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Microhardness of Single Crystals of BeO and Other Wurtzite Compounds

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ABSTRACT

The microhardness of single crystals of BeO, ZnS, AlN, CdS, ZnO, and CdSe has been measured as a function of crystallographic orientation and the results correlated with bond distance, melting point, and band gap.

Thirty-six binary compounds of the elements in Group IV, Groups III/V, Groups II/VI, and Groups I/VII in the periodic table are reported to have structures of the wurtzite type or zincblende type. Of these compounds six show only the wurtzite structure and five are dimorphous with respect to the zincblende form. The 11 compounds are listed in Table I along with some physical properties of interest in this study; included also are two compounds, MnS and MnSe, which have a close relationship to the II/VI compounds.

The wurtzite structure is hexagonal with the space group $P6_3mc$. It is illustrated in Fig. 1 and can be described in several ways. For the purposes of this discussion it is probably clearest to describe the structure as two identical and interpenetrating hexagonal close-packed lattices. The two arrays are shifted with respect to each other so that points of each lattice lie in the center of the tetrahedral interstices of the other lattice. This shift (z parameter) is equal to 0.375 times the c-axis. The cations occupy the points of one lattice and the anions the other lattice. All the atoms then have tetrahedral coordination, with the tetrahedra of one type all pointing in the same direction along the c-axis. The sphalerite structure can be described in a related manner, except that the lattices are cubic close-packed.

The ideal c_0/a_0 ratio (1, 2, 3) for a hexagonal close-packed lattice is 1.633 (*i.e.*, $2\sqrt{2}/\sqrt{3}$). Most of the wurtzite type compounds show some deviation from this ideal value. This deviation requires a distortion of the "ideal" regular coordination tetrahedra. However, this ratio does not give any indication of the magnitude of the shift of the two close-packed lattices. The bond distances listed in Table I have been calculated assuming the shift to be 0.375 for all compounds. It has been shown (3, 4) that for BeO, with $c_0/a_0 = 1.622$, and AlN, with $c_0/a_0 = 1.600$, the shifts are 0.379 and 0.385, respectively. Whether this pattern is the same in other wurtzite compounds remains to be proved. For the purposes of this paper the bond distances in Table I will be adequate.

To understand the processes taking place in crystalline compounds it is necessary to consider various properties of these materials (electrical, physicochemical, mechanical, etc.). Knowledge of such properties should give the distribution of particles in a substance, the nature of these particles, and the way they are bound together, *i.e.*, the electron density distribution or the type of chemical bond.

The hardness of covalent and ionic crystals is one of the properties related in a general way to the type of chemical bond (5, 6). Goldschmidt (7) suggested that the hardness H of a given structure follows the equation $H = \text{constant} \times r^{-m}$, where r is the bond distance and m is an empirical constant related to the type of bonding. Wolff *et al.* (8) have related the hardness of the elements and zincblende III/V compounds to the bond distance using the Goldschmidt formula. They found that the constant

Table I. Properties of wurtzite structures

Compound	c/a	Observed bond distance, A[a]	Optical band gap, ev	Melting point, °C
AlN	1.600	1.86, 1.90	~5.6	2200 (2 atm)
GaN	1.625	1.94, 1.94	3.3	800
InN	1.611	2.13, 2.16	2.4	
BeO	1.623	1.64, 1.65	~15.0	2570
ZnO	1.602	1.95, 1.98	3.14	1970
MgTe	1.622	2.75, 2.76		
CdS[b]	1.622	2.51, 2.53	2.50	1750 (100 atm)
ZnS[b]	1.635	2.33, 2.33	3.5	1850
CdSe[b]	1.630	2.63, 2.64	1.74	—
AgI[b]	1.635	2.81, 2.80		
SiC	1.641	1.89, 1.88	~2.85	
MnS[c]	1.62	2.41, 2.44		
MnSe[c]	1.63	2.52, 2.52		

[a] Calculated from the unit cell dimensions assuming the difference in the z-parameter for the cation and anion is 0.375.
[b] Dimorphous with zincblende structure.
[c] Trimorphous with metastable NaCl structure.

