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A Correlation between Hardness and Bond Ionicity in Crystals

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Abstract: Hardness is a degree of measurement of resistance in materials against permanent deformation. Materials of high hardness are made in use of designing and preparing tools, engine components and dyes. Bond ionicity and hardness are also related to ceramics and glasses. The prominent scale of Mohs is used to design scratch less glass and glasses which are resistant to heat, temperature are designed to shield the modern photo voltaic modules. Not much work is done in determining hardness of a material in terms of chemical properties like bond ionicity. The author attempted successfully in evaluating an empirical formula which relates bond ionicity to the hardness of a material.

Keywords: Bond ionicity, hardness, compressibility, lattice energy, indentation, hardness scale

I. INTRODUCTION

The hardness of a material has been defined as “its resistance scratching” or “to plastic deformation”. The hardness is a measure of resistance to surface penetration by indenter with a force applied to it. The indentation process takes place by plastic deformation in metals and alloys. The hardness is inherently related to plastic flow resistance in these materials. However, brittle solids, such as glass and polycrystalline ceramics at room temperature are subjected to indentation, their hardness tested. The indentation is accomplished by applying a load to a suitable indenter positioned on the surface of the material. To test of the hardness, the indenter material must be harder than the material to be indented. Typical indenters are hardened steel and diamond. The hardness is tested by various methods of combinations of load and indenter on the material to be indented.

The hardness studies on some semiconducting compounds have been attempted by many authors^{[1]-[4]}. Correlation lattice between the micro hardness and other characteristic material parameters like the coordination of atoms in the crystal lattice, the melting or Debye temperature, the interatomic distance, the average atomic mass of the constituent atoms of compounds, the bond ionicity and the elastic properties have been identified and discussed in the literature^{[5]-[7]}. Several attempts have been made in the literature to correlate the bulk modulus and the microhardness. Plendl et al^{[8],[9]} assumed that with in a given class of non-metallic compounds the bulk modulus B directly proportional to the microhardness H . In the case of the tetrahedrally coordinated elemental and binary semiconductors the most successful attempt to quantify the relation between micro hardness and a few well known material parameters have been reported by Garbo et al. and Rucci^[10]. In the case of the diamond and zinc blende semiconductors, it has been shown by various authors that the elastic properties depend only on a few, usually well known material parameters, namely the bond volume and the spectroscopically defined bond ionicity. Micro mechanical hardness testing provides useful information concerning the mechanical behaviour of metals and minerals. Buckle has pointed out the possibility of investigating various material properties by means of microhardness measurements. Plendl and Gieline^{[8],[9]} have given a correlation between hardness, the lattice energy per unit volume and compressibility. Goble and Scott^[11] have established a relation between second derivative of lattice energy and interatomic distance.

There are many scales for the measurement of hardness of materials^[12]. Scales like Moh's hardness, Brinell hardness and Rockwell hardness are used to measure hardness. Other hardness tests are also common. The Vicker's hardness test, Microhardness and the knoop test are other types of tests available in the literature. Many attempts^[13] have been made to relate the hardness of a crystal with many physical properties such as vibrational frequencies, atomic concentrations and surface energy. Oxides, sulphides and silicate compounds are hard materials and have high hardness. Sulphates, carbonates and phosphates are relatively soft. these common features of crystals suggest that stable chemical compositions consisting of different types of bond nature have strong correlation with the degrees of hardness. The bond ionicity is an important physical property which distinguishes a covalent crystal from an ionic crystal Yang et al^[14] have established a relation between compressibility and hardness of the crystal. The present work is an attempt to find a definite correlation between hardness and ionicity of the crystals with different bonding.

II. METHODOLOGY

For calculations of hardness the following different methods are available here with.

- 1) *Experimental details of hardness:* One of the most common hardness tests is in Brinell test¹². In it, the indenter is a 10 mm diameter hardened steel ball, the applied mass is usually 300 kg, the test procedure is shown in fig.1. since a hard material will resist indentation more than a 'soft' material. The average indentation depth, surface area, and projected area are small if the material is hard and relatively large. The Brinell hardness number (BHN) is defined "As the load, 'F' divided by the surface area of indentation". BHN can be evaluated as follows:

$$BHN = \frac{2F}{\pi D \left[D - \sqrt{D^2 - d^2} \right]} = \frac{F}{\pi D t} \text{ ----- (1)}$$

Where 'D' is the ball diameter, 't' is the indentation depth and 'd' is the indentation diameter. In performing the test, 'F' and 'D' are known as priori. So measurements of 'd' allows calculation of the BHN. The BHN has dimensions of stress (N/m²), but hardness numbers are often quoted in terms of mass, rather than force, per unit area eg. (Kg/m²).

