Microhardness and interatomic binding in some cubic crystals

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Abstract. Vicker's microhardness measurements have been carried out on single crystals of CaF_2 , SrF_2 , BaF_2 , CdF_2 , PbF_2 , EuF_2 , ThO_2 , NaClO_3 , NaBrO_3 , $\text{Bi}_4(\text{GeO}_4)_3$, $\text{Bi}_4(\text{SiO}_4)_3$, $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$. The hardness values are discussed *vis-a-vis* the interatomic binding in these crystals. While most of the fluorite-type crystals are highly ionic, covalency is indicated in the bismuth compounds studied.

Keywords. Cubic crystals; microhardness; fluorite-type crystals; interatomic binding.

1. Introduction

Hardness is an important solid state property. Hardness tests are commonly carried out to determine the mechanical strength of materials and it correlates with other mechanical properties like elastic constants (Wooster 1953) and yield stress (Westbrook 1958).

Stillwel (1938) defined hardness as resistance against lattice destruction whereas Ashby (1951) defined it as the resistance offered by a solid to permanent deformation. It is now accepted that hardness is a measure of the resistance that a lattice offers to the motion of dislocations.

The chemical forces in a crystal resist the motion of dislocations as it involves the displacement of atoms. This resistance is the intrinsic hardness of a crystal. Gerk (1977) calls the hardness of a high purity, good quality, well-annealed crystal 'the minimum hardness'. Hardness values obtained from such crystals can thus be correlated with the strength of interatomic binding in these crystals. Plendl and Gielisse (1962) have correlated the hardness of several crystals with their lattice energy. Berzina *et al* (1965) found that the hardness values correlate with surface energy values. Powarjonnynch (1963) and Julg (1978) attempted to draw quantitative information about the bond strength from hardness values. Recently, Chin (1975) suggested that the ratio of microhardness to the shear elastic constant has typical values for different bonding types. Thus, this ratio (hereafter referred to as the Chin parameter) is about 0.1 for covalent solids and 0.05 for ionic solids (Chin *et al* 1978).

In this paper, the results of measurement of microhardness of thirteen cubic crystals are reported; in several cases, this is the first measurement. The results are discussed *vis-a-vis* the interatomic binding.

2. Experimental

Microhardness was measured at room temperature using a Leitz Weitzlar hardness tester fitted with a Vicker's diamond pyramidal indenter, and was calculated using the equation

$$H = 1.854 P/d^2$$

where H is the microhardness (kg/mm^2), P is the load (grams) and d is the length (in microns) of the diagonal of the indentation mark.

Microhardness values show a load dependence at low loads up to 25 g above which they become load-independent (Mott 1956; Sirdeshmukh and Shah 1965). Keeping this in view, the measurements were carried out at loads of 50 g or more. Depending upon the nature of the sample, different loads were chosen for different samples so that the indentation marks were of measurable dimensions. In every case, at least five measurements were made. The final value is the average of these and is accurate to $\pm 2 \text{ kg/mm}^2$.

The crystals of CaF_2 , BaF_2 , SrF_2 , CdF_2 and PbF_2 were from M/s Optovac, the EuF_2 crystal was obtained from Dr H V Lauer of Purdue University and the ThO_2 crystal was a gift from Prof. K Vedam of the Pennsylvania State University. The $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ crystals were grown and cut by Dr W Rehwald of RCA Laboratories. The $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$ crystals were presented by Dr T M Bruton of Mullard Laboratories. The NaClO_3 and NaBrO_3 crystals were grown from aqueous solutions employing standard procedures. All the crystals were annealed at appropriate temperatures before the measurements.

Table 1. Values of microhardness (H), shear constant (C_{44}) and Chin parameter (H/C_{44}) for some cubic crystals.

