Mechanical properties of halide and oxide cubic perovskites

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Abstract: *In this paper, semi empirical formula for the mechanical properties of perovskite solids is elaborated in terms of lattice constant (a in Å) and product of ionic charges of the bonding. Values of bulk modulus(GPa), of the cubic perovskites (halides and oxides) exhibit a linear relationship when plotted against the lattice constant (a°) normalization, but fall on different straight lines according to the product of ionic charges of the compounds and their modulus predictions are in good agreement with the experimental data and those from ab initio calculations.*
Keywords*: Bulk modulus,Perovskites.*

I. Introduction

During last few years, the elastic moduli, which is of great of importance in assessing the competition between the ductile and brittle failures, have been extensively investigated in relation to various microscopic characteristics of different sorts of materials, such as metals and covalently bonded crystals. Due to difficulties associated with experimental processes and their cost, as well as difficulties in obtaining accurate values of physical properties, researchers moved to calculate the physical properties of solids through computational methods[1-10]. Recent developments in modeling, through the use of density functional theory (DFT) and the increased availability of computational power, have made predictions of solid-state properties ab initio from theoretical principles relatively straightforward. Hence it is now common to see calculations for the solid-state properties of binary and ternary compounds. Experimental data to verify these predictions are sparse, especially for non-equilibrium systems, and it can be difficult to interpret the accuracy of published data [11, 12].

Currently, most elastic modulus evaluations are carried out using ab initio techniques; however, one has to keep in mind that the rationalization of these first-principles calculations often requires profound understanding of the nature of the chemical bonding and its attributes in various solid-state systems. But due to the long process, methods involving a as well as complicated computational series of approximations, such a method has always been complicated. These concepts are directly associated with the character of the chemical bond and thus provide means for explaining and classifying many basic properties of molecules and solids.In the past few years [13-14], a number of theoretical calculations based on empirical relations have become an essential part of material research. In many cases empirical relations do not give highly accurate results for each specific material, but they still can be very useful. In particular, the simplicity of empirical relations allows a broader class of researchers to calculate useful properties, and often trends become more evident.[15-17].

II. Mechanical properties of perovskite compounds

The bulk modulus is an important mechanical property of a material and defines its resistance to volume change when compressed. Therefore, we have presented and studied the various models and theories describing the bulk modulus (B) of these materials. Cohen[17] predicted that bulk modulus *B* (GPa) by the semi empirical expression for the covalent materials by the relation,

$$B = \frac{N_C}{4} \frac{(1972 - 220\lambda)}{d^{3.5}}$$

(1)

Where N_C is the bulk coordination number, d is the bond length, and λ is an empirical ionicity parameter that takes the values of 0, 1, and 2 for IV, III-V and II-VI group semiconductors, respectively. Recently, Verma and co-authors [18-21] has been evaluated the structural, electronic, mechanical and ground state properties of binary and ternary crystals with the help of ionic charge theory. This is due to the fact that the ionic charge depends on the number of valence electrons, which changes when a metal forms a compound. In this paper, we improved this formula by replacing the adhoc empirical ionicity parameter with more suitable product of ionic charge of the compounds. Both experimental data and theoretical calculations based on density functional theory follow the correlation.

There have been a number of reports in the past of empirical relations describing the mechanical properties of solids. Anderson and Nafe [22] first proposed an empirical relationship between bulk modulus B at atmospheric pressure and specific volume V_0 of the form B~ V_0^{-x}. They find it to hold for a particular class of compounds.

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Where, the value of x depends on the class of the compounds. For alkali halide, fluorides, sulfides and telluride they find x to be 1 and oxide compounds x is close to 4. One of the earliest attempts at describing bulk modulus B in terms of electronic parameters [23] yielded a simple proportionality relation between B and the product of the electron concentration with Fermi energy. However, the resulting formula is of limited utility, since it usually gives values within a factor of 2 of the experimental values. Recently, Gilman [24] derived expressions for both bulk B and shear G moduli of metals based on simplified quantum-mechanical considerations. The derived expressions also suffer from notable deficiencies, as they ignore the effects induced by ionicity of the bonds and exchange-correlation interactions amongst others.

