Effect of Pressure on the Crystal Structure and the Lattice Parameters of BaO

LIN-GUN LIU AND WILLIAM A. BASSETT

Department of Geological Sciences
University of Rochester, Rochester, New York 14627

An X-ray-diffraction study under pressure has shown that BaO, which has the NaCl-type structure at standard temperature and pressure, transforms to a tetragonal structure with \( a = 4.459 \pm 0.008 \text{ Å}, \ c = 3.606 \pm 0.006 \text{ Å}, \) and \( Z = 2 \) at 92 ± 3 kb and 23 ± 3 °C. At 140 ± 5 kb, it transforms to the tetragonal PH.I-type structure (space group \( P4/nmm \)). At 180 kb, the BaO in this structure has \( a = 4.397 \pm 0.007 \text{ Å}, \ c = 3.196 \pm 0.005 \text{ Å}, \) \( Z = 2, \) and \( u = 0.40. \) These two phase changes are reversible, and the volume changes at the transitions are approximately 5% and 7%, respectively. Using F. Birch's equation of state with an assumed value of 6 for \( (\partial K_r/\partial P)_T, \) the initial isothermal bulk modulus \( K_0 \) has been calculated to be 0.69 ± 0.03 Mb for the phase with the NaCl-type structure. The axial ratios \( c/a \) for the high-pressure phases of BaO appear to be independent of pressure within experimental error.

At standard temperature and pressure, BaO crystallizes in a face-centered cubic NaCl-type structure. Recently, a pressure-induced polymorph of BaO was discovered and reported by Liu [1971]. The structure of the new phase was then described as a PH.I type of distorted body-centered cubic structure. In a brief note, the compression of the NaCl-type structure of BaO was reported by Liu and Bassett [1971]. Since then, a more extensive study of the compression of BaO has revealed an intermediate crystal structure between the NaCl type and the PH.I type. This paper provides the latest data on the two pressure-induced crystal structures and the lattice parameters of BaO compressed to pressures of 290 kb at standard temperature.

**Experimental Method**

A diamond-anvil high-pressure cell designed by Bassett and Takahashi [1965] was used in this study. The BaO with stated purity of 99.999% was purchased from Semi-Elements, Inc. The powdered sample was placed between the polished faces of two gem-quality diamond crystals mounted on the ends of two pistons, which were then driven together by means of a lever and spring assembly. A finely collimated X-ray beam of monochromatized MoK\(_\alpha\) radiation was directed at the small area at the center of the sample between the diamond anvils. The diffracted X-ray beam is recorded on a cylindrical film with a radius of 50 mm. For the compression measurements, Ag was mixed with the BaO as an internal pressure standard. In a few cases where the Ag was found to interfere, the pressure was determined by the spring length, which was calibrated on the basis of Ag and NaCl compressions.

**High-Pressure Transformations in BaO**

X-ray-diffraction patterns of compressed BaO at 25°C show that the NaCl-type structure persists to pressures of about 90 kb. However, an X-ray pattern of BaO taken at 180 kb can be indexed as tetragonal with \( a = 4.397 \pm 0.007 \text{ Å}, \ c = 3.196 \pm 0.005 \text{ Å} \) [Liu, 1971]. The intensities are compatible with a PH.I-type structure (space group \( P4/nmm \)) containing two O atoms in \( 2a(0 0 0; 1/2 1/2 0) \) and two Ba atoms in \( 2c(0 1/2 u; 1/2 0 u), \) where \( u = 0.39 \) or 0.40. The PH.I-type structure is a distorted CsCl-type structure. This structure persists to 290 kb, the highest pressure attained in these studies.

A more detailed study of BaO in the pressure range of 90 to 180 kb has revealed an intermediate crystal structure. At pressures between 90 and 100 kb, the X-ray pattern contains a new set of diffraction lines in addition to those of the NaCl-type structure. The interplanar distances \( (d) \) and line intensities \( (I/I_{\infty}) \) of the X-ray power pattern of this intermediate...
phase taken at a pressure of 100 kb are displayed in Table 1. This pattern can be indexed as tetragonal with parameters $a = 4.459 \pm 0.008$ Å and $c = 3.606 \pm 0.006$ Å. If $Z = 2$ is assumed, the calculated molar volume of this phase is intermediate between those of the NaCl-type and the PH$_2$I-type structures of BaO. We have not been able to find an unambiguous structure that fits the intensity data. Henceforth, the NaCl-type phase will be designated as BaO(I), the intermediate phase as BaO(II), and the PH$_2$I-type as BaO(III). Inversely proportional to the interplanar distance of the X-ray reflections observed with MoK$_{α1}$ radiation at $92 \pm 3$ kb, $100 \pm 5$ kb, and $180 \pm 10$ kb is shown in Figure 1.

