	Pt	60	1100	—	$BaGe_2O_5$ I + $BaGe_2O_5$ II + $BaGe_2O_5$ III	
12	$BaGe_2O_5$	$BaGe_2O_5$	Pt	60	900	60	$BaGe_2O_5$ III	
13	$BaGe_2O_5$	$BaGe_2O_5$	G	60	1200	20	$BaGe_2O_5$ II	$Ba_2Ge_5O_{12}$
14	$BaGe_2O_5$	$BaGe_2O_5$	G	70	1200	20	$BaGe_2O_5$ III	GeO_2(Tet)
15	$BaGe_2O_5$	$BaGe_2O_5$	G	50	850	60	$BaGe_2O_5$ III	GeO_2(Tet)
16	$Ba_2Ge_5O_{12}$	$BaGeO_3 + BaGe_4O_9$	Pt	60	900	30	$BaGe_2O_5$ III + $Ba_2Ge_5O_{12} + GeO_2$(Tet)	GeO_2(Tet)
17	$Ba_2Ge_5O_{12}$	$BaGeO_3 + BaGe_4O_9$	G	60	900	60	$Ba_2Ge_5O_{12}$	GeO_2(Tet)
18[c]	$Ba_2Ge_5O_{12}$	$BaGeO_3 + BaGe_4O_9$	G	60	900	60	$BaGe_2O_5$ III + $Ba_2Ge_5O_{12} + GeO_2$(Tet)	
19	$Ba_2Ge_5O_{12}$	$BaGeO_3 + BaGe_4O_9$	G	60	750	80	$BaGe_2O_5$ III + $Ba_2Ge_5O_{12} + BaGe_4O_9 + GeO_2$(Tet)	
20	$BaGe_3O_7$	$BaGe_4O_9 + BaO_2$	G	60	1100	30	$Ba_2Ge_5O_{12} + GeO_2$(Tet)	
21	$BaGe_4O_9$	$BaGe_4O_9$	G	60	1100	30	$Ba_2Ge_5O_{12} + GeO_2$(Tet)	

[a] Experiments by a cubic anvil apparatus.

[b] Water drop was put in the starting material.

[c] Starting material was insulated by BN sleeve from the heater.

TABLE II

X-Ray Diffraction Data for Atmospheric-Pressure Phase of $BaGe_2O_5$ ($BaGe_2O_5$ I Monoclinic)

$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I
0 1 0	5.535	5.538	w
1 1 0	4.583	4.584	w
−1 0 1	4.513	4.512	w
1 0 1	4.233	4.230	w
2 0 0	4.085	4.084	w
−1 1 1	3.498	3.498	s
1 1 1	3.362	3.362	s
2 1 0	3.286	3.287	vs
0 2 0	2.769	2.769	m
0 0 2	2.581	2.582	m
−3 0 1	2.481	2.483	m
0 2 1	2.441	2.440	w
−1 2 1	2.358	2.360	m
3 0 1	2.340	2.341	w
1 2 1	2.317	2.317	w
−1 1 2	2.290	2.289	w
2 2 0	2.290	2.292	w
−2 0 2	2.257	2.256	w
−2 1 2	2.088	2.089	m
4 0 0	2.042	2.042	w
2 1 2	1.976	1.976	w
4 1 0	1.916	1.916	w
0 2 2	1.888	1.888	m
−3 2 1	1.848	1.848	m
3 2 1	1.788	1.788	m
−1 0 3	1.709	1.709	w
1 0 3	1.660	1.660	w
−1 1 3	1.633	1.633	w
−2 3 1	1.614	1.613	w
1 1 3	1.590	1.590	w

$a = 8.1889(13)$ Å
$b = 5.5380(9)$ Å
$c = 5.1765(5)$ Å
$\beta = 94.089(14)°$
$V = 234.16(6)$ Å^3
$\rho_{calc} = 5.14\ \mathrm{g\ cm^{-3}}\ (Z = 2)$

from those given by Koelmans and Verhagen (*8*). Structure analysis on single crystals of $BaGe_2O_5$ I indicates that these crystals have a monoclinic symmetry with cell parameters $a = 8.1889(13)$, $b = 5.5380(9)$, $c = 5.1765(5)$ Å, and $\beta = 94.089(14)°$. The possible space group is *Pn* (No. 7) or *P2/n* (No. 13). In Table II, both observed and calculated *d*-spacings of the atmospheric-pressure phase of $BaGe_2O_5$ are given on the basis of a monoclinic unit cell. Density measurement was made using a pycnometer. The observed value (5.13 g cm^{-3}) is in very good agreement with that calculated on the basis of the unit cell parameters (5.14 g cm^{-3}).

