

ARTICLES

Phase transformation of BeSe and BeTe to the NiAs structure at high pressure

H. Luo, K. Ghandehari, R. G. Greene, and A. L. Ruoff

Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

S. S. Trail and F. J. DiSalvo

Department of Chemistry, Cornell University, Ithaca, New York 14853

(Received 6 January 1995; revised manuscript received 1 May 1995)

We report the existence of a reversible pressure-induced first-order phase transition between the zinc-blende (*B3*) and the NiAs (*B8*) phase in the beryllium chalcogenides BeSe and BeTe at pressures of 56 ± 5 GPa and 35 ± 5 GPa, respectively. The NiAs phase remains stable in both compounds with further pressure increase up to at least 72 GPa in BeSe and 53 GPa in BeTe. For BeTe, an amorphous phase was observed upon decompression in the pressure range from 47 to 32 GPa. The equation of state is determined for each compound. We discuss the systematic trends of the structural phase transition, the stability of the NiAs structure, amorphization, as well as metallization in the beryllium chalcogenides.

I. INTRODUCTION

Recent observations of pressure-induced structural phase transition in SrSe,¹ three calcium chalcogenides CaX ($X = S, Se, Te$) (Ref. 2) and MgTe (Ref. 3) have left the beryllium chalcogenides BeX ($X = O, S, Se, Te$) and three magnesium chalcogenides MgX ($X = O, S, Se$) the only unknown members in the entire IIA-VI series in regard to high-pressure phase-transition sequence. For all the IIA-VI compounds investigated so far, a first-order phase transition from the sixfold-coordinated NaCl (rocksalt) phase to the eightfold-coordinated CsCl phase has been found except for MgO and BaO where this transition has not yet been observed in the experiments.^{4,5} The NaCl-type IIA-VI compounds are mostly ionic in bonding character and have exhibited a systematic relationship between the transition pressure and ionic radius as summarized in Refs. 2 and 6.

Among the chalcogenides of Group IIA elements (Be, Mg, Ca, Sr, Ba), only BeS, BeSe, and BeTe crystallize in the fourfold-coordinated cubic zinc-blende (zb) structure (sphalerite). The rest have the sixfold-coordinated NaCl (also cubic) structure except for BeO and MgTe, which adopt the fourfold-coordinated wurtzite (hexagonal) structure. A distinguished feature in the beryllium (Be) compounds is that the cations (Be ions) are extremely small as compared to the anions except in BeO. This leads to an excess of the critical ratio of ionic radii, 4.45, for the zb structure in all three Be compounds with the zb structure: BeS, BeSe, and BeTe, implying that they are no longer as ionic as the other IIA-VI compounds. In fact, the Be compounds are more covalent than ionic with the *Phillips* ionicities ranging from 0.169 in BeTe to 0.312 in BeS.⁷ The characteristics of Be compounds in structure and bonding make them analogous to the Group III-V semiconductors which have been extensively

studied at high pressure over the past many years. The Be compounds are featured by having large band gaps ranging from about 2.7 to 5.5 eV,⁸ high bulk moduli, and lattice constant matches with GaAs and ZnSe.^{9,10}

Regarding the pressure-induced phase transition in the zb compounds of the III-V series, the NaCl and β -Sn are the two most common structures observed typically below 20 GPa. Very recently, the sixfold-coordinated hexagonal NiAs (*B8*) structure was found in the zb compounds AlAs and AlP at high pressure.^{11,12} Typically, the relative volume decrease at the fourfold to sixfold structural transformation is around 17% and the high-pressure phases are all metallic.

To the best of our knowledge, there had been no reported experimental work on BeS, BeSe, and BeTe at high pressure before this study. For the other two tetrahedral IIA-VI compounds MgTe and BeO, the wurtzite structure becomes unstable in the former at a very low pressure³ and is stable in the latter to, at least, 55 GPa.¹³ The experimental results of BeO are in disagreement with the theories which predicted that BeO would transform to the NaCl phase at 20 GPa (*ab initio* pseudopotential calculations^{14,15}) or at 40 GPa (potential-induced breathing model¹³).

The Be compounds are particularly similar to the boron (B) compounds BN, BP, and BAs of the III-V series in that both have the same crystal structure at ambient conditions, wide band gaps, and high bulk moduli. All of the three B compounds were expected to transform to the sixfold-coordinated structure in the megabar region¹⁶ but no experimental confirmation has been achieved. Thus, understanding the high-pressure structural behavior of the Be compounds is significant in that it could provide a clue on the high-pressure behavior of the B compounds and hence motivate further experimental and theoretical work on these compounds.

