High-pressure phase transitions and the equations of state of BaS and BaO

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(Received 24 October 1985)

The high-pressure phase transitions and the equations of state of the barium chalcogenides BaS and BaO were investigated by energy-dispersive x-ray diffraction using the Cornell High Energy Synchrotron Source (CHESS). For BaS, the rocksalt ($B1$) phase was found to be stable between 0 and 6.5 GPa and the cesium chloride ($B2$) phase was stable between 6.5 and 89.0 GPa, the highest pressure reached in this experiment. For BaO, three structural phases were found between 0 GPa and the highest pressure of 60.5 GPa. BaO(I) is in the rocksalt phase between 0 and 10.0 GPa, BaO(II) is in the hexagonal NiAs phase between 10.0 and 15.0 GPa, and BaO(III) is in the tetragonal PH_4I phase from 15.0 GPa up to the highest pressure of 60.5 GPa. From the variation in the intensities of the diffraction lines for BaO(III) with pressure, we conclude that this tetragonal PH_4I phase is continuously approaching a cesium-chloride-type structure as the pressure increases. This behavior of BaO(III) is a new phenomenon in the study of barium chalcogenides and alkaline-earth oxides. The potential for metallization of BaS and BaO under high pressure is also discussed.

INTRODUCTION

The pressure-induced structural phase transitions and metallization transitions of closed-shell systems such as the alkali-metal halides and the alkaline-earth chalcogenides (AX; X =O,S,Se,Te) are of great theoretical interest. BaTe was the first closed-shell compound to be metallized by the application of high pressures with a metallization pressure of 20 GPa.[1] There is substantial interest in the metallization of CsI under high pressures.[2] Local density-functional total energy calculations for BaTe (Ref. 3) and CsI (Ref. 4) are consistent with these experimental observations[1,2] regarding the structural and metallization transitions. The success of these first-principles calculations of the P-V relations and phase transitions for these compounds has stimulated further experimental work on alkali-metal halides and alkaline-earth chalcogenides.

In this paper we report the results of our high pressure studies on the two barium chalcogenides BaS (to 89.0 GPa) and BaO (to 60.5 GPa). Earlier high-pressure x-ray investigations of BaS (Ref. 5) (to 10.4 GPa) and of BaSe and BaTe (Refs. 1 and 6) reported phase transitions from the rocksalt ($B1$) phase to the cesium-chloride ($B2$) phase at pressures of 6.5, 6.0, and 4.8 GPa, respectively. BaO, which has been studied up to 29 GPa, shows, on the other hand, a different phase-transition sequence.[7,8] The low-pressure rocksalt phase of BaO, rather than transforming directly to the $B2$ phase, transforms to an intermediate BaO(II) phase at 9.2 GPa and then to a tetragonal PH_4I structure (distorted $B2$ phase) above 14.0 GPa. In a previous work,[8] the BaO(II) phase was assigned to a tetragonal structure ($c/a \approx 0.84$) by indexing the observed lines but no atomic positions were suggested. In our studies we have extended the range of high-pressure measurements on BaS and BaO, determined the crystal structure of

BaO(II), and explained the cause of the intensity variation of the BaO(III) diffraction peaks.

EXPERIMENTAL TECHNIQUES

The BaS and BaO samples were pressurized with a diamond anvil cell and their structures were determined under high pressure by the energy-dispersive x-ray diffraction (EDXD) technique using the intense white x-ray beam at the Cornell High Energy Synchrotron Source (CHESS). For details of the experimental technique, see Baublitz, Arnold, and Ruoff.[9] The instrumentation now used at CHESS incorporates several modifications: motorized loading of the diamond anvil cell, a rotatable detector arm, and a new collimator system capable of illuminating sample regions as small as 10 μm in diameter with x rays.[10] The diamond flats were 300 μm in diameter and the sample regions were 75 μm in diameter. Normally, a 50 μm collimator was used and the region illuminated was adjusted by two motors which drove the collimator in the two directions perpendicular to the x-ray beam.

