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Elastic moduli of perovskite-type rare earth rhodium borides and carbides

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ABSTRACT

In this paper, semi-empirical formula for the bulk modulus (B in GPa) and shear modulus (G in GPa) of perovskite structured solids are elaborated in terms of lattice constant (a in Å) and product of ionic charges (Z_a Z_x) of the bonding. Values of bulk modulus, of the group ARh_3X, (X = B and C) perovskite-type materials 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. The resulting expressions can be applied to a broad selection of perovskite (ARh_3X = A: large cation with different valence and X: borides and carbides) materials and their modulus predictions are in good agreement with the experimental data and those from ab initio calculations. Copyright © 2014 VBRI press.

Keywords: Rare earth borides; rare earth carbides; bulk modulus; shear modulus microwave-assisted synthesis; spin glass; magnetic.

Introduction

Perovskite-type oxides are of great interest in materials science because the relatively simple crystal structure displays many diverse electric, magnetic, piezoelectric, optical, catalytic and magnetoresistive properties. This is one of the most frequently encountered structures in solid-state physics, and it accommodates most of the metallic ions in the periodic table with a significant number of different anions **[1-5]**.

On the other hand, studies on non-oxide perovskite-type compounds such as the ternary rare earth rhodium borides ARh_3B and carbides ARh_3C (A = rare earth) have been comparatively rare. It is of interest to systematically investigate the properties of non-oxide perovskite-type compounds because boron makes many technologically important compounds with mechanical hardness. It is also an interesting problem to analyze the effects of carbon doping in place of boron in these systems. The structural, elastic, dielectric and optical properties of the cubic perovskites are very important **[6]**.

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 **[1, 5]**. 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 **[7, 8]**.

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. As a result, analytical and semiempirical methods need to be elaborated in concert with computational approaches and estimations. Empirical concepts such as valence, empirical radii, ionicity and plasmon energy are then useful **[3, 4, & 9]**. 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.

As for covalent materials, it was found by Cohen **[10]** that their bulk modulus *B* (GPa) can be estimated by the following semiempirical expression:

$$B = \frac{N_C}{4}\frac{(1972 - 220\lambda)}{d^{3.5}} \qquad (1)$$

where N_C is the bulk coordination number, d is the bond length, and λ is an empirical ionicity parameter that tkes the values of 0, 1, and 2 for IV, III-V and II-VI group semiconductors, respectively. Recently, Verma and co-authors **[3, 4, & 7]** 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 ad hoc 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.

Theory

There have been a number of reports in the past of empirical relations describing the mechanical properties of solids. Anderson and Nafe **[11]** first proposed an empirical relationship between bulk modulus B at atmospheric pressure and specific volume V_0 of the form $B \sim V_0^{-x}$. They find it to hold for a particular class of compounds. Where the value of x depend on the class of 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 **[12]** 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 **[13]** 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 [10]:

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

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

where Ω and δ stand for volume and dimensionless deformation parameter, respectively. From Eqs. (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 **[14]** like those occurring under elastic deformation; while the valence electrons are completely affected by such phenomena. Consequently, the core electrons do not have a significant contribution to the elastic response of a material deforming within the limits of the elastic regime; whereas, the valence electrons are fully involved in the distortion process. Since the involvement of core electrons in the elastic deformation is insignificant, the variation of their energy is also negligible. 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 **[15]** 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:

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

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 [10] that Philips' homopolar band gap energy is the dominant energy parameter in covalent solids. Recently, relationships connecting inherent traits such as thermal activation energies **[16]** and hardness **[17]** 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: [15]

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

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), 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 encloses the largest electron concentration [10]. Thus Eqs. (2)–(6) yield

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

and

$$G \, \alpha \, \frac{1}{d^{5.5}} \qquad (8)$$

The author in previous research **[3, 4, 7]** found that substantially reduced ionic charges must be used to get better agreement with experimental values. Goldshmidt **[18]** has pointed out that a term A = Z_aZ_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 **[19]** 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.

Linear regression lines have been plotted for the bulk modulus (in GPa) and shear modulus (in GPa) which result in equation of the form

$$B\left(GPa\right) = S + V\frac{(Z_aZ_x)^{0.25}}{a^{3.5}} \qquad (9)$$

and

$$G\left(GPa\right) = S + V\frac{(Z_aZ_x)}{a^{5.5}} \qquad (10)$$

where Z_a, and Z_x are the ionic charges on the A and X, respectively and a is lattice parameter in Å. The constants S and V are given in table 1 along with the correlation coefficient (R) obtained from the regression analysis.