This paper presents the results of the first high-

pressure experimental study on the two Be chalcogenides BeSe and BeTe to 72.1 and 53.0 GPa, respectively. The major results of this study include determinations of crystal structure of the high-pressure phases and the equations of state. This work is a part of our global investigation of the structural and electronic properties of the Groups II-VI and III-V compounds under static compression.

II. EXPERIMENTAL

A. Sample synthesis

BeSe and BeTe samples were synthesized by the reaction of beryllium foil (99.999% pure) with selenium powder (99.999% pure) or tellurium powder (99.99% pure) in an alumina crucible sealed in an evacuated quartz tube at 1200°C for 48 h. The x-ray-diffraction data indicated that both samples had the zb structure with fairly good interplanar spacing and intensity agreements with the calculated values. The purity of sample was estimated to be higher than 98% based on the x-ray-diffraction data. Both samples also showed sharp vibrational phonon signals when examined by Raman spectroscopy. The BeSe sample had a light gray color and was transparent in the visible range, while the BeTe sample appeared in a light brown color and was opaque.

B. DAC preparation and EDXD measurements

Diamond-anvil cells (DAC) were used to generate static compression on sample. The sample was ground into fine powder and loaded into the DAC. A small amount of gold powder was placed in the center region of the sample which served as an internal pressure marker. The pressure was determined by the isothermal equation of state of gold obtained from the shock-wave method.¹⁷ In detail, the converted bulk modulus of gold $B_0 = 177.3$ GPa and its first-order pressure derivative $B'_0 = 4.77$ were used in the two-parameter *Birch* equation shown in the next section. The BeSe and BeTe samples were studied in two DAC's with diamond flats of 200 and 450 μm in diameter, respectively. No pressure medium was used with the sample and the state of stress in the sample was consequently nonhydrostatic. The nonhydrostaticity in a sample under a uniaxial compression has been approximately analyzed for the cubic symmetry.¹⁸

The energy-dispersive x-ray diffraction (EDXD) measurements on BeSe and BeTe were performed at the Cornell High Energy Synchrotron Source (CHESS). The details of the EDXD techniques are given in Refs. 19 and 20. The diffraction data were collected at a Bragg angle of 6.378° for BeSe and 6.137° for BeTe. All the measurements presented in this paper were carried on at room temperature.

III. RESULTS

In this section, we show the results of BeTe first because it is representative by having the largest difference between the anion and cation radius among all the zb compounds.

A. Beryllium telluride

The lattice constant of BeTe at 1 atm measured by this work is $a_0 = 5.617 \pm 0.001$ Å in deviation of 0.01 Å from an earlier value of 5.6269 ± 0.0005 Å.⁸ We do not know why there exists such a deviation. Certainly, the sample quality is one reason, and the measurement error is the other. The zb phase of BeTe is stable with increasing pressure up to about 37.1 GPa. The measured relative volume V/V_0 at this pressure is 0.733. A diffraction spectrum at this pressure is shown in Fig. 1(a). The interplanar spacings (d) and integrated intensities (I) are listed in Table I along with the corresponding values from the calculation. The intensity comparison between the measured and calculated values presented in Table I implies that the sample was textured along the $\langle 111 \rangle$ direction under compression.

In addition to the diffraction peaks from the sample and gold (Au), the fluorescence of tellurium (K_β), and the escape peaks from the Ge detector (e), we also observed one weak peak labeled as Te at 23.8 KeV in Fig. 1(a). This weak peak appeared first above 3 GPa on the lower energy side of the BeTe (200) peak in each of the two separate experiments on BeTe. Since this unknown peak shifted much faster with pressure than any of the diffraction peaks from the sample and, particularly, was still present in the diffraction spectra of the transformed sample as shown in Figs. 1(b) and 1(c), it is not likely it was a diffraction peak from any high-pressure phase of BeTe. We attribute this peak to the diffraction from a small amount of unreacted tellurium metal in the sample.

When the pressure was increased to 39.3 GPa, there was a dramatic change in the diffraction pattern as shown in Fig. 1(b). The first two peaks (111) and (200) from the zb phase were still visible but much weaker at this pressure and disappeared above 43 GPa, indicating that BeTe was in a coexistence of two phases between 39 and 43 GPa and transformed to a single phase above 43 GPa.

The new diffraction spectra above 39 GPa can be indexed well to the NiAs structure (space group $P6_3/mmc$) that has a hexagonal unit cell containing two pairs of BeTe units. At 39.3 GPa, at which the NiAs phase was first observed, the measured lattice constants of the hex-

TABLE I. List of the observed interplanar spacings d and intensities I in BeTe at a pressure of 37.1 GPa along with the corresponding theoretical values based on the zb structure. The measured lattice constant at this pressure is $a = 5.064 \pm 0.001$ Å. The method of the relative intensity calculation has been described in Ref. 19.