The present $BaGe_2O_5$ I crystals always show fine polysynthetic twinning on (100) besides two other twinnings of which the axes are *b* and *c*, respectively. Therefore, a single crystal free from twinnings could not be obtained. Sanborite crystal ($BaSi_2O_5$) is known to undergo a reversible high–low transformation at about 1350°C (*9*). It is expected from the structural analogy between silicate and germanate that the twinnings in $BaGe_2O_5$ could similarly result from transformation of the high-temperature phase, if we assume an unquenchable high-temperature phase of $BaGe_2O_5$.

Experimental results on the high-pressure transformations of $BaGe_2O_5$ are given in Table I. At pressures of 40 to 60 kbar, two high-pressure phases of $BaGe_2O_5$, i.e., $BaGe_2O_5$ II and $BaGe_2O_5$ III, were identified. The stability field for these two high-pressure phases of $BaGe_2O_5$ is shown in Fig. 2. The phase boundary curve between $BaGe_2O_5$ II and $BaGe_2O_5$ III was preliminarily determined as $P(\mathrm{kbar}) = 7.7 + 0.047T\ (°\mathrm{C})$ from Fig. 2.

At 60 kbar, when the graphite heater is used, in the runs at 1100°C, a migration of BaO component through the graphite heater proceeded and a precipitation of $Ba_2Ge_5O_{12}$ (high-pressure phase) was observed at the outer shell of the sample (Nos. 8 and 9 in Table I). The run product at 60 kbar and at 750°C using a graphite heater was confirmed by the XMA to be a completely homogeneous sample of $BaGe_2O_5$ ($BaGe_2O_5$ III) (No. 10 in Table I) and no migration of the BaO component took

TABLE III

X-RAY DIFFRACTION DATA FOR THE HIGH-PRESSURE PHASE OF BaGe$_2$O$_5$(BaGe$_2$O$_5$ II MONOCLINIC)

h k l	d_{obs} (Å)	d_{calc} (Å)	*I*
-2 2 2	3.407	3.408	m
4 0 0	3.294	3.296	w
2 2 2	3.241	3.245	m
-2 0 3	2.941	2.939	w
-4 2 1	2.860	2.863	s
0 2 3	2.855	2.854	w
-2 4 1	2.820	2.826	m
-4 0 2	2.807	2.803	w
2 0 3	2.780	2.783	m
2 4 1	2.780	2.777	m
4 2 1	2.765	2.764	s
0 4 2	2.690	2.696	w
4 0 2	2.626	2.625	w
-2 5 3	1.955	1.955	w
-6 3 1	1.945	1.946	w
6 0 2	1.945	1.944	w
-2 6 2	1.917	1.915	w
5 2 3	1.880	1.879	w
4 0 4	1.867	1.868	m
0 2 5	1.828	1.827	w
3 5 3	1.806	1.805	w
2 0 5	1.795	1.795	m
1 6 3	1.771	1.772	w
3 4 4	1.726	1.727	w
5 5 2	1.703	1.702	m
-4 1 5	1.686	1.686	w
8 0 0	1.648	1.648	w
4 4 4	1.622	1.622	m

$a = 13.218(4)$ Å
$b = 13.091(5)$ Å
$c = 9.538(3)$ Å
$\beta = 94.008(27)°$
$V = 1646.3(9)$ Å^3
$\rho_{calc} = 5.85$ g cm^{-3} ($Z = 16$)

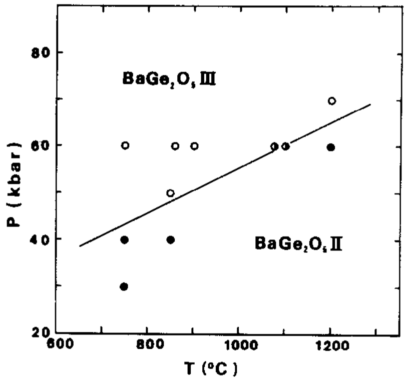

FIG. 2. Stability diagram for the high-pressure and high-temperature transformations of BaGe$_2$O$_5$.