Vickers¹⁵ micro hardness measures have been performed by Vickers indenter attached to the Universal Research Microscope. All the indentations were done at room temperature on freshly cleaned samples. The indentations were performed on a load of 100 P and the time of indentation being 10 seconds. The microhardness value is calculated using the expression.

$$BHN = \frac{1.8544 P}{d^2} \text{ ----- (2)}$$

where 'P' is the load applied in grams and 'd' is the length of the diagonal of the indenter impression in mm. the length of the diagonal was measured using a micrometer. At least ten indentations were performed on each sample and a number of specimens were taken from each crystal. Microhardness value is an average of all such measurements.

- 2) *Julg Method:* Julg¹⁶ proposed an empirical relation between the ionicity (I) and the Moh's hardness (H) of a crystal. The relation is as follows.

$$H = k - \frac{2}{3} K I^4 \text{ ----- (3)}$$

Here the value of 'K' is purely determined by the rows to which atoms in the chemical bond belongs in the periodic table. This means 'K' must be either related to atomic number, atomic weight or atomic radius. From the above equation it is inconceivable that which of these atomic properties come with the ionicity term to give the hardness value. Although the validity of the above equation has been claimed and verified by Julg. But it is admitted that a great uncertainty arises due to the presence of the fourth power of the ionicity term and therefore for weak bond ionicity values of electron charges and hardness estimated may not be accurate.

The procedure has been followed by Sreedharan Pillai¹³ suggested a straightforward relationship between hardness (H) and ionicity (I) without incorporating additional parameters. The proposed empirical relation is in the form of second degree polynomial of the type:-

$$H = aI^2 + bI + C \text{ ----- (4) where a, b and c are the constants.}$$

Yang et al¹⁴, have been correlated the hardness of a solid and compressibility and proposed a relation as

$$H = \frac{1}{n\beta} \text{ ----- (5) of the solid this formula becomes}$$

Where 'n' is the number of densities. In terms of weight density ρ (gram/cc)

$$H = \frac{M}{q\rho\beta} = \frac{M_a}{\rho\beta} \text{ ----- (6)}$$

Where 'M' is the molecular weight, 'q' is the number of atoms in the molecule and $M_a = \frac{M}{q}$ is the average atomic weight.

- 3) *Present method:* Sreedharan Pillai has applied a second degree polynomial relation for some crystals only. In view of Moh's hardness data for different crystals listed by Yang et al., the quadratic relation of the following type is proposed.

$$H = 14.455 - 27.511 I + 16.002 I^2 \text{ ----- (7)}$$

Where 'H' and 'I' are Moh's hardness and ionicity of the compounds respectively.