(hkl)	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
(111)	2.922	2.924	100.0	100.0
(200)	2.538	2.532	40.9	57.5
(220)	1.796	1.790	14.0	55.3
(311)	1.527	1.527	14.9	52.5
(222)	1.463	1.462	8.3	12.9
(400)	1.267	1.266	1.3	5.5
(331)	1.167	1.162	2.9	12.0
(420)	1.129	1.132	2.8	9.2

TABLE II. List of the observed interplanar spacings d and intensities I of BeTe at a pressure of 45.8 GPa along with the theoretical corresponding values based on the hexagonal NiAs structure. The measured lattice parameters at this pressure are $a = 3.418 \pm 0.001 \text{ \AA}$, $c = 5.496 \pm 0.001 \text{ \AA}$, and $c/a = 1.608$.

(hkl)	$d_{\text{obs}} (\text{\AA})$	$d_{\text{calc}} (\text{\AA})$	$I_{\text{obs}} (\%)$	$I_{\text{calc}} (\%)$
(100)	2.968	2.960	12.1	15.0
(002)	2.748	2.748	38.6	21.3
(101)	2.602	2.606	100.0	100.0
(102)	2.015	2.014	2.7 ^a	22.4
(110)	1.710	1.709	50.4	46.4
(103)	1.554	1.558	~1	19.4
(112)	1.450	1.451	19.9	18.7
(201)	1.431	1.429	15.5	14.3

^aThe energy of this line happened to be just above the absorption edge of tellurium, resulting in an exceptionally low intensity as compared to the calculated value.

agonal cell are $a = 3.423 \pm 0.001 \text{ \AA}$, $c = 5.528 \pm 0.001 \text{ \AA}$, and $c/a = 1.615$. The measured diffraction intensity fits the best with the following basis in the unit cell: Te ions at $(1/3, 2/3, 1/4)$ and $(2/3, 1/3, 3/4)$; and Be ions at (000) and $(0, 0, 1/2)$. It should be noted that the atomic sites in

the NiAs structure are not equivalent or interchangeable for cations and anions. Since the c/a ratio ($=1.615$) in the NiAs structure is very close to the ideal value of 1.633, the Te ions form a hexagonal close-packed (hcp) lattice, whereas the Be ions occupy the octahedral sites in a simple hexagonal arrangement. Figure 1(c) shows a fully transformed sample diffraction spectrum at 45.8 GPa, and Table II lists the measured and calculated d spacings and intensities in BeTe at the same pressure. Comparing Table II with Table I, we notice that the degree of texturing is reduced in the NiAs phase.

The c/a ratio in the NiAs phase remained unchanged with increasing pressure and no further phase transformation was found up to at least 53 GPa, the highest pressure attempted for BeTe. It should be noted that an increasing intense background appeared between 20 and 25 KeV and the diffraction peaks became broad after the phase transition [see Figs. 1(b) and 1(c)]. This could indicate an onset of a disordered structure associated with the phase transition. In the coexistence of the zb and NiAs phases at 39.3 GPa, the relative volume V/V_0 is 0.714 for the zb phase and 0.633 for the NiAs phase. The relative volume decrease $-\left[\Delta V/V(\text{zb})\right]$ at the transition on uploading is consequently 11.3%.

When the pressure was released, BeTe remained in the NiAs phase only for a narrow pressure range of about 5 GPa. At 50.3 GPa, the sample diffraction became very weak and was barely indexed to the NiAs structure [see Fig. 2(a)]. In the pressure range from about 47 down to 32 GPa, no BeTe diffraction peak was recorded. On the contrary, the diffraction from the gold powder used as a pressure marker remained strong throughout the experiment. A selected diffraction spectrum at 35.6 GPa is shown in Fig. 2(b). From the view of x-ray diffraction,