Table 1. Linear regression results from the data for ARh_3B and ARh_3C perovskites.

Properties	S	V	R
Bulk modulus B	-2.825±16.48	15754.75±1330	0.97227
Shear modulus G	196.5±9.72	43054±2267	0.98903

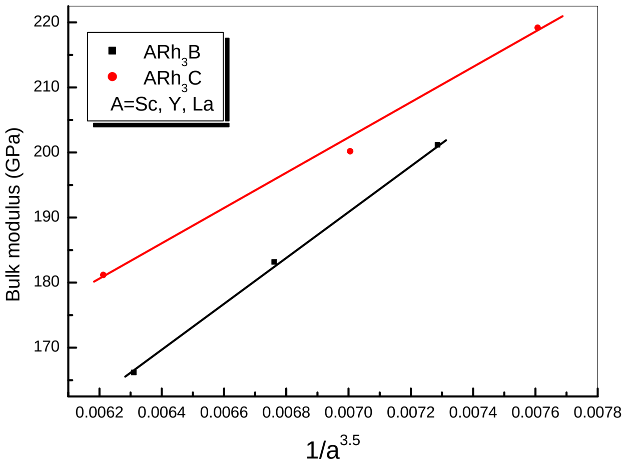

Fig. 1. Plot of bulk modulus B (GPa) and lattice constant (a in Å) for the group ARh_3B and ARh_3C perovskites and found at two positions, which is depending upon the product of ionic charges. In this figure bulk modulus and lattice constant values are taken from Reference **[6]**.

Results and discussion

The knowledge of elastic moduli is necessary in order to come to a better theoretical understanding of material properties that are essentially 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.

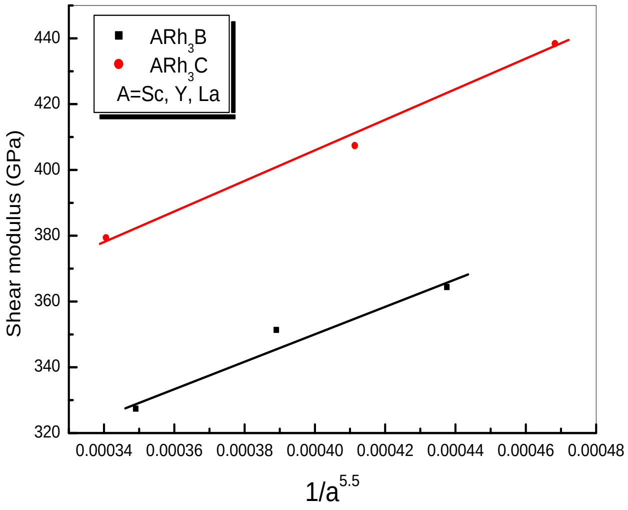

Fig. 2. Plot of shear modulus G (GPa) and lattice constant (a in Å) for the group ARh_3B and ARh_3C perovskites and found at two positions, which is depending upon the product of ionic charges. In this figure shear modulus and lattice constant values are taken from Reference **[6]**.

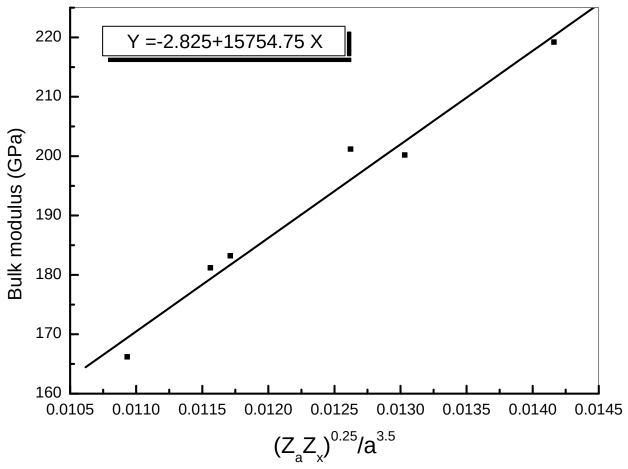

Fig. 3. Bulk modulus B (GPa) for perovskites (ARh_3B and ARh_3C) as a function of $(Z_aZ_x)^{0.25}/a^{3.5}$. This line show linear relationship as determined by regression analysis. In this figure bulk modulus and lattice constant values are taken from Reference **[6]**.