Both bulk B and shear G moduli can be derived from the second derivative of the total energy E with respect to the appropriate deformation parameter at the equilibrium state as follows [17, 25]:

$$B = \Omega \frac{\partial^2 E}{\partial \Omega^2}\bigg|_{\Omega=\Omega_0} \qquad (2)$$

$$G = \frac{1}{\Omega} \frac{\partial^2 E}{\partial \delta^2}\bigg|_{\gamma=\gamma_0} \qquad (3)$$

Where Ω and δ stand for volume and dimensionless deformation parameter, respectively. From Esq. (2) and (3), it is evident that the first step in establishing the formulae for bulk and shear moduli is to approximate the energy derivatives in terms of chemical bonding parameters. Due to their spherical symmetry and tight-binding character, the core electrons are nearly unresponsive to low-energy perturbations [26]like those occurring under elastic deformation; while the valence electrons are completely affected by such phenomena. Therefore, within the limits of the elastic regime, the second derivative of the total energy can be approximated by the variation of the valence electrons' force. In the case of covalently bonded materials, as discussed by Philips [16]the band gap energy $E_g$provides an estimation of the valence bond strength and it results from homopolar and heteropolar or ionic contributions of the atoms to the bonds as follows:

$$E_g^2 = E_h^2 + E_c^2 \quad (4)$$

Here E_h refers to the homopolar or covalent contribution to the bonding, while E_c corresponds to the ionic contribution or the charge transfer to the bonds. In the case of purely covalent group IV crystals, such as diamond, silicon, or germanium, E_g is equal to E_h. Consequently, E_h characterizes the strength of the covalent bond. Cohen was the first to maintain [17] that Philips' homopolar band gap energy is the dominant energy parameter in covalent solids. Recently, relationships connecting inherent traits such as thermal activation energies [27] and hardness [28] to the homopolar band gap energy were elaborated in the case of covalent crystals. These works further confirm that the intrinsic properties of covalent materials are predominantly dictated by E_h. Using a scaling argument, E_h can be expressed in terms of d as follows: [16]

$$E_h = \frac{39.74}{d^{2.5}} \qquad (5)$$

where the units of E_h are in eV and d (nearest neighbour distance) is in Å. Since for small amounts of deformation, the strain parameter is a linear function of the nearest neighbour distance, from Eq. (5.5), it follows that

$$\frac{\partial^2 E}{\partial \delta^2} \alpha \frac{1}{d^{4.5}} \qquad (6)$$

The cylindrical-shaped charge volume of covalent crystals is a linear function of the nearest neighbour distance, $\Omega \approx \pi (2a_B)^2 d$ ($a_B$is Bohr radius) and it can be used in Eqs. (2) and (3), since it enclose the largest electron concentration [17]. Thus Equations (2) – (6) yield

$$B \alpha \frac{1}{d^{3.5}} \qquad (7)$$

III. Bulk modulusandIonic charge theory

On the basis of concept of ionic charge theory, a chemical bond is formed when the atoms with incomplete valence shells combine. The valence electrons refer to the electrons that take part in chemical bonding. These electrons reside in the outer most electron shell of the atom. Ionic charge depends on the outermost-shell electrons of an atom.In previous research [13, 19], we found that substantially reduced ionic charges must be used to get better agreement with experimental values. Goldschmidt [29] has pointed out that a term $A = Z_a Z_c$, where Z_a and Z_c are the valence number of anion and cation, respectively, may be considered for a direct comparison of the hardness. Further it is well known that the hardness is closely related to the elastic properties of crystals [30] Ionic charge depends on the outermost-shell electrons of an atom. Thus, there must be a correlation between ionic charge and the properties of solids[40].It has been verified[17]that elastic moduli assume a decreasing linear trend with increasing lattice parameter. Therefore, based on Equation (7), the fact, that bulk modulus (B) is linear functions of lattice parameter. The bulk modulus is expected to exhibit the