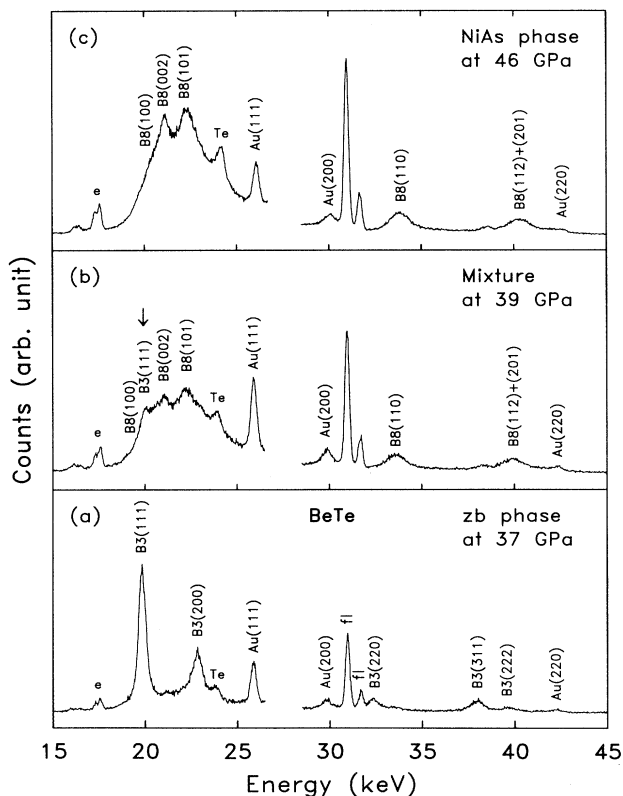


FIG. 1. EDXD spectra of BeTe around the zb ($B3$) to NiAs ($B8$) transition during compression. Au stands for the gold diffraction lines; e for the escape peaks; Te for the tellurium metal; and fl for the fluorescence (K_{β}) of tellurium. In all three patterns, the strong $K\alpha$ lines of tellurium at 27.19 and 27.46 KeV are not shown for clarity. The phase assignment is indicated in each spectrum.

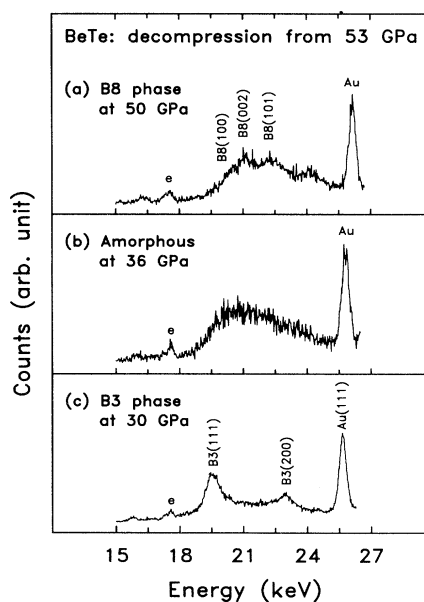


FIG. 2. EDXD spectra of BeTe during decompression: (a) at 50 GPa and indexed to the NiAs ($B8$) structure; (b) at 36 GPa and assigned as an amorphous phase; and (c) at 30 GPa and indexed to the zb ($B3$) structure.

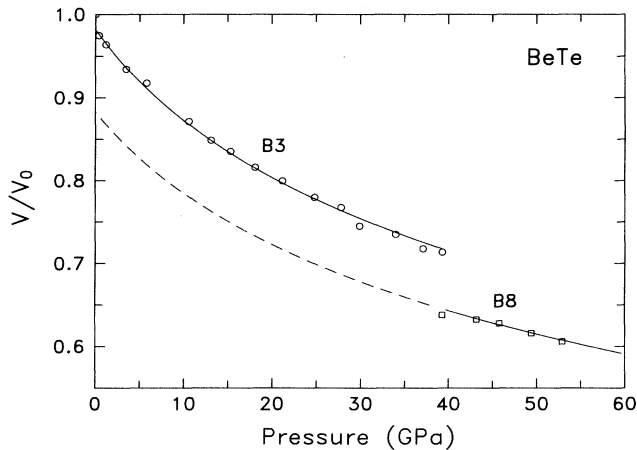


FIG. 3. Plot of the relative volume V/V_0 versus pressure for BeTe. Only the uploading data are shown here. The solid lines are the plots of the Birch fit. The relative volume decrease at the transition is 11.3%.

the featureless diffraction spectrum at 35.6 GPa indicates that BeTe is in an amorphous phase. A brief discussion is given in Sec. IV on the likely reasons for BeTe to transform to an amorphous phase.

When the pressure was further released to 30.2 GPa, BeTe suddenly transformed back to the original zb phase and exhibited fairly good diffraction peaks as shown in Fig. 2(c). Thus, the equilibrium zb to NiAs transition pressure (an average value of uploading and downloading transition pressures) in BeTe is determined to be 35 ± 5 GPa. Because of the kinetic effects in the pressure-induced phase transition, the equilibrium transition pressure determined here (i.e., 35 GPa) should be referred in comparison with theoretical calculations.

The pressure-volume (P - V) relation of BeTe is plotted in Fig. 3, along with a fit to the two-parameter Birch equation²¹

$$P = \frac{3}{2} B_0 (x^{7/3} - x^{5/3}) \left[1 + \frac{3}{4} (B'_0 - 4) (x^{2/3} - 1) \right], \quad (1)$$

where $x = V_0/V$, B_0 is the isothermal bulk modulus at zero pressure, and B'_0 is the first-order pressure derivative of the bulk modulus evaluated at zero pressure. Both zb and NiAs phases have nearly the same value of B_0 determined to be 67 ± 1 GPa when B'_0 is fixed at 4. The extrapolated relative volume of the NiAs phase at zero pressure is $V_0(\text{NiAs})/V_0(\text{zb}) = 0.88$.