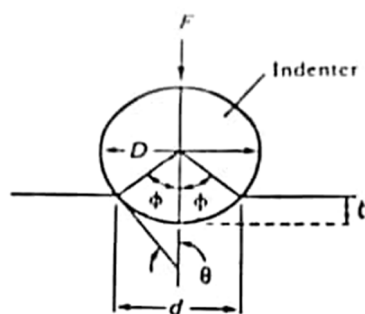


Figure 1

Table 1. Bond energy, D_{AB} of semiconductors

| S.No | Compound | Ionicity(I) | Hardness, H (Mohs) | | |
|------|----------|-------------|---------------------|---------------------|------------------------|
| | | | Experimental Equ. | Yang et al Equ. (6) | Present study Equ.(21) |
| 1 | AgBr | 0.850 | 2.50 | 5.90 | 2.63 |
| 2 | CuBr | 0.785 | 2.40 | 4.96 | 2.72 |
| 3 | CuCl | 0.746 | 2.25 | 4.76 | 2.24 |
| 4 | CuI | 0.692 | 2.50 | 5.64 | 3.08 |
| 5 | CaO | 0.913 | 4.50 | 9.59 | 2.68 |
| 6 | PbS | 0.633 | 2.65 | 9.71 | 3.45 |
| 7 | HgS | 0.640 | 2.50 | 3.46 | 3.40 |
| 8 | PbTe | 0.551 | 3.00 | 8.36 | 4.16 |
| 9 | SrO | 0.926 | 3.50 | 9.08 | 2.70 |
| 10 | SrS | 0.914 | 2.61 | --- | 2.68 |
| 11 | CdTe | 0.675 | 2.80 | 8.69 | 3.18 |
| 12 | ZnTe | 0.546 | 2.80 | 7.76 | 4.20 |
| 13 | ZnS | 0.623 | 3.75 | 9.06 | 3.53 |
| 14 | SiC | 0.177 | 9.50 | 15.35 | 10.09 |
| 15 | ZnSe | 0.676 | 3.75 | 7.92 | 3.17 |
| 16 | CdS | 0.685 | 3.20 | 9.18 | 3.12 |
| 17 | CdSe | 0.699 | 3.00 | 8.84 | 3.04 |
| 18 | KBr | 0.952 | 2.00 | 3.26 | 2.77 |
| 19 | KCl | 0.953 | 2.00 | 3.38 | 2.77 |
| 20 | KF | 0.955 | 2.80 | 3.78 | 2.78 |
| 21 | KI | 0.950 | 2.20 | 2.22 | 2.70 |
| 22 | LiBr | 0.899 | 2.50 | 3.22 | 2.66 |
| 23 | LiCl | 0.935 | 3.00 | 3.22 | 2.72 |
| 24 | LiF | 0.915 | 3.75 | 3.26 | 2.68 |
| 25 | LiI | 0.890 | 2.80 | 3.08 | 2.65 |
| 26 | NaBr | 0.934 | 2.45 | 3.02 | 2.72 |
| 27 | NaCl | 0.935 | 2.00 | 3.29 | 2.72 |
| 28 | NaF | 0.946 | 2.25 | 4.02 | 2.75 |
| 29 | NaI | 0.92 | 2.30 | 3.29 | 84.86 |

| | | | | | |
|----|--------------------------------|-------|------|-------|------|
| 30 | RbBr | 0.957 | 2.70 | 3.40 | 2.78 |
| 31 | RbCl | 0.955 | 2.60 | 3.45 | 2.78 |
| 32 | RbF | 0.960 | 2.30 | 4.01 | 2.79 |
| 33 | RbI | 0.951 | 2.68 | 3.32 | 2.76 |
| 34 | BaS | 0.935 | 3.00 | 6.87 | 2.72 |
| 35 | BaF ₂ | 0.890 | 3.00 | 6.77 | 2.65 |
| 36 | CaF ₂ | 0.980 | 4.00 | 7.04 | 2.86 |
| 37 | CdF ₂ | 0.790 | 4.00 | 6.74 | 2.71 |
| 38 | SrF ₂ | 0.900 | 3.50 | 6.90 | 2.66 |
| 39 | CaCl ₂ | 0.890 | 3.00 | 3.94 | 2.65 |
| 40 | Al ₂ O ₃ | 0.450 | 9.00 | 12.45 | 5.32 |

III. CONCLUSIONS

The bond ionicity data are available for many crystals and minerals^{[13],[18]}. Recently Yang et al^[14], have given an extensive hardness data for different crystals. This prompted the author to correlate the hardness and the ionicity of the crystal. The quadratic form of the relation yielded two values of I , of which one was always very small or negative. Higher values were considered for covalent nature of chemical bond eq.(7), is found suitable in estimating the hardness of the crystal, the evaluated values are in good agreement with the hardness values quoted by Yang et al^[14].

The bond between the positive and negative ions in an ionic compound results exclusively due to electrostatic attraction. The electron cloud repels the positive, negative ions to come too close to each other. As the two ions approach each other, the spherical electron cloud of the negative ion become much distorted by the influence of the electron cloud of positive ion which results in gradual change of ionic picture to covalent nature of crystal. There are the two extreme types of bond character. In mixed bond nature, as the anions are larger than cations, a portion of electron cloud of the anions becomes pulled over towards the region of the cation. As the distortion is increased, the bond between anion and cation takes more and more covalent character^[13]. The bond energies of different semiconductors, were given by Sanderson^[17].

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