Since the crystallographic nature of the phases of BaS is rather simple, the pressure of the BaS sample was measured with the internal pressure marker of platinum. The BaS powder (> 99.9% purity) was ground into a fine powder and mixed with the platinum powder in the proportion of 87% BaS and 13% Pt by weight. The pressure calibration was based on the equation of state for platinum given by Jamieson, Fritz, and Manghnani.[11]

Since the diffraction patterns of BaO are very complicated and since the exact atomic structures of BaO(II) and BaO(III) had not been previously determined, we used the ruby fluorescence technique[12] for the pressure measurements of BaO. The BaO sample used in our studies had a stated purity of 99.999%. All data were collected with the CHESS electron beam energy at 5.3 GeV. The typical beam current was 25 mA.
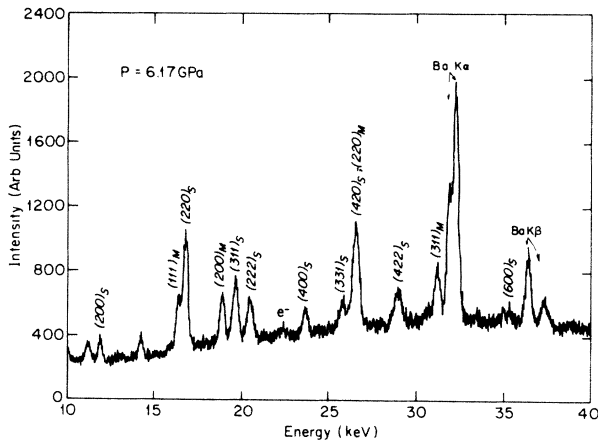
FIG. 1. EDXD spectrum of BaS plus platinum mixture taken at a pressure of 6.17 GPa. The peaks labeled by an S are diffraction peaks from the BaS sample; those labeled by an M are from the platinum pressure marker. The BaS at this pressure is still in the $B1$ phase. The detector angle (θ) is 9.728°. The peak labeled e^- is an escape peak from the germanium detector.

RESULTS

Barium sulfide

The EDXD spectrum of a BaS plus platinum mixture at a pressure of 6.17 GPa is shown in Fig. 1. At this pressure the sample is still in the low-pressure $B1$ phase and remains in this phase up to the transition pressure of 6.5 GPa. At 6.5 GPa the sample undergoes a structural phase transition to the $B2$ phase and remains in this phase up to 89.1 GPa, the highest pressure reached for this sample. The EDXD spectrum of the sample at 76.1 GPa is shown in Fig. 2. The six diffraction lines of BaS in this spectrum attest to the fact that the BaS is still in the cubic cesium-chloride $B2$ phase; there is no evidence of any anomalous line broadening or line splitting which would indicate a distortion of the $B2$ phase. Finally, the P-V equation of state of BaS up to 89.1 GPa ($V/V_0 = 0.514$) is given in Fig. 3 and the equation of state parameters obtained by a computer fit to the data points are listed in Table I.

Barium oxide

At normal room temperature and under normal atmospheric pressure, BaO is stable in the rocksalt ($B1$) structure (space group F_{m3m}). Figure 4 shows the EDXD pat-
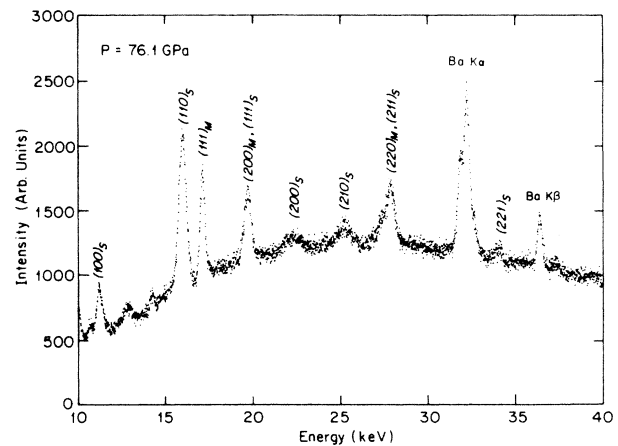

FIG. 2. EDXD spectrum of BaS plus platinum mixture taken at a pressure of 76.1 GPa. The BaS is in the $B2$ phase at this pressure.

tern of the low-pressure $B1$ phase of BaO at a pressure of 10.2 GPa just before the phase transition to BaO(II). There was no x-ray pressure marker in this sample; the pressure was determined using the ruby fluorescence technique.

