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Observation of Shocked and Unshocked $BaZnGeO_4$ by Means of Electron Microscopy

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Electron microscopic observations were performed on shocked and unshocked $BaZnGeO_4$ (BZG). Particular attention was given to the superlattice relation. A specimen shocked to the pressure range of 19–27 GPa, showed a small distortion from the original hexagonal lattice, to an orthorhombic symmetry. Along with this distortion, weak superlattice reflections along the c^* direction in the unshocked BZG were found to disappear completely, while the repetition mode of superlattice reflections along the b^* direction ([110]* direction in the hexagonal structure) as found to change from three to six, and then to four, with increasing shock pressure. A single crystal—single crystal transition, on a submicrometer scale, was shown to occur due to a small displacement of atoms during shock process.

Introduction

The crystal structure of the high-temperature form of $BaZnGeO_4$ (BZG) is fundamentally understood to be a derivative of $BaAl_2O_4$, a stuffed trydimite structure with hexagonal symmetry, where six tetrahedra consisting of ZnO_4 and GeO_4 are corner-linked to form layers normal to the c axis, and Ba ions fill the cavities enclosed by the hexagonal ring (*1*, *2*). However, with decreasing temperature, BZG shows several polymorphs with various superstructures which may be due to the ordering of Zn and Ge ions. Considerable interest has been taken in elucidating the structure relations of these polymorphs to throw light on the mechanism of the phase transitions. Very recently, by means of X-ray powder diffraction technique (*3*) we observed new crystalline polymorphs in the shock-loaded product for the peak pressure range of 19–27 GPa. Infrared spectroscopy revealed the structural similarity of the shock-induced phases to of the original unshocked BZG, corroborating some resemblance between powder diffraction patterns of the shocked and unshocked substances. In the present study, electron microscopy has been used to obtain more detailed information on the structures of the shock-induced phases as well as of the original unshocked phase of BZG.

Experimental

Specimens for the shock-loading experiments were single crystals of BZG grown by the Czochralski technique (*1*). They were platelets of 1 mm thickness either par-

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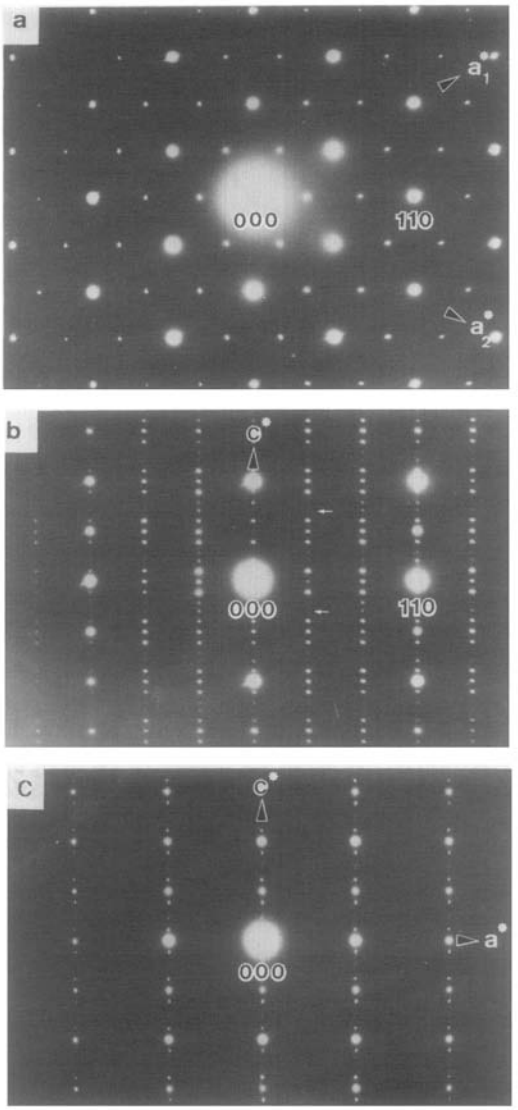

FIG. 1. Electron diffraction patterns of original unshocked $BaZnGeO_4$. (a) Basal plane, (b) c^*–[110]* reciprocal plane, (c) c^*–a^* reciprocal plane.

allel or perpendicular to the c axis and were encased in a stainless-steel container. Shock-loading experiments were carried out by using a 25-mm propellant gun or a 20-mm two-stage light gas gun (*4*). The shocked state was estimated from the measured projectile velocity on the basis of the impedance match concept. Experimental details have already been reported elsewhere (*4*).

The shocked specimens were examined by electron microscopy and by X-ray diffraction analysis. A 200-kV transmission electron microscope was used to observe the electron diffraction pattern. X-Ray powder diffraction patterns were obtained by a diffractometer equipped with a graphite monochrometer.