B. Beryllium selenide

The BeSe sample was in a single phase of the zb type with $a_0 = 5.137 \pm 0.001$ Å in good agreement with the literature value of 5.139 Å.²² The phase transition sequence in BeSe was found to be the same as in BeTe in both uploading and downloading cases except that no amorphous phase was observed.

Three selected spectra around the zb to NiAs phase transition on uploading are shown in Fig. 4. Only a nar-

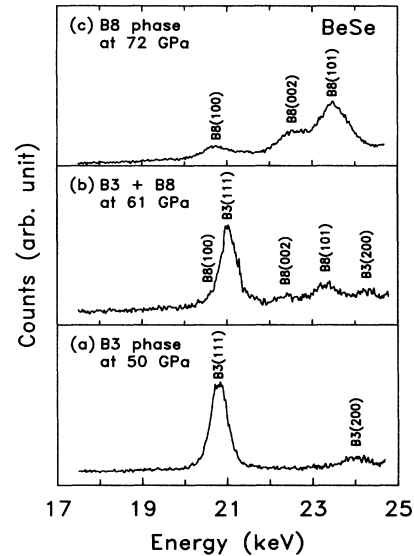


FIG. 4. EDXD spectra of BeSe around the zb ($B3$) to NiAs ($B8$) phase transition on uploading.

row spectral range is plotted in Fig. 4 because the rest part of spectra contains strong diffraction peaks from the tungsten/rhenium gasket. The phase transition in BeSe started at about 61 GPa and completed at about 69 GPa. At 72.1 GPa, the highest pressure attempted, BeSe was in a single phase fully indexed to the NiAs structure with $a = 3.123 \pm 0.001$ Å, $c = 4.955 \pm 0.001$ Å and $c/a = 1.587$. The diffraction intensity data supports the following basis in the hexagonal unit cell: the anions (Se ions) at positions of $(1/3, 2/3, 1/4)$ and $(2/3, 1/3, 3/4)$, and the cations (Be ions) at positions of (000) and $(0, 0, 1/2)$.

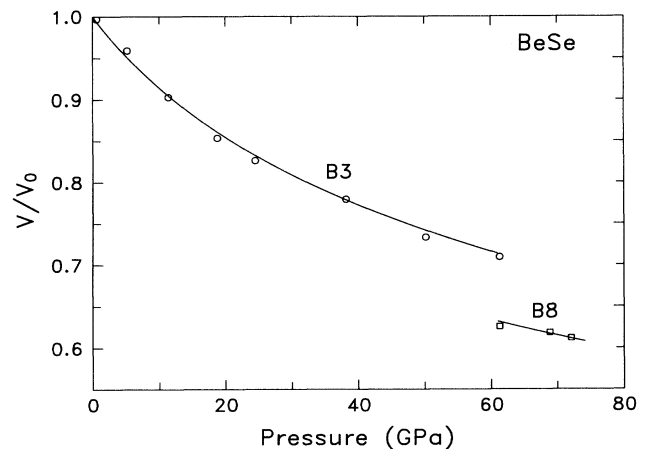


FIG. 5. Plot of the relative volume V/V_0 versus pressure for BeSe. The solid line in the zb ($B3$) phase is the plot of the Birch fit. The solid line in the NiAs ($B8$) phase serves as a guideline for the eyes.

TABLE III. List of the observed interplanar spacings d and intensities I of BeSe at a pressure of 50.2 GPa along with the theoretical corresponding values based on the zb structure. The measured lattice constant at this pressure is $a = 4.647 \pm 0.001$ Å.

(hkl)	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
(111)	2.683	2.683	100.0	100.0
(200)	2.327	2.323	11.9	55.2
(220)	1.646	1.643	6.4	47.5
(311)	1.403	1.401	4.7	43.0
(222)	1.345	1.341	2.2	10.4
(400)	1.164	1.162	3.5	4.2

In the beginning of the two phase mixture at 61.3 GPa, the relative volume is 0.716 for the zb phase and 0.632 for the NiAs phase. The relative volume decrease at the zb to NiAs transition is therefore 11.8%. Tables III and IV list the d and I data for the zb and NiAs phase at 50.2 and 72.1 GPa, respectively. Similar to what happened in BeTe, the high-pressure NiAs phase was less textured than the low-pressure zb phase in BeSe.