The phase changes BaO(I)–BaO(II) and BaO(II)–BaO(III) are reversible. The first occurs at a pressure of $92 \pm 3$ kb and the second at $140 \pm 5$ kb at $23 \pm 3$ °C. The volume changes at the transitions are approximately 5% and 7%, respectively.

**ISOTHERMAL COMPRESSION**

The variations of the lattice parameters of BaO with pressure have been obtained using mixtures with silver as an internal standard. The pressure-volume relation for Ag used in this study was that reported by Vaidya and Kennedy [1970] for 0–45 kb and a new static compression curve measured in our laboratory using a Bassett cell and a NaCl pressure calibrant for 45–290 kb. At a compression of $V/V_o = 0.95$, this new scale yields a pressure of 66 kb. At the same compression, the Ag scale used by Drickamer et al. [1966] yields a pressure of 59 kb. However, at a compression of $V/V_o = 0.86$, both our new scale and the one used by Drickamer et al. yield the same pressure of 247.5 kb.

For calculations of the lattice parameters, the following diffraction lines were used:

- For BaO(I) (111), (200), (220), (311), (222), (400), (331), (420), and (422).
- For BaO(II) (110), (101), (200), (002), (211), (112), and (300).
- For BaO(III) (001), (110), (101), (111), (201), (211), (220), and (102).
- For Ag (111), (200), (220), (311), and (222).

In some runs, interference between sample reflections causes one or two reflections from each pattern to be rejected.

The results of the measurements at $23 \pm 3$ °C are listed in Table 1 and displayed in Figure 2. No attempt is made to report the initial isothermal bulk modulus $K_o$ for the high-pressure phases BaO(II) and BaO(III). The value of $K_o$ for BaO(I) was evaluated by a least squares fit of its compressional data to the Birch's equation of state,

$$P = \frac{3}{2}K_o[(V/V_o)^{-7/3} - (V/V_o)^{-5/3}] + [1 - \xi(V/V_o)^{-2/3} - 1]$$

where $\xi = 3(4 - K_o')/4$ is a function of temperature only, and $K_o'$ is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure. Since the largest amount of compression for BaO(I) is about $V/V_o = 0.88$, we feel that an attempt to determine $K_o'$ directly from the data is not justified. Hence, the value of $K_o$ of BaO(I) calculated using the Birch's equation of state for each of three fixed $K_o'$ values is

$$K_o' = 5 \quad K_o = 0.72 \pm 0.03 \text{ Mb}$$

$$K_o' = 6 \quad K_o = 0.69 \pm 0.03$$

$$K_o' = 7 \quad K_o = 0.66 \pm 0.03$$

where the plus and minus values indicate 1 standard deviation of the data points. On the
other hand, the \( K_o' \) values for MgO and CaO have been measured by means of ultrasonic techniques. The \( K_o' \) values of MgO were compiled by Soga [1968]. Since BaO is more compressible than MgO and CaO, it is reasonable to assume a higher value for \( K_o' \). We therefore assume \( K_o' = 6 \). \( K_o \) calculated on this assumption is 0.69 ± 0.03 Mb.