Results and Discussion

Figure 1 shows electron diffraction patterns of the original unshocked phase of BZG. The superlattice spots are likely to be interpreted in terms of a large hexagonal cell, with $a = \sqrt{3}a_0$ and $c = 4c_0$ which was adopted by Iijima *et al.* (*2*), where a_0 and c_0 are lattice constants of the basic hexagonal cell. The higher order weak superlattice along the c^* axis is indicated with arrows (Fig. 1b), which are inclined with respect to the c^* axis, and which show a nonintegral and nonparallel relation of superlattice cell, i.e., a spacing and an orientation anomaly.

Electron diffraction analysis of the specimen shocked to the pressure range of 19–27 GPa (*3*), showed a small distortion from the original hexagonal lattice to the orthorhombic symmetry (Fig. 2). The top and bottom figures are the electron diffraction patterns of the shock-induced phase in the orthorhombic b^*–a^* and b^*–c^* reciprocal plane, respectively, where the orthorhombic a^* axis of the shock-induced phase is taken to correspond to the original hexagonal lattice. These figures correspond to the electron diffraction patterns of the unshocked BZG in the hexagonal basal plane and [110]*–c* in Fig. 1, respectively. The orthorhombic symmetry of the crystal lattice of the shock-induced phase is evident from these diffraction patterns, although the distortion from the original hexagonal lattice is very small. Along with this distortion, weak superstructure reflections along

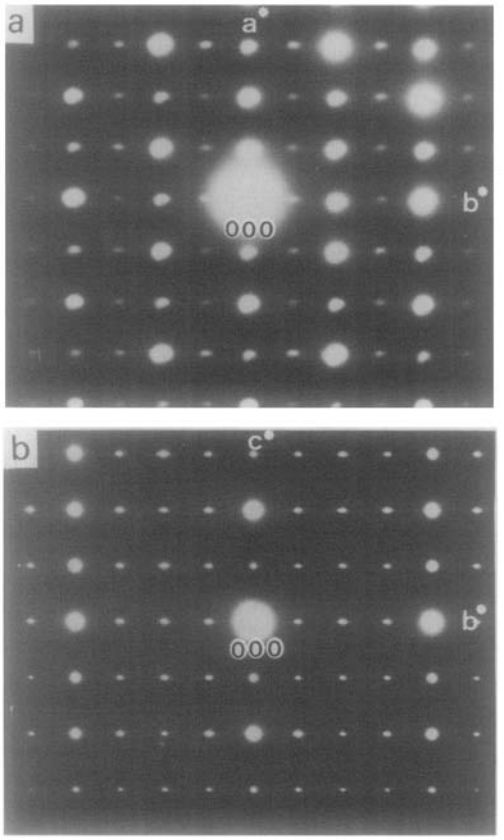

FIG. 2. Electron diffraction patterns of $BaZnGeO_4$ with the orthorhombic structure obtained by shock-loading to 27 GPa. (a) b^*–a^* reciprocal plane, (b) b^*–c^* reciprocal plane.

the c^* direction, observed in the unshocked BZG, are found to disappear completely in the shock-induced phase, similar to the high-temperature form of BZG. However, the superstructure mode with the three-unit repetition along the [110]* direction in the original hexagonal lattice is found to change to the superstructure mode with a four-unit repetition along the b^* direction in the shock-induced phase, unlike the high-temperature form. Furthermore, we also encountered another intermediate phase with a superstructure mode with a six-unit repetition, in the run product shocked to 19 GPa, as shown in Fig. 3, although it was found to coexist as well with the four-unit repetition phase. These shock-induced phases are unstable: Heating by the electron beam during prolonged observation easily lead to reversion to the original phase.

We tried to explain the powder diffraction pattern of the shock-induced phase, as previously reported by Takei *et al.* (*3*), on the basis of the information obtained from the electron diffraction analysis: The reflections ($3n$, 0, l) of the original hexagonal lattice should split into orthorhombic ($3n$, $2n$, l) and (0, $4n$, l) reflections, and those of (n, n, l), into orthorhombic (n, $2n$, l) and ($2n$,

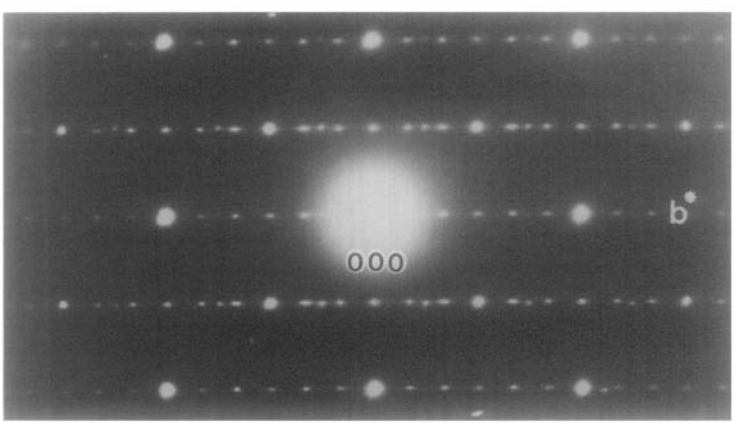

FIG. 3. Electron diffraction pattern in the reciprocal plane of an intermediate orthorhombic phase obtained by shock-loading to 19 GPa, which shows a superstructure along the b^* axis with six-unit repetition. Reflections from the phase with four-unit repetition (see Fig. 2) are superimposed.