Above 10 GPa the BaO often shows mixed phase patterns of BaO(I) + BaO(II). All of the diffraction patterns reported in an earlier study[8] were mixtures of these two phases in the range from 10 to 15 GPa. We were, however, able to get a single phase pattern for BaO(II) at a pressure of 13.9 GPa (Fig. 5). The earlier study[8] also assigned a tetragonal lattice ($c/a = 0.84$ and two ion pairs per unit cell) to the BaO(II) structure but was unable to give a definite atomic structure that was in good agreement with the experimental diffraction line intensities. We have, though, been able to get an excellent fit of the data by assigning the BaO(II) structure to a hexagonal cell of the NiAs type[13] (space group $P6_3/mmc$, $c/a \approx 1.75$, and two ion pairs per unit cell). In this structure the oxygen atoms occupy the positions of (0,0,0) and (0,0,$\frac{1}{2}$) while the barium atoms occupy ($\frac{1}{3},\frac{2}{3},\frac{1}{4}$) and ($\frac{2}{3},\frac{1}{3},\frac{3}{4}$). It should be noted that the atomic sites of the oxygen atoms are not equivalent to those of the barium atoms in the hexagonal NiAs structure. This NiAs crystal structure, a hexagonal analog of the rocksalt structure, not only gives a good fit to the observed interplanar spacings but, in addition, is in very good agreement with the observed relative intensities of the diffraction peaks. This agreement can be seen in Fig. 5 where the theoretically calculated relative intensities for NiAs with $a = 3.617$ Å and $c = 6.349$ Å is shown

TABLE I. Fit of BaS data points to a first-order Birch equation.

Phase	Pressure range (GPa)	B_0 (GPa)	B_0'	$(V/V_0)_{P=0}$
$B1$	0—6.5	55.1 ± 1.4	5.5^a	1
$B2$	6.5—89	21.4 ± 0.3	7.8 ± 0.1	0.91 ± 0.01

^{a} In view of the limited data for the $B1$ phase, the value of B_0' was fixed to 5.5, a typical value for the B_0' of ionic solids.
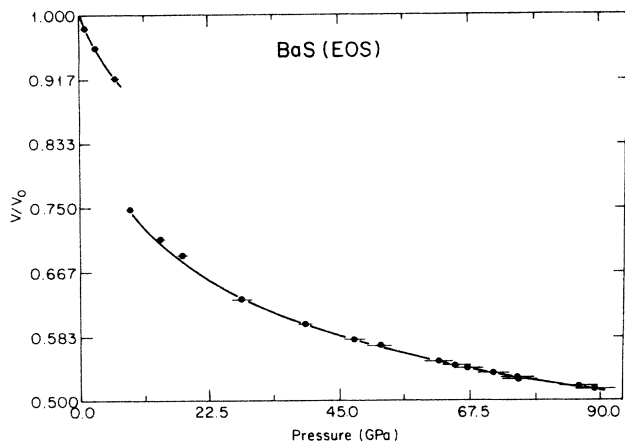
FIG. 3. Plot of the reduced volume V/V_0 of BaS versus pressure. Fits of both the $B1$ phase and the $B2$ phase to a first-order Birch equation are also shown on this figure by solid curves.

FIG. 5. EDXD pattern of BaO at a pressure of 13.9 GPa. BaO(II) is shown in the upper panel. The lower panel shows the calculated relative line intensities based on the hexagonal NiAs structure with $a = 3.617$ Å and $c = 6.349$ Å.

below the EDXD pattern taken at 13.9 GPa. Table II lists the observed and calculated interplanar spacings as well as the calculated and experimental intensities for the BaO(II) Debye-Scherrer spectrum of Liu and Barrett.[8]. Again, the data are in excellent agreement with the fit to the NiAs structure. The c/a ratio here of 1.76 is greater than the ideal close-packed c/a ratio of 1.63 for the NiAs structure. It is interesting to note that Froyen and Cohen[14] predicted c/a ratios higher than the ideal value for certain III-V compounds in their high-pressure NiAs phases.