TABLE IV

X-RAY DIFFRACTION DATA FOR THE HIGH-PRESSURE PHASE OF BaGe$_2$O$_5$(BaGe$_2$O$_5$ III TETRAGONAL)

h k l	d_{obs} (Å)	d_{calc} (Å)	*I*
1 0 2	3.569	3.561	vs
1 1 2	3.424	3.439	w
3 3 1	2.873	2.885	m
1 3 2	2.770	2.776	m
4 0 2	2.471	2.471	w
1 4 2	2.428	2.430	w
1 1 3	2.381	2.383	m
1 6 0	2.187	2.186	m
3 0 3	2.153	2.153	m
5 5 0	1.880	1.880	m
4 6 0	1.843	1.844	w
2 2 4	1.716	1.720	w
5 5 2	1.677	1.676	w
1 7 2	1.677	1.676	w
6 0 3	1.647	1.648	w
2 7 2	1.637	1.637	w
8 0 1	1.618	1.621	w
2 6 3	1.599	1.599	w
2 4 4	1.571	1.569	w
3 8 0	1.558	1.556	w
3 5 4	1.436	1.436	w
1 6 4	1.412	1.411	w
5 8 1	1.384	1.384	w
2 3 5	1.373	1.372	w

$a = 13.295(4)$ Å
$c = 7.391(3)$ Å
$V = 1306(1)$ Å^3
$\rho_{calc} = 7.37$ g cm^{-3} ($Z = 16$)

place. At 40 kbar, on the other hand, even at 750°C, a migration of the BaO component proceeded, showing a ring structure in the transverse section of the sample, that is, the center is BaGe$_2$O$_5$ II and the rim is high-pressure phase of Ba$_2$Ge$_5$O$_{12}$ (No. 6 in Table I). When the platinum heater is used, at 60 kbar and at 900°C no migration of the BaO

TABLE V

X-RAY DIFFRACTION DATA FOR THE HIGH-PRESSURE PHASE OF $Ba_2Ge_5O_{12}$ (HEXAGONAL)

h k l	d_{obs} (Å)	d_{calc} (Å)	*I*
1 1 1	5.601	5.591	vw
2 0 0	5.062	5.060	vw
1 1 3	4.322	4.320	vw
2 0 4	3.484	3.487	vw
3 0 0	3.372	3.374	m
2 1 3	3.286	3.286	vw
1 1 5	3.215	3.215	vs
1 0 6	3.059	3.058	vw
2 1 4	2.994	2.994	vw
2 2 0	2.921	2.922	m
2 2 1	2.886	2.889	vs
1 1 6	2.811	2.812	vw
3 0 4	2.761	2.762	vs
2 1 5	2.712	2.714	vw
1 3 2	2.692	2.695	vw
2 2 3	2.658	2.659	m
1 1 7	2.490	2.488	w
3 2 0	2.322	2.322	w
4 0 4	2.239	2.240	w
4 1 1	2.194	2.194	w
1 4 3	2.089	2.088	vw
1 4 4	2.007	2.007	w
3 1 7	1.965	1.964	vw
0 0 10	1.925	1.925	w
4 1 5	1.915	1.916	m
5 0 4	1.867	1.866	vw
3 3 4	1.805	1.805	m
2 2 9	1.726	1.726	m
4 2 5	1.713	1.713	vw
6 0 0	1.687	1.687	s
4 1 8	1.626	1.627	w
2 5 0	1.621	1.621	w
6 0 6	1.494	1.493	w
5 2 5	1.494	1.494	w
4 4 1	1.456	1.457	vw
6 0 8	1.381	1.381	w

$a = 11.6864(9)$ Å
$c = 19.249(3)$ Å
$V = 2276.7(5)$ Å^3
$\rho_{calc} = 7.26\ g\ cm^{-3}\ (Z = 12)$

component was observed (No. 12 in Table I), while at 40 kbar and at 850°C, a migration of the BaO component was still observed (No. 7 in Table I).

Single crystals of $BaGe_2O_5$ II (chemical compositions were confirmed by XMA, see Fig. 1) were successfully obtained from the run at 60 kbar and 1200°C (No. 13 in Table I) and also from the run for the $BaGeO_3$ composition as a decomposition product at 60 kbar and 1100°C with a graphite heater (No. 5 in Table I). The crystal symmetry was studied using these single crystals. $BaGe_2O_5$ II has a monoclinic cell with $a = 13.218(4)$, $b = 13.091(5)$, $c = 9.538(3)$ Å, and $\beta = 94.008(27)°$, and the space group is $P2_1/a$ (No. 14). It is seen that a and b of this phase are almost the same and β is close to 90°. This implies that this crystal has a slightly distorted tetragonal symmetry. In Table III, both observed and calculated d-spacings of $BaGe_2O_5$ II are given on the basis of a monoclinic unit cell.