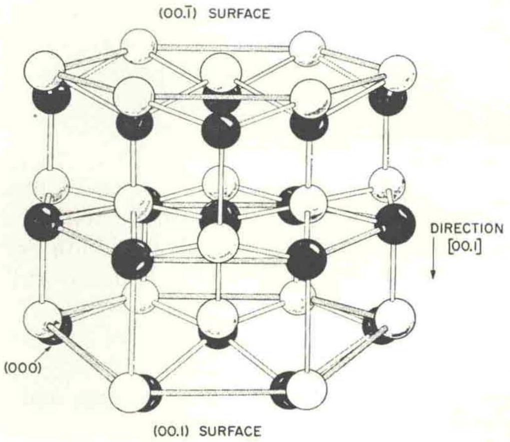

Fig. 1. Wurtzite structure

Table II. Knoop hardness[a] of wurtzite compounds

Compound	Plane indented	Indentation direction	Hardness, kg/mm^2	Remarks
BeO	(00.1)	[10.0], [11.0]	1300	No orientation dependence
	(00.$\bar{1}$)	[10.0], [11.0]	1100	No orientation dependence
	(10.0)	[00.1]	1175	
	(10.0)	[10.0]	917	
ZnO	(00.1)	[10.0], [11.0]	274	No orientation dependence
	(00.$\bar{1}$)	[10.0], [11.0]	238	No orientation dependence
	(10.0)	[00.1]	241	
	(10.0)	[10.0]	170	
CdS	(00.1)	[10.0], [11.0]	118	No orientation dependence
	(10.0)	[00.1]	91	No orientation dependence
	(10.0)	[10.0]	53	
CdSe	(00.1)	[10.0], [11.0]	83	
	(11.0)	[11.0]	63	
	(11.0)	[00.1]	49	
ZnS	(00.1)	[10.0], [11.0]	246	No orientation dependence
	(11.0)	[11.0]	158	
	(11.0)	[00.1]	—	
AlN	(00.1)	[10.0], [11.0]	1187	No orientation dependence

[a] 100g load.

m assumes the approximate value 5 and 9 for the elements and III/V compounds, respectively.

Wolff has recently found the same relationship to hold for II/VI compounds as well (9).

Experimental Results

The microhardness of the single crystals of BeO, AlN, ZnO, CdS, and CdSe was determined as a function of orientation using a Leitz Durimet hardness tester with a Knoop diamond. The crystals were either mounted in Bakelite mounds and polished before testing, or tested in the as-grown state. Indentations on each specimen were made independently by the authors and the results compared and averaged. The latter represent at least 25 measurements. All indentations were examined at 1600X magnification. Those associated with cracks of any sort were not included in the study. No evidence of twinning was observed. The indentation load was varied between 15 and 200g; no load dependence was found. The rate of indentation was also varied between 1 sec and 10 min; no rate dependence was apparent. However, the incidence of cracking was related to the rate of loading. The faster the loading, the greater the incidence of cracking. With respect to BeO, the cracking incidence was also associated with the surface environment of the crystal. Cracking was essentially eliminated when an organic solvent such as kerosene was applied to the crystal prior to indenting it. The experimental data are tabulated in Table II. In Fig. 2, 3, and 4, the hardness is graphically related to bond distance, band gap, and melting point; it can be seen that a logarithmic relation exists.

The band gaps for most of the compounds were obtained from Bube and others (10-12). The gap for BeO was obtained in our laboratories using a vacuum ultraviolet spectrograph where the fundamental absorption occurred at approximately 800Å, indicating a very large band gap.

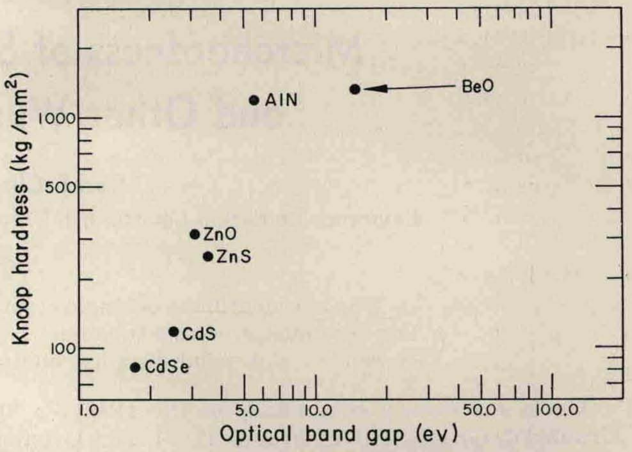

Fig. 2. Knoop hardness as a function of optical band gap. Basal plane (0001).