Crystal	Face on which hardness was measured	H (kg/mm^2)	C_{44} (kg/mm^2)	H/C_{44}
CaF_2	(111)	185	3450 ^a	0.05
SrF_2	(111)	163	3100 ^a	0.05
BaF_2	(111)	149	2400 ^a	0.06
PbF_2	(111)	133	2500 ^a	0.05
CdF_2	(111)	153	2100 ^b	0.07
EuF_2	(111)	264	3050 ^c	0.09
ThO_2	(111)	750	8100 ^a	0.09
NaClO_3	(100)	107	1179 ^d	0.09
NaBrO_3	(100)	136	1536 ^d	0.09
$\text{Bi}_4(\text{GeO}_4)_3$	(100)	561	5280 ^e	0.11
$\text{Bi}_4(\text{SiO}_4)_3$	(100)	593	4440 ^e	0.12
$\text{Bi}_{12}\text{GeO}_{20}(\text{BGO})$	(100)	372	2600 ^f	0.14
$\text{Bi}_{12}\text{SiO}_{20}(\text{BSO})$	(100)	473		

^a Chung and Buessem (1968); ^b Alterovitz and Gerlich (1970); ^c Lauer *et al* (1971);

^d Haussuhl (1964); ^e Rehwald and Widmer (1973); ^f Slobodnik and Sethares (1972).

3. Results and discussion

The microhardness values for thirteen cubic crystals are given in table 1. The value of 185 kg/mm^2 obtained for CaF_2 agrees well with the value 175 kg/mm^2 quoted by Mott (1956). For NaClO_3 and NaBrO_3 , Haussuhl (1964) reported values 123 kg/mm^2 and 195 kg/mm^2 respectively. The present values are also of the same order but smaller in both cases. In the case of the remaining crystals, this appears to be the first measurement of Vicker's hardness.

It is now established that the hardness of sodium bromate is more than that of sodium chlorate. In this respect these two crystals differ from the corresponding halides where the hardness of sodium bromide is less than that of a sodium chloride (Berzina *et al* 1965). Radha and Gopal (1968) pointed out that the difference in the behaviour of sodium chlorate and sodium bromate on the one hand and sodium chloride and sodium bromide on the other, is manifested in several other physical properties like elastic constants, thermal expansion etc. They have suggested that this difference arises out of the fact that the NaCl distance in sodium chlorate is larger than the NaBr distance in sodium bromate whereas in the sodium halides the NaCl distance is shorter than the NaBr distance. This may explain the difference between the relative values of the hardness of the sodium halates and the sodium halides.

In $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$, the hardness of the orthosilicate is more than that of orthogermanate. This is consistent with the conclusions drawn by Rao *et al* (1981) from the values of the elastic constants and Debye temperatures. Again, in the case of $\text{Bi}_{12}\text{GeO}_{20}$ (BGO) and $\text{Bi}_{12}\text{SiO}_{20}$ (BSO), the hardness of BSO is much greater than that of BGO indicating the stronger binding in the former. Structural data (Abrahams *et al* 1979) on these crystals show that most of the interatomic distances in BSO are shorter than the corresponding distances in BGO. Thus, it appears reasonable that the hardness of BSO should be more than that of BGO.

The hardness values are now examined in terms of the Chin parameter. As mentioned in § 1, Chin (1975) has pointed out that the ratio H/C_{44} (where C_{44} is the shear elastic constant) is characteristic of the bonding in cubic solids. This parameter has a value of about 0.1 for covalent solids and a value of 0.04–0.06 for ionic solids (Chin *et al* 1978). The C_{44} values and those of the Chin parameter (H/C_{44}) are given in table 1. Some interesting features are observed. The Chin parameter value for CaF_2 , SrF_2 , BaF_2 , CdF_2 and PbF_2 is about 0.06 showing that these are essentially ionic like the alkali halides. This conclusion is consistent with that drawn from other properties like lattice energies (Ladd and Lee 1964), and thermal expansion (Sirdeshmukh and Rao 1972). On the other hand, the Chin parameter value is about 0.1 for BGO, $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ indicating the existence of a covalent component in the binding in these crystals. In EuF_2 , ThO_2 , NaClO_3 and NaBrO_3 , the Chin parameter has a value 0.09 which suggests a partial ionic character.

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