Table IV shows X-ray powder diffraction data for $BaGe_2O_5$ III. A single crystal of this phase could not be obtained even at 70 kbar and 1200°C (No. 14 in Table I), but the d-spacings of this phase are well indexed on the basis of a tetragonal system. The cell constants refined by the least-squares method are $a = 13.295(4)$ and $c = 7.391(3)$ Å.

One-bar densities for these three phases of $BaGe_2O_5$ are calculated on the basis of the cell dimensions obtained in this study as follows: for $BaGe_2O_5$ I, $\rho_{calc} = 5.14\ g\ cm^{-3}$ $(Z = 2)$; for $BaGe_2O_5$ II, $\rho_{calc} = 5.85\ g\ cm^{-3}$ $(Z = 16)$; for $BaGe_2O_5$ III, $\rho_{calc} = 7.37\ g\ cm^{-3}$ $(Z = 16)$. Increase in density from $BaGe_2O_5$ I to $BaGe_2O_5$ II is 14% and from $BaGe_2O_5$ II to $BaGe_2O_5$ III is 26%.

$Ba_2Ge_5O_{12}$

It was confirmed that at atmospheric pressure, $Ba_2Ge_5O_{12}$ cannot exist as a single phase but decomposes into $BaGe_4O_9$ plus $BaGeO_3$ or BaO_2. Experimental results on the high-pressure stability relations of the $Ba_2Ge_5O_{12}$ composition are also given in Table I. As seen in Fig. 1 and Table I, we successfully obtained a high-pressure phase

TABLE VI

SUMMARY OF THE HIGH-PRESSURE STABILITY RELATIONS OF THE SYSTEM $BaO-GeO_2$ UP TO 60 kbar

Pressure (kbar)	Ba_2GeO_4	$BaGeO_3$	$BaGe_2O_5$	$Ba_2Ge_5O_{12}$	$BaGe_3O_7$	$BaGe_4O_9$
0	Orthorhombic (13) $\rho_{calc} = 5.808$	Hexagonal (4, 5) (low-temperature phase) $\rho_{calc} = 4.72$ Orthorhombic (7) (high-temperature phase) $\rho_{calc} = 5.159$	Monoclinic $\rho_{calc} = 5.14$	$BaGe_4O_9$ + $BaGeO_3/BaO_2$[a]	$BaGe_4O_9$ + $BaGeO_3/BaO_2$[a]	Hexagonal (10) $\rho_{calc} = 5.145$
~40		Ba_2GeO_4 + $BaGe_2O_5$ (monoclinic)	Monoclinic $\rho_{calc} = 5.85$	Hexagonal $\rho_{calc} = 7.26$	$Ba_2Ge_5O_{12}$ (hexagonal) + GeO_2 (tetragonal)	$Ba_2Ge_5O_{12}$ (hexagonal) + 3 GeO_2 (tetragonal)
~60		Ba_2GeO_4 + $BaGe_2O_5$ (tetragonal)	Tetragonal $\rho_{calc} = 7.37$			

[a] When sintered at around 1000°C, $BaGe_4O_9 + BaGeO_3$, and when melted at around 1400°C, $BaGe_4O_9 + BaO_2$.

for this composition in the pressure range 20–60 kbar. As also shown in Table I, all the runs for this composition showed precipitation of GeO_2 (tetragonal) in the outer part of the sample due to the inevitable effect of the graphite and platinum heater. Single crystals of $Ba_2Ge_5O_{12}$ were obtained at the central part of the sample in the run at 60 kbar and 900°C with a graphite heater (No. 17 in Table I). A single crystal of this phase was also obtained at the outer portion in the runs for the $BaGe_2O_5$ composition at 60 kbar and 1100°C (Nos. 8, 9 in Table I) and the $BaGeO_3$ composition at 30 kbar and 750°C (No. 4 in Table I) with a graphite heater. Precession photographs indicate that the crystal of $Ba_2Ge_5O_{12}$ has hexagonal symmetry. Observed and calculated *d*-spacings based on hexagonal indexing are given in Table V. The cell constants refined by the least-squares method for run 17 in Table I are $a = 11.6864(9)$ and $c = 19.249(3)$ Å. The possible space group is $P6_3cm$ (No. 185) or $P\bar{6}c2$ (No. 188) or $P6_3/mcm$ (No. 193).