The P - V relation of BeSe is plotted in Fig. 5 with a fit of the Birch equation [Eq. (1)] shown by the solid line. The resulting value of B_0 is 92.2 ± 1.8 GPa when B'_0 is fixed at 4. No fitting was made for the NiAs phase because of the lack of data points in that phase.

In contrast to that in BeTe, there was no amorphous phase formed in BeSe on downloading. The reverse transition from the NiAs back to the zb phase occurred at 50.5 GPa. Thus, the equilibrium zb to NiAs transition pressure in BeSe is determined to be 56 ± 5 GPa.

IV. DISCUSSION

Including the present results, the zb to NiAs structural transformation has been observed in four compounds AIP, AlAs, BeSe, and BeTe in the entire binary II-VI and III-V systems. In terms of chemical bonding, each of these four compounds has a small value Phillips ionicity $f_i \leq 0.307$. While the other zb compounds with

TABLE IV. List of the observed interplanar spacings d and intensities I of BeSe at a pressure of 72.1 GPa along with the theoretical corresponding values based on the hexagonal NiAs structure. The measured lattice parameters at this pressure are $a = 3.123 \pm 0.001$ Å, $c = 4.955 \pm 0.001$ Å, and $c/a = 1.587$.

(hkl)	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
(100)	2.696	2.705	14.8	14.0
(002)	2.476	2.477	40.2	20.3
(101)	2.375	2.374	100.0	100.0
(102)	1.834	1.827	6.3	21.9
(110)	1.559	1.562	26.3	42.5
(103)	1.414	1.410	6.6	17.4
(112)	1.322	1.321	10.8	14.3
(201)	1.300	1.305	4.9	11.7

$f_i \geq 0.307$ often transform to the NaCl [e.g., InAs (Ref. 23)] or the β -Sn structure [e.g., GaP (Ref. 24)]. The boron compounds BN, BP, and BAs are analogous to AIP, AlAs, BeSe, and BeTe in structural and bonding aspects, and, therefore, are likely to transform to the NiAs structure eventually at high pressure. Theoretically, the three boron compounds were expected to transform to the NaCl structure,¹⁶ which has a very small total-energy difference from the NiAs structure. To find out which structure the boron compounds will transform to would be of considerable experimental and theoretical interest.

For both BeSe and BeTe, the zb structure becomes unstable at a volume reduction $V/V_0 \approx 0.715$ and the transition is accompanied by a relative volume decrease of $-\Delta V/V \approx 11.5\%$, the smallest volume collapse ever observed at the first-order fourfold–sixfold phase transition. The average value at this type of transition is around 17%. Small volume collapses at transition also exist in CaSe and CaTe,² where the sixfold–eightfold phase transition has a relative volume decrease of 7.7 and 4.6%, respectively, in comparison to a typical value of 12% at this type of transition. One common feature of these compounds with small volume collapses at transition (BeSe, BeTe, CaSe, CaTe) is that the cations are much smaller than anions. As a result, the interionic Coulomb interaction is ineffective in these compounds and the Pauling repulsive force between the large anions resists the reduction of the cation-anion distance and hence the collapse of volume at the transition. Quantitatively, our diffraction results show that the nearest Be-ion and Te-ion distance increases notably from 2.17 to 2.41 Å at the transition from the zb to the NiAs structure.

Up to date, only those NiAs structures with c/a ratios greater than the ideal value 1.633 have become unstable under compression [e.g., FeS and FeSe,²⁵ MnTe,²⁶ and BaO (Ref. 4)]. The NiAs structure in BeSe and BeTe has a c/a ratio of 1.587 and 1.615, respectively, and is, therefore, expected to remain stable in a large pressure range. Further experimental and theoretical efforts are needed on the stability of the NiAs structure.

We do not know if the fourfold to sixfold structural transformations in BeSe and BeTe is accompanied by an insulator to metal transition, although such an electronic transition has taken place in many other, if not all, first-order structural changes in the III-V and II-VI compounds investigated so far. On one side, it is likely that the high-pressure NiAs phase in BeSe and BeTe has become metallic for the NiAs structure has always been adopted by metallic and intermetallic compounds at either ambient or high-pressure conditions. On the other side, however, the two Be compounds are special in that both have a large band gap and experience a relatively small volume collapse at the transition. As a result, a nonmetallic NiAs phase is likely in BeSe and BeTe. If so, the current observation would serve as the first exception in which a NiAs phase is not metallic. Visual examinations were made under a microscope on both samples at their highest compression with no metallic appearance observed. Further optical and/or electrical measurements are needed in order to conclude this issue.