TABLE I

OBSERVED AND CALCULATED *d*-SPACING OF $BaZnGeO_4$ WITH THE ORTHORHOMBIC STRUCTURE BY SHOCK-LOADING TO 27 GPa

k h l	d_{obs} (Å)	d_{calc} (Å)	*I*	*h k l*	d_{obs} (Å)	d_{calc} (Å)	*I*
1 2 0	4.683	4.676	w	—	2.207	—	vw
2 0 0	4.611	4.609	w	0 5 0	2.172	2.170	vw
—	4.349	—	vw	0 0 4	2.162	2.160	w
1 2 1	4.123	4.112	w	1 1 4	2.064	2.064	m
—	3.813	—	w	2 4 2	2.056	2.056	m
—	3.267	—	vw	1 5 1	2.050	2.052	m
1 2 2	3.175	3.173	vs	3 4 0	2.032	2.034	w
2 0 2	3.156	3.152	s	4 0 2			
0 4 0	2.717	2.713	s	—	1.9935	—	vw
3 2 0	2.679	2.674	s	1 2 4	1.9612	1.9606	w
1 1 3	2.667	2.664	m	1 6 0	1.7746	1.7748	w
0 4 1	2.592	2.588	vw	1 5 3	1.7039	1.7033	vw
—	2.567	—	vw	0 4 4	1.6908	1.6896	w
—	2.488	—	vw	3 2 4	1.6788	1.6801	w
—	2.382	—	vw	0 2 5	1.6453	1.6463	w
0 4 2	2.299	2.297	vw	1 6 2	1.6407	1.6416	w
—	2.269	—	vw	1 2 5	1.6208	1.6206	w

Note. $a = 9.2185$ Å, $b = 10.851$ Å, $c = 8.6385$ Å, $V = 864.16$ Å^3.

0, *l*) reflections, if the shock-recovered material consists solely of the four-unit repetition crystal. The observed diffraction pattern was not completely explained by the indexing based on the orthorhombic symmetry of the four-unit repetition crystal, as summarized in Table I; a few weak reflections remained unindexed. This might be due to the existence of similar phases such as a six-unit repetition crystal observed in electron diffraction. Furthermore, a detailed analysis is complicated by the gradual change in the X-ray diffraction pattern itself with time, which may correspond to the instability of the shock-induced phase as revealed in the electron diffraction analysis. The ratio of unit cell length, $a : b : c = 0.850 : 1 : 0.796$, determined from the X-ray powder diffraction analysis was found to be in close agreement with that obtained from the electron diffraction pattern, i.e., $0.855 : 1 : 0.796$, lending support to the result of the X-ray diffraction analysis. The reciprocal unit vectors, a^*, b^*, c^*, of the orthorhombic shock-induced phase (with 4-unit repetition) correspond to $\frac{1}{2} \cdot a_h^*$, $\frac{1}{2} \cdot a_h^* \cos 30°$, and c_h^* of the hexagonal unshocked phase, yielding real space correspondence of $a \leftrightarrow \sqrt{3}a_h$, $b \leftrightarrow 2a_h$, and $c \leftrightarrow c_h$. The changes in length along the three principal axes, *a*, *b*, and *c*, of the orthorhombic cell produced by the shock-induced transition are then estimated to be -0.8, $+1.2$, and -1.2%, respectively, resulting in volume contraction by 0.9% during the transition.

Single crystal-to-single crystal transition observed in BZG, though in a submicrometer scale, can be realized by a small cooperative displacement of atoms under shock process. Owing to the relatively open structure of the stuffed trydimite, several distorted polymorphs with similar atomic configurations and internal energies might be metastably formed under shock loading or unloading processes. Examples of such phase transformations due to similar displacive mechanism would be rather frequently encountered in such open-structure compounds under detailed examination.

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References

1. H. TAKEI, S. TSUNEKAWA, AND M. MAEDA, *J. Mater. Sci.* **15,** 2612 (1980).
2. K. IIJIMA, F. MARUMO, AND H. TAKEI, *Acta Crystallogr.*, **38,** 1112 (1982).
3. H. TAKEI, Y. SYONO, T. GOTO, AND M. KIKUCHI, *Phys. Chem. Mineral.* **10,** 16 (1983).
4. T. GOTO AND Y. SYONO, "Materials Science of the Earth's Interior," p. 605, Terra/Reidel, Tokyo/Dordrecht (1984).