$BaGe_3O_7$ and $BaGe_4O_9$

Experimental results on these two compositions in the system $BaO-GeO_2$ are also shown in Table I. $BaGe_3O_7$ does not exist as a single phase at atmospheric pressure and decomposed into a mixed phase of $BaGe_4O_9$ and $BaGeO_3$ in a proportion of 2 : 1. $BaGe_4O_9$ has a well-established structure of hexagonal symmetry (*10*) at atmospheric pressure. Both $BaGe_3O_7$ and $BaGe_4O_9$ decomposed into the high-pressure phase of $Ba_2Ge_5O_{12}$ plus tetragonal GeO_2 at 60 kbar and 1100°C.

Summary

In Table VI, all the experimental results are summarzied together with some previous data for the system $BaO-GeO_2$. On the basis of the cell dimensions obtained in this study and also using those in references, 1-bar densities for the atmospheric- and high-pressure phases of the system $BaO-GeO_2$ are calculated and listed in Table VI. Volume decrease associated with the decomposition and synthesis reactions in Table VI for $BaGeO_3$, $Ba_2Ge_5O_{12}$, $BaGe_3O_7$, and $BaGe_4O_9$ are calculated, respectively, as follows:

$$(1)\quad 3BaGeO_3 \rightarrow Ba_2GeO_4 + BaGe_2O_5\ \text{(II or III)},\quad -\Delta V/V = 12 \text{ or } 20\%,$$

$$(2)\quad BaGe_4O_9 + BaGeO_3 \rightarrow Ba_2Ge_5O_{12},\quad 31\%,$$

$$(3)\quad 2BaGe_4O_9 + BaGeO_3 \rightarrow \tfrac{3}{2}Ba_2Ge_5O_{12} + \tfrac{3}{2}GeO_2,\quad 29\%,$$

$$(4)\quad 2BaGe_4O_9 \rightarrow Ba_2Ge_5O_{12} + 3GeO_2,\quad 26\%.$$

In these calculations, we adopted a value of 6.276 g cm^{-3} for the density of tetragonal GeO_2 according to the crystal data in NBS circular (*11*).

Detailed structure analysis on the four new phases that have appeared in the present study (an atmospheric-pressure phase of $BaGe_2O_5$ ($BaGe_2O_5$ I), two high-pressure phases of $BaGe_2O_5$ ($BaGe_2O_5$ II and $BaGe_2O_5$ III), and a high-pressure phase of $Ba_2Ge_5O_{12}$) are now in progress.

Acknowledgment

We are grateful to H. Takei for his kind advice in the synthetic and structural studies on the present $BaO-GeO_2$ system.

References

1. R. G. GREBENSHCHIKOV, N. A. TOROPOV, AND V. I. SHITOVA, *Dokl. Akad. Nauk SSSR* **153**(4), 842 (1963).
2. R. G. GREBENSHCHIKOV, A. K. SHIRVINSKAYA, V. I. SHITOVA, AND N. A. TOROPOV, *Khim. Vysokotemp. Mater. Tr. Vses. Soveshch. 2nd,* 105 (1965).
3. R. G. GREBENSHCHIKOV, N. A. TOROPOV, AND V. I. SHITOVA, *Izv. Akad. Nauk SSSR Neorg. Mater.* **1**, 1130 (1965).

4. R. G. Grebenshchikov, V. I. Shitova, and N. A. Toropov, *Izv. Akad. Nauk SSSR Neorg. Mater.* **3**, 1620 (1967).
5. Y. Shimizu, Y. Syono, and S. Akimoto, *High Temp.–High Pressures* **2**, 113 (1970).
6. F. Liebau, *Neues Jahrb. Mineral. Abh.* **94**, 1209 (1960).
7. W. Hilmer, *Acta Crystallogr.* **15**, 1101 (1962).
8. H. Koelmans and C. M. C. Verhagen, *J. Electrochem. Soc.* **106**, 677 (1959).
9. H. A. Klasens, A. H. Hoekstra, and A. P. M. Cox, *J. Electrochem. Soc.* **104**, 93 (1957).
10. C. R. Robbins and E. M. Levin, *J. Res. Nat. Bur. Stand. Sect. A* **65**(2), 127 (1961).
11. *Nat. Bur. Stand. Circ.* **8**, 539 (1958).
12. Yu. A. Malinovskii, E. A. Pobedimskaya, V. A. Kuznetsov, and N. V. Belov, *Kristallografiya* **20**(6), 1197 (1975).
13. H. Strunz and P. Jacob, *Neues Jahrb. Mineral. Monatsh.*, 78 (1960).