explicit dependences on lattice parameter (a) and ionic charge (Z). As an example, for verification of ionic charge theory, we have plotted the curves between B Vs $a^{3.5}$ (B = bulk modulus in GPa, a = lattice parameter in Å) for group $A^{+1}B^{+2}X_3$, (X = F. Cl, Br), $A^{+2}B^{+4}O_3$ and $A^{+3}B^{+3}O_3$ cubic perovskites and plotted in the figure 1.
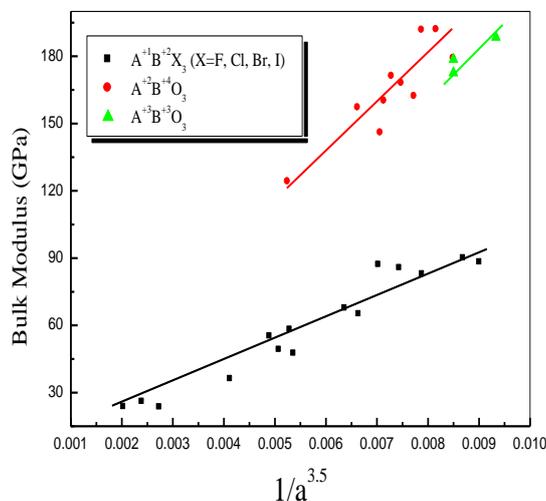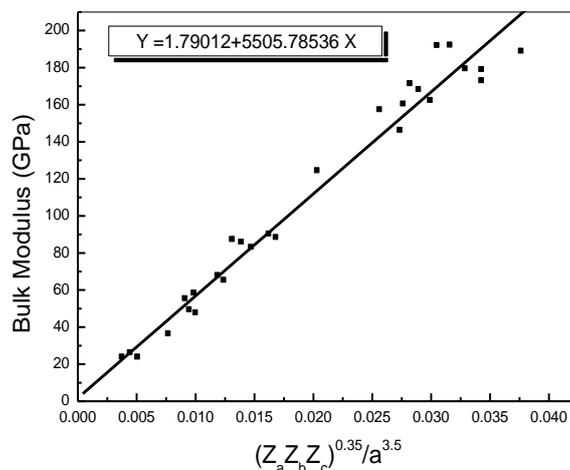

Figure 1. Plot of bulk modulus B (GPa) and lattice constant (a in Å) for the group $A^{+1}B^{+2}X_3$, (X = F. Cl, Br), $A^{+2}B^{+4}O_3$ and $A^{+3}B^{+3}O_3$ perovskites and found at three positions, which is depending upon the product of ionic charges. In this figure bulk modulus and lattice constant values are taken from Reference [1-10, 31-38].

We observe that in this plot of B Vs $a^{3.5}$normalization, the group $A^{+1}B^{+2}X_3$, (X = F. Cl, Br), $A^{+2}B^{+4}O_3$ and $A^{+3}B^{+3}O_3$ cubic perovskites exhibit three positions in this figure. These effects induced by the ionic charges of the compounds in the case of group $A^{+1}B^{+2}X_3$, (X = F. Cl, Br), $A^{+2}B^{+4}O_3$ and $A^{+3}B^{+3}O_3$ perovskites. If all data of bulk modulus (in GPa) plots with product of ionic charges ($Z_a Z_b Z_c$) of group $A^{+1}B^{+2}X_3$, (X = F. Cl, Br), $A^{+2}B^{+4}O_3$ and $A^{+3}B^{+3}O_3$ perovskites and found a straight line for all groups, which are presented in figure 2. We note the procedure for determining B (in GPa) from these techniques considers a difference between experimental measurements, and this could magnify errors. Linear regression lines have been plotted for the bulk modulus (in GPa), which result in equations of the form

$$B\,(GPa) = S + V\,\frac{(Z_a Z_b Z_c)^{0.35}}{a^{3.5}} \qquad (8)$$

where Z_a, Z_b and Z_c are the ionic charges on the A, B and X, respectively and a is lattice parameter in Å. The parameters S (1.79±4.15) and V (5505.785±186.86) are constants. The correlation coefficient R (0.97092) obtained from the regression analysis. The significance of the regression is given as the probability P (<0.0001) of the null hypothesis (that there is no correlation) for ABX_3 (X = F. Cl, Br) perovskites materials.

