Phase Transformation of BeS to the NiAs Structure at High Pressure

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Pressure-induced transitions have previously been observed at room temperature in all the alkaline chalcogenides except MgS, MgO, BeS and BeO. This paper reports on studies to 96 GPa on BeS in which a phase transformation from the four-fold zincblende structure occurs at 51 ± 8 GPa to the six-fold nickel arsenide structure, which persists to the highest pressure studied. The equation of state is given.

[phase transition, NiAs structure, equation of state, transition pressure dependence on ionic radius ratio]

1. Introduction

A summary of the high pressure behavior of BeS, BeSe and BeTe is given. The expectation that BeO will behave differently is noted.

The beryllium chalcogenides differ from the other alkaline chalcogenides (except for MgTe) in that they do not have the six-fold coordinated rocksalt (B1) structure, but rather are four-fold coordinated. Both BeTe and BeSe have the zincblende structure and transform at pressure to the NiAs (B8) structure [1]. The ideal NiAs structure (c/a = 4/3) has on the average a seven-fold coordinated structure (Te surrounded by six equidistant Be and Be surrounded by eight equidistant atoms, two being Be and six being Te).

2. Experimental

The present paper describes the behavior of BeS which has the zincblende structure at atmospheric pressure. Energy dispersive x-ray diffraction studies were carried out at CHESS to 96 GPa as before [1]. The BeS had a purity of 99%. Only the zincblende peaks were present initially. The lattice parameter was 4.870 Å. The sample had a light gray color and was opaque.

Table 1. List of the observed interplanar spacings and relative intensities I of BeS at 0.6 GPa along with the theoretical corresponding values based on the zincblende structure. The fitted lattice parameter is 4.860 Å. The CESR energy was 5.28 GeV and the energy-interplanar spacing product was Ed = 46.685 keV-Å.

hkl	d _{obs} (Å)	d _{calc} (Å)	I _{obs} (%)	I _{calc} (%)
111	2.806	2.806	100	100
200	2.431	2.430	22.6	36.0
220	1.718	1.719	48.1	40.7
311	1.466	1.466	16.0	26.3
222	1.404	1.403	3.8	4.33
400	1.216	1.215	1.6	2.90
331	1.116	1.115	4.2	4.72
420	1.087	1.087	2.7	2.46
422	0.992	0.992	2.8	2.72
511+333	0.936	0.935	1.1	1.24
440	0.859	0.859	0.34	0.41

3. Results and Discussion

Table 1 shows the diffraction results for BeS at 0.6 GPa. As the pressure was increased, new peaks appeared at 59 GPa and the transition was soon complete. Table 2 summarizes the diffraction results at 66 GPa. The new phase was shown to be the NiAs structure which persisted to 96 GPa. During unloading, peaks of zincblende phase began to reappear at 43 GPa. The transition pressure is taken to be the average of 59 GPa and 43 GPa, i.e., 51 ± 8 GPa. The volume change at the 51 GPa transition is 11%. The c/a ratio of the NiAs phase varied as c/a = 1.61 - 0.0002P (GPa).

Table 2. List of the observed interplanar spacing and relative intensities I of the NiAs structure of BeS at 66.0 GPa along with the theoretical corresponding values. The fitted lattice parameters are a = 2.971 Å and c = 4.711 Å. The CESR energy was 5.28 GeV and the energy-interplanar spacing product was Ed = 46.685 kev-Å. The reduced volume is $V/V_0 = 0.624$.

hkl	d _{obs} (Å)	d _{calc} (Å)	I _{obs} (%)	I _{calc}
100	2.576	2.573	18.4	9.52
002	2.353	2.354	48.8	16.1
101	2.256	2.256	100	100
102	1.740	1.736	45.4	22.7
110	1.486	1.484	29.6	15.2
103	1.338	1.339	18.4	8.94
200		1.287		0.43
112	1.257	1.255	15.6	5.34
201		1.241		5.76
004		1.177	^a	1.30
202		1.128		1.90
104		1.071		0.25
203	0.995	0.994	3.1	2.05
210	0.972	0.972	0.31	0.12
211	0.940	0.952	1.1	1.43

^aThere is a diamond dip very near to this peak which precludes measuring this. The dip is caused by the fact that this energy generates a Laue spot of diamond and the absorption which causes this peak decreases the intensity.