**TABLE 2. Compressional Data for BaO at 23 ± 3 °C**

<table>
<thead>
<tr>
<th>Run</th>
<th>( a ) ( V/V_0 )</th>
<th>( b )</th>
<th>( c/a )</th>
<th>( V/V_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLD 164</td>
<td>4.0853</td>
<td>0.978</td>
<td>0.547</td>
<td>0.965</td>
</tr>
<tr>
<td>SLD 166</td>
<td>4.041</td>
<td>0.968</td>
<td>0.440</td>
<td>0.947</td>
</tr>
<tr>
<td>SLD 163</td>
<td>4.033</td>
<td>0.962</td>
<td>0.427</td>
<td>0.940</td>
</tr>
<tr>
<td>SLD 167</td>
<td>4.008</td>
<td>0.944</td>
<td>0.387</td>
<td>0.920</td>
</tr>
<tr>
<td>SLD 168</td>
<td>3.995</td>
<td>0.935</td>
<td>0.357</td>
<td>0.905</td>
</tr>
<tr>
<td>SLD 172</td>
<td>100</td>
<td>0.904</td>
<td>3.606</td>
<td>4.459</td>
</tr>
<tr>
<td>SLD 170</td>
<td>3.955</td>
<td>0.907</td>
<td>3.596</td>
<td>4.455</td>
</tr>
<tr>
<td>SLD 171</td>
<td>3.936</td>
<td>0.894</td>
<td>3.583</td>
<td>4.423</td>
</tr>
<tr>
<td>SLD 156</td>
<td>180</td>
<td>5.311</td>
<td>0.882</td>
<td>2.616</td>
</tr>
<tr>
<td>SLD 157</td>
<td>122</td>
<td>0.894</td>
<td>2.609</td>
<td>4.414</td>
</tr>
<tr>
<td>SLD 158</td>
<td>100</td>
<td>0.894</td>
<td>2.596</td>
<td>4.397</td>
</tr>
<tr>
<td>SLD 159</td>
<td>122</td>
<td>0.894</td>
<td>2.585</td>
<td>4.346</td>
</tr>
<tr>
<td>SLD 160</td>
<td>242</td>
<td>0.888</td>
<td>2.573</td>
<td>4.332</td>
</tr>
</tbody>
</table>

*Pressures estimated from the length of the spring, which was calibrated using NaCl and Ag.*

---

**Fig. 1.** Intensity versus interplanar distance of the X-ray reflections observed with MoKα radiation of BaO compressed to pressures of 92 ± 3, 100 ± 5, and 180 ± 10 kb at 23 ± 3 °C.
EFFECT OF PRESSURE ON BaO

Fig. 2. BaO compression curve to 290 kb. The curve for BaO(I) is the plot of the Birch equation with \( K_0 = 690 \) kb and \( K'_0 = 6 \). The curves for BaO(II) and BaO(III) were estimated. Open circles are data points for which the pressure was calculated on the basis of internal pressure standard of Ag, and solid circles are data points for which the pressure was estimated from the length of spring.

The axial ratios \( c/a \) for both BaO(II) and BaO(III) appear to be independent of pressure within the experimental error of this study.

DISCUSSION

The physical properties and crystal structures of the alkali-earth oxides, MgO and CaO, have been of interest to geophysicists since Birch [1952] first suggested that the simple oxides may dominate the earth's lower mantle. It was hoped that a study of BaO under pressure might shed light on the behavior of the other members of this important group. Although analog studies are a nonrigorous means of estimating the behavior of certain substances, they have played an important role by leading to some insights into relationships that might otherwise have been missed. There is one rule that seems to hold particularly well: for a series of compounds in which the anion is the same and the cations are the elements of a column in the periodic table, the compounds having higher atomic numbers are isostructural with the high-pressure polymorphs of the compounds having lower atomic numbers. For example, the high-pressure phases of NaCl, KCl, and RbCl are isostructural with zero-pressure CsCl; the high-pressure phase of SiO\(_2\) (stishovite) is isostructural with the 1-bar phase of TiO\(_2\) (rutile) and GeO\(_2\); the high-pressure phase of ZnO is isostructural with the 1-bar phase of CdO (NaCl-type structure). Applied to the alkali-earth oxides, this rule predicts that, up to very high pressure, MgO probably remains in the NaCl-type structure, since all the members of this group have the NaCl-type structure at 1 bar. If a phase change occurs at very high pressures, the structures of BaO(II) and BaO(III) are likely candidates. It seems reasonable to assume that such a phase change would take place only at pressures in excess of those found in the earth’s mantle.

Acknowledgments. This work was supported by the Earth Sciences Section, National Science Foundation, NSF GA-25718 and GA-31902.

REFERENCES


(Received January 20, 1972; revised May 11, 1972.)