Figure 2 Bulk modulus B (GPa) for perovskites ($A^{+1}B^{+2}X_3$; X = F, Cl, Br, $A^{+2}B^{+4}O_3$ and $A^{+3}B^{+3}O_3$) as a function of $(Z_a Z_b Z_c)^{0.35}/a^{3.5}$. This line show linear relationship as determined by regression analysis. In this figure bulk modulus and lattice constant values are taken from Reference [1-10, 31-38].

From the comparison figures 1 and 2, we see that three lines found in figure 1 due to different ionic charges of the compounds. In figure 2, it has been verified that bulk modulus assumes a linear trend with lattice parameter. The facts that Bulk modulus is linear function of product of ionic charges and $1/a^{3.5}$

Table 1. Values of bulk modulus (B in GPa) defined by Eq. (8) obtained for $A^{+1}B^{+2}X_3$, (X = F. Cl, Br), perovskites.

Solids	a (Å) [5]	B (GPa) [1-4]	B (GPa) this work	Solids	a (Å) [5]	B (GPa) [3, 4]	B (GPa) this work
$CsCdF_3$	4.47	58	54.6	$RbPbF_3$	4.79		42.9
$CsCaF_3$	4.523	49	52.4	$KCaF_3$	4.38		58.6
$CsHgF_3$	4.57	55	50.5	$KCdF_3$	4.293		62.9
$CsSrF_3$	4.75		44.1	$KMgF_3$	3.989	82.7	81.3
$CsEuF_3$	4.78		43.2	$KNiF_3$	4.013		79.6
$CsPbF_3$	4.8	36	42.6	$KZnF_3$	4.056	85.5	76.7
$CsYbF_3$	4.61		49.0	$KCoF_3$	4.071		75.7
$CsCaCl_3$	5.396	23.4	28.2	KVF_3	4.1		73.9
$CsCdCl_3$	5.21		31.9	$KFeF_3$	4.121		72.6
$CsPbCl_3$	5.605	25.8	24.7	$KMnF_3$	4.189	64.9	68.5
$CsHgCl_3$	5.41		28.0	$NaVF_3$	3.94		84.9
$CsEuCl_3$	5.627		24.4	$NaMgF_3$	3.84	87.9	92.9
$CsTmCl_3$	5.476		26.8	$NaZnF_3$	3.88	89.8	89.6
$CsYbCl_3$	5.437		27.5	$NaCoF_3$	3.9		88.0
$CsPbBr_3$	5.874	23.5	21.0	$AgMgF_3$	3.918		86.6
$CsPbI_3$	6..29	19.8	16.5	$AgNiF_3$	3.936		85.2
$RbZnF_3$	4.11	86.9	73	$AgZnF_3$	3.972		82.5
$RbCoF_3$	4.141		71.3	$AgCoF_3$	3.983		81.8
$RbVF_3$	4.17		69.6	$AgMnF_3$	4.03		78.5
$RbFeF_3$	4.174		69.4	$LiBaF_3$	3.992		81.1
$RbMnF_3$	4.24	67.5	65.7	$TlCoF_3$	4.138		71.5

Table 2. Values of bulk modulus (B in GPa) defined by Eq. (8) obtained for $A^{+2}B^{+4}O_3$ perovskites. The values of bulk modulus are tabulated as experimental (E) for comparison.