It has been verified **[10]** that elastic moduli assume a decreasing linear trend with increasing lattice parameter. Therefore, based on Eqs. (7) and (8), the fact that B and G are linear functions of lattice constant. These elastic moduli are expected to exhibit the explicit dependences on lattice parameter (a in Å) and ionic charge (Z). As an example to 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) and G Vs $a^{5.5}$ (G = shear modulus in GPa, a = lattice parameter in Å) for the group ARh_3B and ARh_3C perovskite-type compounds and data are presented in the following **Fig. 1** and **2**. We observe that in the plot of B Vs $a^{3.5}$ and G Vs $d^{5.5}$, the group ARh_3B and ARh_3C perovskite-type compounds exhibit two positions in these figures. This effect induced by the ionic charges of the compounds in the case of group ARh_3B and ARh_3C perovskite-type compounds. If all data of bulk modulus (in GPa) and shear modulus (in GPa) plots with product of ionic charges $(Z_aZ_x)/a$ normalization of group ARh_3B and ARh_3C perovskite-type compounds and found a straight line for all groups, which are presented in **Fig. 3** and **4**.

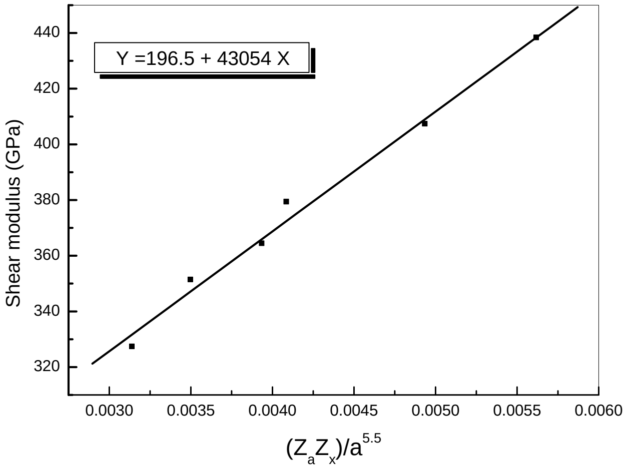

Fig. 4. Shear modulus G (GPa) for perovskites (ARh_3B and ARh_3C) as a function of $(Z_aZ_x)/a^{3.5}$. This line show linear relationship as determined by regression analysis. In this figure shear modulus and lattice constant values are taken from Reference **[6]**.

Table 2. Values of bulk modulus (B in GPa) and shear modulus (G in GPa) defined by Eq. (9) & (10) obtained for ARh_3B and ARh_3C perovskites.

Solids	**a (Å) [6]**	**Z_aZ_x**	**B (GPa) [6]**	**B (GPa) this work**	**% error**	**G (GPa) [6]**	**G (GPa) this work**	**% error**
$ScRh_3B$	4.08	9	201	196	2	364	366	0.6
YRh_3B	4.168	9	183	182	1	351	347	1.0
$LaRh_3B$	4.251	9	166	169	2	327	332	1.5
$ScRh_3C$	4.03	12	219	220	1	438	439	0.1
YRh_3C	4.126	12	200	203	1	407	409	0.5
$LaRh_3C$	4.27	12	181	179	1	379	373	1.7

From the comparison **Fig. 1-4**, we see that three lines found in **Fig. 1** & **2** due to different ionic charges of the compounds. In **Fig. 3** & **4**, it has been verified that bulk modulus and shear modulus assume a linear trend with lattice parameter. We note the procedure for determining B (in GPa) and G (in GPa) from these techniques considers a difference between experimental measurements, and this could magnify errors.

In the **Table 2**, we have presented bulk modulus values evaluated by Sahara et al. **[6]** for the sake of comparison. The simple trend when a larger lattice constant leads to a smaller bulk modulus and shear modulus. It has been demonstrated also for different perovskites AB_3X **[20]**. 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 and shear modulus from their ionic charges. We note that the evaluated values of elastic moduli by the proposed relation are in close agreement with the experimental data as compared to the values reported by previous researchers so far. Consequently, the reliability and accuracy of proposed formula is well verified.

Conclusion

There are several methods in determining elastic properties in materials, but due to the small changes of the unit cell dimensions, the accuracy of determining these parameters always have been unpredictable. We developed a semi-empirical formula for shear modulus of perovskite-type materials and obtained an improved universal formula for their bulk modulus. The investigation of the ratio of these formulae, whose accuracy is comparable to that of the first-principles calculations, clearly demonstrated the predominance of the lattice parameter in assessing brittle characteristics of perovskite-type materials. The method presented in this work will be helpful to material scientists for finding new materials with desired elastic properties among a series of structurally similar materials.

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