Just above 15 GPa BaO shows mixed phase patterns of BaO(II) + BaO(III). Single-phase patterns of BaO(III) were obtained above 18 GPa. Figure 6 shows the EDXD pattern of BaO(III) at a pressure of 18.8 GPa. As pointed out in a previous study,[7] BaO(III) is of the tetragonal PH$_4$I type structure. The space group is $P4/nmm$ with two ion pairs per unit cell, oxygen atoms at (0,0,0) and
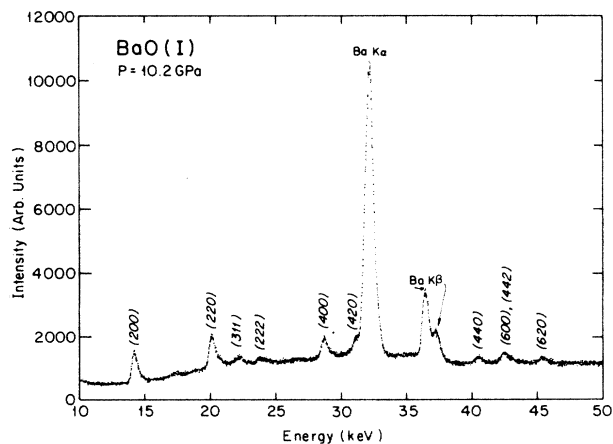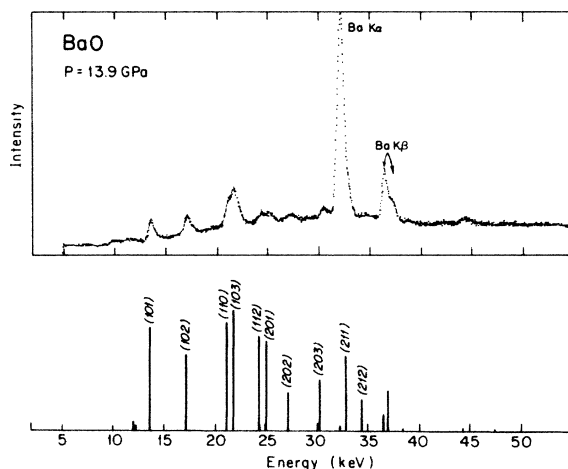
$(\frac{1}{2},\frac{1}{2},0)$ and barium atoms at $(\frac{1}{2},0,\frac{1}{2}+\Delta)$ and $(0,\frac{1}{2},\frac{1}{2}-\Delta)$. Again, the atomic sites are not equivalent and the atoms are not interchangeable. The coordination for each atom in this structure is pseudoeightfold for small Δ. If the atomic position parameter $\Delta=0$ and $c/a =1/\sqrt{2}$, then the structure is of the undistorted cesium-chloride ($B2$) type and the coordination number of each atom is eight. The theoretical calculation of relative line intensities in Fig. 6 with $a =4.375$ Å, $c =3.248$ Å, $c/a =0.742$, and $\Delta=0.12$ shows good agreement with the actual EDXD pattern. With increasing pressure the relative intensities of the peaks in phase III show dramatic, although continuous, change; diffraction peaks with $(h +k)$ even increase in intensity as the pressure increases whereas those with $(h +k)$ odd decrease in intensity. This variation in relative intensities is the result of the Δ

FIG. 4. EDXD spectrum of BaO at a pressure of 10.2 GPa. BaO is in the rocksalt phase [BaO(I)]. The diffraction angle (θ) is 9.377°.
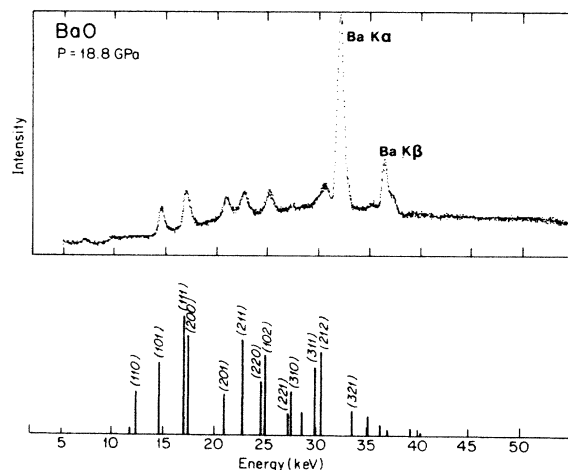

FIG. 6. EDXD pattern of BaO at a pressure of 18.8 GPa. BaO(III) is shown in the upper panel. The lower panel shows the calculated relative line intensities based on the tetragonal PH$_4$I structure with $a =4.375$ Å, $c =3.248$ Å, and $\Delta=0.12$.

TABLE II. Fit of hexagonal NiAs structure to the BaO(II) Debye-Scherrer data of Liu and Bassett (Ref. 8) at a pressure of 10 GPa. The lattice parameters obtained from our fit were $a = 3.6149$ Å and $c = 6.2384$ Å. Listed below are the observed interplanar spacings, calculated interplanar spacings, observed line intensities, and theoretically calculated intensities assuming a NiAs structure. The calculated line intensities include a Lorentz polarization factor. The value of the fitting parameter R and its expression from Ref. 18 are also given.