Solids	a (Å) [5]	B (GPa) [7-10, 31]	B(GPa) thiswork	Solids	a (Å) [5]	B (GPa) [32-35]	B (GPa) this work
$BaMnO3$	3.846	196	191.3	$SrVO_3$	3.89	181.5	183.9
$BaFeO_3$	3.994		167.6	$SrFeO_3$	3.85		190.6
$BaMoO_3$	4.04		161.0	$SrTiO_3$	3.905	179 [E]	181
$BaNbO_3$	4.08	171	155.6	$SrTcO_3$	3.949		174.4
$BaSnO_3$	4.116	145.8 [E]	150.9	$SrMoO_3$	3.975		170.5
$BaHfO_3$	4.171		144.0	$SrNbO_3$	4.016	173	164.4
$BaZrO_3$	4.193	127 [E]	141	$SrSnO_3$	4.034	164	161.9
$BaIrO_3$	4.1		152.9	$SrHfO_3$	4.069		157.1
$BaPbO_3$	4.265		133.2	$SrTbO_3$	4.18		142.9
$BaTbO_3$	4.285		131.1	$SrAmO_3$	4.23		137.1
$BaPrO_3$	4.354		123.9	$SrPuO_3$	4.28		131.6
$BaCeO_3$	4.397		119.7	$SrCoO_3$	3.85		190.6
$BaAmO_3$	4.357		123.6	$SrZrO_3$	4.104	151	152.4
$BaTiO_3$	4.012	162 [E]	165.0	$CaZrO_3$	4.01		165.3

Table 3. Values of bulk modulus (B in GPa) defined by Eq. (8) obtained for $A^{+3}B^{+3}O_3$ perovskites.

Solids	a (Å) [5]	B (GPa) [36, 37]	B (GPa) this work	Solids	a (Å) [5]	B (GPa) [37, 38]	B (GPa) this work
$EuTiO_3$	3.905	172.6	189.0	$NdCrO_3$	3.835		201.4
$EuAlO_3$	3.725		223.0	$NdFeO_3$	3.87		195.1
$EuCrO_3$	3.803		207.4	$NdMnO_3$	3.8		207.9
$EuFeO_3$	3.836		201.2	$PrAlO_3$	3.757		216.4
$EuGaO_3$	3.84		200.5	$PrCrO_3$	3.852		198.3
$EuInO_3$	4.03		169.3	$PrFeO_3$	3.887		192.1
$CeAlO_3$	3.772		213.4	$PrGaO_3$	3.863		196.3
$GdAlO_3$	3.71		226.1	$PrMnO_3$	3.82		204.2
$GdCrO_3$	3.795		208.9	$PrVO_3$	3.89		191.6
$GdFeO_3$	3.82		204.2	$PrCoO_3$	3.78	130	211.8
$LaAlO_3$	3.778		212.2	$SmAlO_3$	3.734		221.1
$LaCrO_3$	3.874		194.4	$SmCoO_3$	3.75		217.8
$LaFeO_3$	3.92		186.5	$SmVO_3$	3.89		191.6

IV. Results and discussion

Elastic moduli are important for theoretical understanding of material properties. It is determined by the phonon density of states and lattice anharmonicity effects or by electron-phonon interaction processes mediated via deformation potentials. In view of the still unsatisfactory and contradictory data on the mechanical properties of the compounds on the one hand and of the importance of their knowledge for a comprehensive analysis of a wide variety of material characteristics on the other hand it was the aim of the present study to critically evaluate and review related experimental and theoretical data reported in the literature so far. In the tables 1-3, we have presented experimental and theoretical bulk modulus values evaluated by different researchers [1-4, 7-10, 31-38] for the sake of comparison. The simple trend when a larger lattice constant leads to a smaller bulk modulus. It has been demonstrated also for different perovskites ABO_3[39,40]. In the present work it is shown that analogous relation exists for the perovskite materials, which can be successfully employed to estimate the bulk modulus from their ionic charges.

V. Summary and conclusions

From the above results and discussion obtained by using the proposed empirical relation, it is quite obvious that the parameter such as bulk modulus reflecting the mechanical property can be expressed in terms of ionic charge, pressure, volume and temperature of the material. We note that the evaluated values of bulk modulus by the proposed relation (5.8) are in close agreement with the experimental data as compared to the values reported by previous researchers so far. For example, the results for bulk modulus differ from experimental by 1% ($SrTiO_3$), 1.8% ($BaTiO_3$), 3.5% ($BaSnO_3$) and 11% ($BaZrO_3$) in the current study.

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