This work is significant for a systematic understanding

of the pressure-induced structural phase transition in binary systems. Now, only BeO, BeS, BN, and BP remain experimentally unknown in regard to their high-pressure sixfold-coordinated structures in the entire IIA-VI and III-V tetrahedral systems. Based on the transition sequence found in BeSe and BeTe, BeS is expected to transform to the NiAs structure; and based on the theoretical calculations, the rest (BeO, BN, and BP) are predicted to adopt the rocksalt (NaCl) structure.^{13,16}

It is known that there exist relationships between phase transition sequence and lattice constant, and between bulk modulus and nearest-neighbor distance in a homologous series. For the ionic calcium and strontium chalcogenides, the transition pressure and bulk modulus were found to follow simple relations with the ionic radius and the lattice constant.^{2,6} For the III-V zb compounds, an empirical formula $B_0 = 1761d^{-3.5}$,²⁷ where B_0 is the bulk modulus and d is the nearest-neighbor distance, gives B_0 values very close to the measured ones. For the Be chalcogenides, three bulk moduli were measured by x-ray diffraction except for BeS. By fitting the three known B_0 to the same type of relationship as for the III-V compounds, we obtained $B_0 = 868d^{-2.84}$. The computed B_0 is within $\pm 3\%$ from the measured value for each of the three Be compounds and is 105 GPa for BeS. Using this value with $B'_0 = 4$ in the Birch equation [Eq. (1)] and assuming $V/V_0 = 0.715$ at the phase transition, we expect BeS to transform to the NiAs phase at $P_t \approx 69$ GPa on uploading. The estimated transition pressure for BeO is $P_t \approx 139$ GPa, which may not be accurate since BeO has a wurtzite structure other than a zb type and is much less covalent than the other three Be compounds.

Finally, we discuss the observed amorphous phase in BeTe during decompression. Pressure-induced crystalline-to-amorphous transition has been observed in a number of solids of different forms, including semiconductors [GaAs,²⁸ GaP,²⁹ and BAs (Ref. 30)], molecular solids [C₆H₆ (Ref. 31) and sulfur³²], and large band-gap insulators [SiO₂ (Ref. 33) and CaSiO₃ (Ref. 34)]. Some amorphous phases are intermediate states in transition between two crystalline phases (sulfur on uploading,³² and GaP on downloading²⁹), and others are metastable phases created on either uploading or downloading and persist even back to the ambient conditions [GaAs,²⁸ BAs,³⁰ and C₆H₆ (Ref. 31)]. In general, amorphization at high pressure and/or low temperature is ascribed to the kinetic reasons such as potential barriers between crystalline energy states. In BeTe, where an amorphous phase is formed on decompressing from about 47 to 32 GPa, the kinetic barrier is high for the reverse transition from the

NiAs to the zb phase for the following reason. In BeTe, the cations are so small that the anions are repelled from getting close to the cations by the overlap of their own charge distributions. The strong repulsive force among anions in BeTe also explains why it has the largest hysteresis (i.e., kinetics) of about 10 GPa in the reverse transformation among the IIA-VI compounds.

V. CONCLUSIONS

In conclusion, we have obtained the following results from the high-pressure EDXD experiments on BeSe and BeTe.

(1) BeSe transforms from the zinc-blende to the NiAs phase at 61.3 GPa on uploading with a relative volume decrease of 11.8% at the transition. The NiAs phase is stable up to at least 72.1 GPa. This transition is reversible with large hysteresis of about 10 GPa. The bulk modulus of BeSe is determined to be 92.2 ± 1.8 GPa when the B'_0 fixed at 4.

(2) BeTe transforms from the zinc-blende to the NiAs phase at 39.3 GPa on uploading with a relative volume decrease of 11.3% at the transition. The NiAs phase is stable up to at least 52.9 GPa. Upon a release of pressure, BeTe first transforms to an amorphous phase at about 47 GPa and then to its original phase at 30.2 GPa. The bulk modulus of BeTe is determined to be 66.8 ± 0.7 GPa when the B'_0 fixed at 4.

(3) For both BeSe and BeTe, the zinc-blende structure becomes unstable at a relative volume of 0.715 ± 0.001 . The volume collapses (or decreases) at the phase transition are significantly smaller than that in most other fourfold to sixfold phase transitions. We expect the NiAs phase in both BeSe and BeTe to be stable over a large pressure range.

(4) Based on the phase-transition trends found in BeSe and BeTe, we expect BeS to transform to the NiAs phase at about 69 GPa. This needs to be verified experimentally.

(5) This work raises an important question about the electrical property of BeSe and BeTe in the NiAs phase. Further optical (absorption and reflection) and electrical resistance measurements are needed.

ACKNOWLEDGMENTS

We acknowledge the support by the Cornell Materials Science Center through the National Science Foundation under Grant No. DMR 91-21654 and by the National Science Foundation under Grant No. DMR 92-18249. We thank the CHESS staff for their technical assistance.