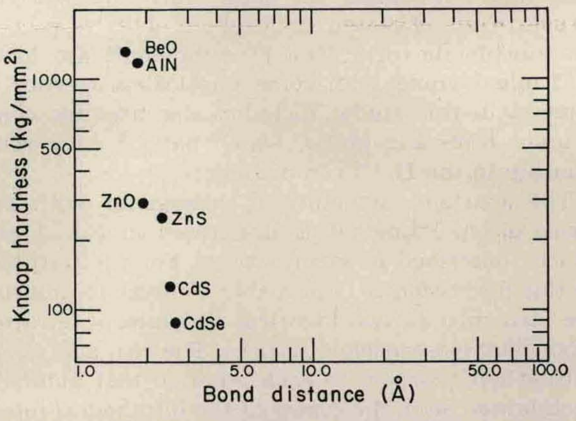

Fig. 3. Microhardness of wurtzite compounds on basal plane as a function of bond distance. (Knoop, 100g load).

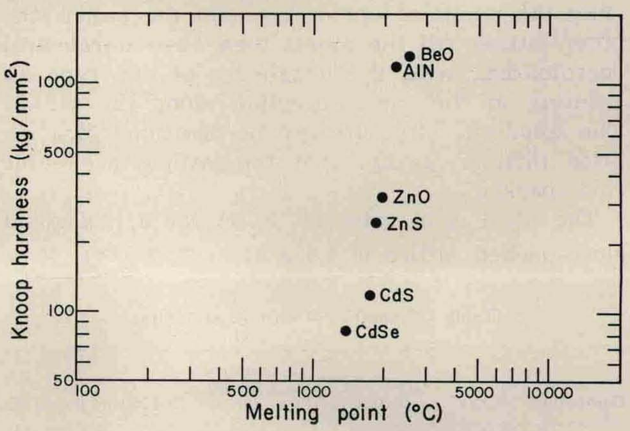

Fig. 4. Relation between Knoop hardness and melting point

Discussion of Results

The hardness measurements for CdS, CdSe, and ZnO agree with data by Wolff (9), while the hardness data for BeO and AlN disagree with reported data. The absence of any studies on the slip crystallography of the wurtzite compounds precludes any discussion of its relationship to hardness. However, current studies at this laboratory are aimed at elucidating this relationship.

BeO is reported (13, 14) to have a Mohs hardness of 9, which would correspond to a Knoop hardness of approximately 2000 kg/mm^2. It can be seen from our data that its true hardness is closer to 8 than 9. In view of the correlations obtained with bond distance, band gap, etc., it is felt that hardness reflects a measure of the bonding energy of the compounds.

The anisotropy of the hardness measurements for the wurtzite compounds is felt to be a true reflection of the differential bonding. Hardness values are lower on the $(10\bar{1}0)$ than on the basal plane where the hardness is isotropic. On the $(10\bar{1}0)$ surface the highest hardness parallels the (0001) face. The lower hardness parallels the prismatic cleavages (15-18).

The explanation presumably lies in the fact that basal cleavage, with the breaking of one bond per unit cell area, leaves the two halves oppositely charged, while breaking the same number of bonds along $(10\bar{1}0)$ and $(11\bar{2}0)$ leaves both halves neutral. In order to leave both cleaved basal planes neutral it would be necessary to break two bonds per unit cell.

The differential hardness on the (0001) and $(000\bar{1})$ as found on BeO and ZnO is at this time difficult to explain, but it is felt that either dislocation density or strain is responsible for the difference.

Summary

The microhardness of BeO, ZnO, AlN, CdS, ZnS, and CdSe have been measured as a function of orientation and compared with the literature. Their hardness can be correlated with band gaps, bond distance, and melting point.

It is felt that the orientation dependence of the hardness can be explained by the crystal structure.

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