hkl	d_{obs} (Å)	d_{cal} (Å)	Obs. int. (%)	Calc. int. (%)
(002),(100)	3.145	3.119,3.131	35	31.7
(101)	2.802	2.798	100	100.0
(102)	2.221	2.210	40	34.1
(110)	1.805	1.807	50	34.9
(103)	1.748	1.732	40	37.5
(112)	1.565	1.564	30	29.0
(201)	1.490	1.518	30	26.6
(202)	1.405	1.399	10	12.9
(203)	1.245	1.251	10	17.9
(211)	1.159	1.163	10	30.6

$$R = \sum_{h,k,l} \left| \frac{I_{obs}(h,k,l)}{\sum_{h',k',l'} I_{obs}(h',k',l')} - \frac{I_{cal}(h,k,l)}{\sum_{h',k',l'} I_{cal}(h',k',l')} \right| = 0.177 .$$

TABLE III. Fit of BaO data points to a first-order Birch equation.

Phase	Pressure range (GPa)	B_0 (GPa)	B_0'	$(V/V_0)_{P=0}$
BaO(I)	0—10	66.2±0.8	5.67[a]	1.0
BaO(III)	18—60.5	33.2±1.9	6.02±0.3	0.94±0.02

[a] In view of the limited data on the $B1$ phase in our experiment, B_0' was fixed to the ultrasonically measured value (Ref. 19). The zero pressure isothermal bulk modulus from ultrasonic measurement is 74.1 GPa.
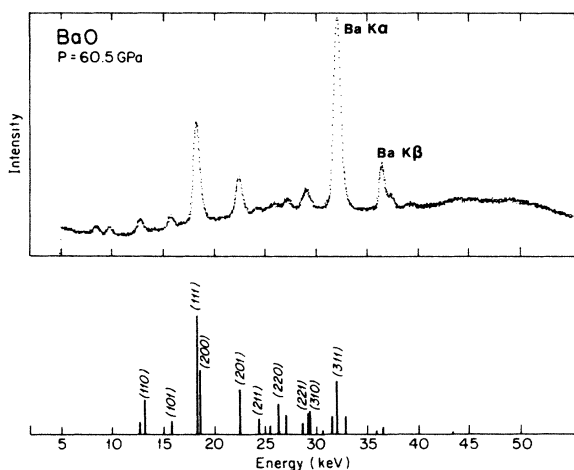

FIG. 7. EDXD pattern of BaO at a pressure of 60.5 GPa. BaO(III) is shown in the upper panel. The lower panel shows the calculated relative line intensities based on the tetragonal PH₄I structure with $a = 4.100$ Å, $c = 2.998$ Å, and $\Delta = 0.06$.
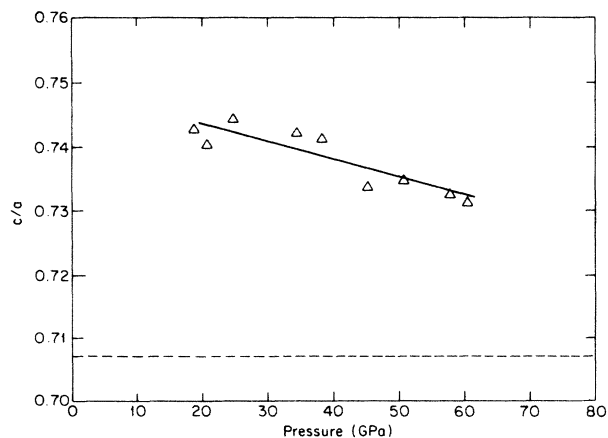

FIG. 8. The axial ratio (c/a) for the BaO(III) phase as a function of pressure. The value of $1/\sqrt{2}$, which corresponds to the $B2$ structure, is indicated by the dashed line.
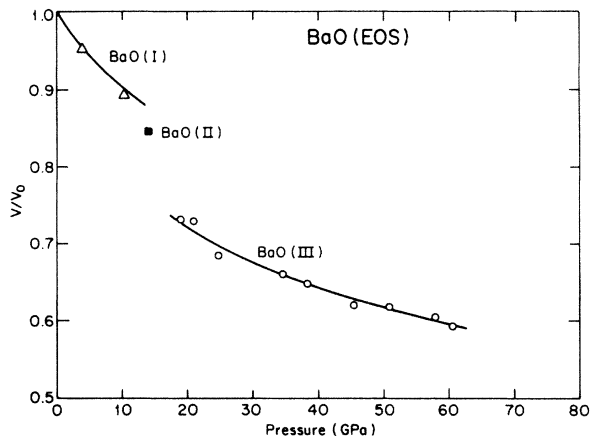
FIG. 9. Plot of the reduced volume V/V_0 of BaO versus pressure. The different symbols correspond to different phases. The solid curves show the first-order Birch fits to phase I and phase III.