¹H. Luo, R. G. Greene, and A. L. Ruoff, Phys. Rev. B **49**, 15 341 (1994).

²H. Luo, R. G. Greene, K. Ghandehari, T. Li, and A. L. Ruoff, Phys. Rev. B **50**, 16 232 (1994).

³T. Li, H. Luo, R. G. Greene, A. L. Ruoff, S. S. Trail, and F. J. DiSalvo, Phys. Rev. Lett. (to be published).

⁴S. T. Weir, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. B **33**, 4221 (1986).

⁵M. S. Vassiliou and T. J. Ahrens, Geophys. Res. Lett. **8**, 729 (1981).

⁶K. Syassen, Physica B **139&140**, 277 (1986).

⁷J. A. Van Vechten, Phys. Rev. **187**, 1007 (1969).

- ⁸W. M. Yim, J. P. Dismukes, E. J. Stofko, and R. J. Paff, *J. Phys. Chem. Solids* **33**, 501 (1972).
- ⁹R. G. Dandrea and C. B. Duke, *Appl. Phys. Lett.* **64**, 2145 (1994).
- ¹⁰P. M. Mensz, *Appl. Phys. Lett.* **64**, 2148 (1994).
- ¹¹R. G. Greene, H. Luo, T. Li, and A. L. Ruoff, *Phys. Rev. Lett.* **72**, 2045 (1994).
- ¹²R. G. Greene, H. Luo, and A. L. Ruoff, *J. Appl. Phys.* **76**, 7296 (1994).
- ¹³A. P. Jephcoat, R. J. Hemley, and H. K. Mao, R. E. Cohen, and M. J. Mehl, *Phys. Rev. B* **37**, 4727 (1988).
- ¹⁴K. J. Chang, S. Froyen, and M. L. Cohen, *J. Phys. C* **16**, 3475 (1983).
- ¹⁵K. J. Chang and M. L. Cohen, *Solid State Commun.* **50**, 487 (1984).
- ¹⁶R. M. Wentzcovitch, M. L. Cohen, and P. K. Lam, *Phys. Rev. B* **36**, 6058 (1987).
- ¹⁷J. C. Jamieson, J. Fritz, and M. H. Manghnani, *Adv. Earth Planet. Sci.* **12**, 27 (1980).
- ¹⁸A. L. Ruoff, H. Luo, H. Xia, and Y. K. Vohra, *High Pressure Res.* **6**, 183 (1991).
- ¹⁹M. Baublitz, Jr., V. Arnold, and A. L. Ruoff, *Rev. Sci. Instrum.* **52**, 1616 (1981).
- ²⁰K. E. Brister, Y. K. Vohra, and A. L. Ruoff, *Rev. Sci. Instrum.* **57**, 2560 (1986).
- ²¹F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).
- ²²B. R. Pamplin, in *Handbook of Chemistry and Physics*, 60th ed. (CRC, Boca Raton, FL, 1980), p. E-102.
- ²³J. C. Jamieson, *Science* **139**, 762 (1963).
- ²⁴M. Baublitz, Jr. and A. L. Ruoff, *J. Appl. Phys.* **53**, 6179 (1982).
- ²⁵T. Kamimura, M. Sato, H. Takahashi, N. Mori, H. Yoshida, and T. Kaneko, *J. Magn. Magn. Mater.* **104-107**, 255 (1992).
- ²⁶M. Mimasaka, I. Sakamoto, K. Murata, Y. Fujii, and A. Onodera, *J. Phys. C* **20**, 4689 (1987).
- ²⁷S. B. Zhang and M. L. Cohen, *Phys. Rev. B* **35**, 7604 (1987).
- ²⁸Y. K. Vohra, H. Xia, and A. L. Ruoff, *Phys. Rev. Lett.* **57**, 2666 (1990).
- ²⁹K. Tsuji, Y. Katayama, Y. Yamamoto, H. Kanda, and H. Notsaka, *J. Phys. Chem. Solids* **56**, 559 (1995).
- ³⁰R. G. Greene, H. Luo, and A. L. Ruoff, *Phys. Rev. Lett.* **73**, 2476 (1994).
- ³¹J. M. Besson, M. M. Thiery, and Ph. Pruzan, in *Molecular Systems Under High Pressure*, edited by R. Pucci and G. Piccitto (Elsevier, North-Holland, 1991), pp. 341-359.
- ³²H. Luo and A. L. Ruoff, *Phys. Rev. B* **48**, 569 (1993).
- ³³R. J. Hemley, A. P. Jephcoat, H. K. Mao, M. C. Ming, and M. H. Manghnani, *Nature (London)* **52**, 334 (1988).
- ³⁴M. B. Kruger and R. Jeanloz, *Science* **249**, 647 (1990).