Fig. 1. Fractional volume vs pressure for BeS.

Figure 1 shows the P-V behavior. The data for the zincblende phase was fitted to a Birch equation [2]

$$P = \frac{3}{2} B_{0} \left\{ \left(\frac{V_{0}}{V} \right)^{\frac{7}{3}} - \left(\frac{V_{0}}{V} \right)^{\frac{5}{3}} \right\} \left\{ 1 + \frac{3}{4} \left(B_{0}' - 4 \right) \left[\left(\frac{V_{0}}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}$$

with $B_0 = 105$ GPa and $B_0 / = 3.5$.

Table 3 shows for the BeX compounds the measured and calculated values of V_0 , B_0 , B_0 , P_1 , V/V_{01} [3-8]. It is found that B_0 is related to the molecular volume, V_0 , at one atmosphere by

 $B_0(GPa = 3231/[\Omega]^{1.018})$

where Ω is atomic volume (Å³). For BeO the average available B₀ = 227.6 GPa was used. For the III-V compounds Zhang and Chen [9] gave a similar relationship with an exponent of 1.16. An ionic solid with a $1/r^n$ repulsive potential would have an exponent of 4/3. The BeX compounds which transform at high pressure to the NiAs structure have low Phillips ionicities [10]: BeS (0.286), BeSe (0.261) and BeTe (0.169). The same is true



Fig. 2. Dependence of the transition pressure versus the ratio of the cation radius to the anion radius for the beryllium chalcogenides. The experimental BeSe value is complicated by the fact that an amorphous phase found between crystalline states suggesting extreme sluggishness which could affect the experimental transition pressure.

of AlAs (0.274) and AlP (0.307) which also transform to the NiAs structure at high pressure [11, 12]. Thus all of these compounds have ionicities less than 0.31. However, BeO, which has not been taken to a pressure sufficient, 55 GPa [13] and 66 GPa [14], to cause a phase transition has an ionicity of 0.602; it is expected based on this ionicity that it might transform from the wurzite structure to a NaCl-structure such as did GaN (0.500) [15]. Figure 2 shows the pressure dependence of the transition as a function of the ionic radius ratio r_c/r_a . We do not include earlier calculations for BeO as we consider the calculation of Ref. 4 to be much more reliable.

Table 3. Experimental and Computed Properties for BeS, BeSe, BeTe

	V _o (Å ³)		B _o (GPa) B _o /			P _t (GPa)		V/V _{ot}		ΔV/V x 100%		
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
BeO	13.49 ^a	12.97 ^c	227.7 ^f	227.b ^c		3.96 ^c		137 ^c		0.73 ^c		11.2 ^c
BeS	28.72	27.19 ^d 26.71 ^e	105	101.9 ^d 113.4 ^e	3.5	3.7 ^d 3.5 ^e	51	58 ^d 52.4 ^e	0.724	0.727 ^d 0.757 ^e	11	10.9 ^d 14 ^e
BeSe	33.89 ^b	31.95 ^e	92.2 ^b	92.2 ^e		3.7 ^e	56 ^b	42.8 ^e	0.715 ^b	0.759 ^e	11.5 ^b	13.3 ^e
BeTe	44.31 ^b	42.30 ^e	67 ^b	68.2 ^e		3.4 ^e	35 ^b	32.2 ^e	0.715 ^b	0.758 ^e	11.5 ^b	14.0 ^e

^aRef. 3; ^bRef. 1; ^cRef. 4; ^dRef. 5; ^eSee Ref. 6; ^fThis is the average of the three values 210 (Ref. 3), 224 (Ref. 7) and 249 (Ref. 8).

Calculations clearly indicate a zincblende to NiAs transitions in BeTe, BeSe, BeS [6] and a wurzite to NaCl transition in BeO [4]. From Fig. 1 of Ref. 16, the subsequent transition from the B1 structure to the B2 structure of BeO (assuming it is this transition which occurs) would be in the neighborhood of 1 TPa.

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