parameter steadily decreasing with increasing pressure. Figure 7 shows the EDXD pattern taken at 60.5 GPa along with the theoretically calculated lines with $a = 4.100$ Å, $c = 2.998$ Å, $c/a = 0.731$, and $\Delta = 0.06$. The c/a ratio is slowly decreasing with increasing pressure as is the Δ parameter. A plot of this variation of c/a with pressure is given in Fig. 8. Extrapolation of the c/a plot suggests that BaO may adopt the undistorted cesium chloride phase ($c/a = 1/\sqrt{2}, \Delta = 0$) only above 100 GPa (1 Mbar) in the absence of any intervening first-order transition.

The equation of state of BaO obtained from our experiment is shown in Fig. 9 along with a first-order Birch fit to the data points. Parameters for the Birch equation obtained are given in Table III.

METALLIZATION

A phenomenon of interest in high-pressure studies of normally insulating or semiconducting materials is the metallization of the material under a sufficiently high pressure. The metallization may occur either as a result of a structural phase transition in which the band structure of the new phase has an unfilled band, or as a result of a gradual overlap of the valence band with the conduction band. Most of the barium chalcogenides appear to metallize by the band-overlap mechanism. The compound BaTe has been shown to be a metal at a pressure of approximately 20.0 GPa through the use of optical and resistivity measurements.[1] For BaS, it appears that much higher pressures are needed to achieve metallization. Band-structure calculations by Carlsson and Wilkins[15] for BaS predict band-overlap metallization at a BaS volume ratio of $V/V_0 = 0.60$ which, from the equation of state (EOS) of BaS presented here, corresponds to a pressure of about 39 GPa. The Herzfeld criterion[16] for metallization predicts metallization to occur at $V/V_0 = 0.55$ or, according to our EOS, a pressure of about 62.2 GPa. The true metallization pressure is believed to lie between the band-structure calculated value and the Herzfeld calculated

value, as was the case for BaTe.[1] Since the pressure of 89 GPa attained in the present experiment is much higher than any of these expected metallization pressures, the BaS sample is believed to have become metallic. Optical and resistivity measurement projects are underway to verify this.

The pressure induced metallization of alkaline-earth oxides BaO and CaO was examined theoretically by Bukowinski and Hauser[17] using augmented plane wave band-structure calculations. As a result of these calculations, the metallization pressure of BaO was estimated to be about 1 Mbar assuming that the BaO is in the $B2$ phase when it metallizes. This estimate may have to be revised in view of the results obtained in our experiment. Since the BaO sample is transparent and colorless at 60.5 GPa, the band gap must still be above 3 eV at this pressure and it is not likely that this gap will be reduced to 0 eV at 100 GPa (1 Mbar) unless some first order transition intervenes. Excluding this possibility, according to our equation of state BaO must be pressurized to 1.4 Mbar before the volume is reduced to $V/V_0 = 0.5$, the Herzfeld predicted volume for metallization. It appears, then, that BaO may only metallize at pressures well above 1 Mbar unless there is some as yet undiscovered first order transition above 60.5 GPa.

CONCLUSIONS

In conclusion, we have obtained the following results from our experiments on the two barium chalcogenides BaS and BaO.

(1) BaO transforms from the $B1$ phase to an intermediate BaO(II) phase at about 10 GPa rather than transforming directly to the $B2$ phase as other barium chalcogenides do. This intermediate BaO(II) phase is in the hexagonal NiAs structure. At about 15 GPa this phase transforms to BaO(III).

(2) The high-pressure BaO(III) phase is a tetragonal PH_4I type with pseudoeightfold coordination and seems to be steadily approaching a cesium-chloride- ($B2$) type structure with increasing pressure. Extrapolations of the c/a data points indicates that pressures exceeding 1 Mbar may be required for BaO to finally adopt the $B2$ phase in the absence of a first-order transition.

(3) The $B2$ phase of BaS is stable up to 89 GPa, the highest pressure reached in our experiment. It is believed that the BaS became metallic around 62 GPa in the cesium-chloride phase by band overlap. This must be verified by optical and resistivity measurements now underway.

(4) The equations of state of BaS to 89 GPa and of BaO to 60.5 GPa are given and their low-pressure behavior is in good agreement with ultrasonic bulk modulus measurements.

ACKNOWLEDGMENTS

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