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A Novel Strategy for Comprehensive Estimation of Lattice Energy, Bulk Modulus, Chemical Hardness and Electronic Polarizability of $A^{N}B^{8\text{-}N}$ Binary Inorganic Crystals

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Abstract: How to search for a convenient method without a complicated calculation process to predict the physicochemical properties of inorganic crystals through a simple micro-parameter is a greatly important issue in the field of materials science. Herein, this paper presents a new and facile technique for the comprehensive estimation of lattice energy (U), bulk modulus (B), chemical hardness (η), and electronic polarizability (α), just by using a simple mathematic fitting formula with a few structure parameters, such as the systems of rock salt crystals (group I–VII, II–VI) and tetrahedral coordinated crystals (group II–VI, III–V). For the typical binary $A^{N}B^{8\text{-}N}$ crystal systems, our present conclusions suggest that a good quantitative correlation between U, B, η, α and chemical bond length (d) is observed, the normal mathematical expression is $P = a{\cdot}d^{b}$ (P represents these physicochemical parameters), constants a and b depend on the type of crystals, and the relevant squares of the correlation coefficient (R^2) are larger than 0.9. The results indicate that lattice energy, bulk modulus, and chemical hardness decrease with increases in chemical bond length, but electronic polarizability increases with an increase in chemical bond length. Meanwhile, the new data on the lattice energy, bulk modulus, chemical hardness, and electronic polarizability values of binary $A^{N}B^{8\text{-}N}$ crystal systems considered in the present study are calculated via the obtained curve fitting equations without any complex calculation process. We find that there is a very good linear trend in our calculated results along with the values reported in the literature. The present study will be important in solid-state chemistry, which may give researchers useful guidance in searching for relevant data for predicting the properties of new materials or synthetic routes based on a simple mathematic empirical model.

Keywords: inorganic crystals; lattice energy; bulk modulus; chemical hardness; electronic polarizability; chemical bond length

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1. Introduction

One of the main aims of theoretical chemistry is to present a useful correlation between chemical concepts, which provides great convenience and important information to researchers for the prediction of molecular properties, such as reactivity and stability of chemical species, and to build a bridge between physics and chemistry in the field of materials science [1–5]. In the past few decades, a considerable number of theoretical calculations in terms of the empirical model have become an essential part of materials research, because of the simplicity allowing a broader class of researchers to understand useful properties in order to help them reduce experimental complexity during the process of exploring the synthetic techniques of novel materials [6–11]. In the description of different characteristics of chemical species related to their stability, reactivity, and mechanical and optical-electrical property, popular chemical concepts, such as lattice energy, bulk modulus, chemical hardness, and electronic polarizability are commonly mentioned [12–15]. It is also worth noting that there is an intrinsic relationship between these concepts based on the other structural parameters, and the detailed description will be discussed in the following section.

The lattice energy of inorganic crystals plays a significant role in the exploration of the existence and stability of materials based on the analysis of thermodynamics [16–19]. Namely, this energy is considered to be one of most important quantities in the matter of whether new inorganic materials can be synthesized by using designed synthetic routes [16–19]. Hence, the computation and estimation of lattice energy has attracted great attention in the field of modern materials science. Normally, lattice energy of inorganic crystals can be determined by means of the Born–Fajans–Haber (BFH) thermochemical cycle based on the experimental data, such as standard formation enthalpy, bond dissociation energy, sublimation enthalpy, ionization energy, and electron affinity [12,18,19]. Such an experimental method can provide important original data needed for precise establishment of a theoretical fitting model. Recently, different theoretical models have been proposed for the evaluation of the lattice energy of inorganic crystals [12,16–19]. By means of the dielectric theory of chemical bond of complex crystals, Zhang's group presented an empirical method for the estimation of the lattice energy of inorganic ionic crystals [12]. In their subsequent study, a relationship between the lattice energy and bulk modulus of binary inorganic crystals was obtained through introducing the concept of lattice energy density [19]. At the same time, the bulk modulus of binary inorganic crystals was calculated by using the empirical fitting equation, which shows that there is an existing close relationship between lattice energy and the bulk modulus.

The bulk modulus is a macroscopic physical parameter in evaluating a material's mechanical performance, which has unique and valuable contributions to predict the ability of solids to resist compression deformation within the limits of the elastic regime [13,20]. In other words, materials with a high bulk modulus are often taken as potential superhard materials [1,19]. Meanwhile, the bulk modulus can offer some useful information on the geometry of minerals' compression, which has been relevant to geophysics and has been used for the interpretation of Earth's seismic properties [13,21,22]. Hence, extensive relevant studies have been focused on estimating the bulk modulus of crystal materials for either a theoretical basis or experimental technique [13,19]. An accurate determination of bulk modulus requires complicated engineering, involving a careful analysis of elastic parameters, plastic deformation, and even complex experiment measurement processes. In response to this, most researchers tend to choose the computational route to obtain such physical properties of solid materials. Currently, most theoretical calculations of the bulk modulus are performed by using state-of-the-art ab initio techniques [23]. However, these first-principles calculations are relatively complex and require significant effort due to the long computational process and rigorous mathematical formulae involving a series of approximations, which lead to difficulty in constructing relationships among the chemical composition, crystal structure, and intrinsic properties for ordinary researchers. Therefore, it is necessary to search for an effective method to estimate the bulk modulus of different types of crystals from the viewpoint of a simple and convenient operation. Wang et al. presented an empirical model based on the bond valence model in terms of bond length, bond valence, and bond density to predict the bulk modulus of crystal materials [13]. Xue's group estimated the elastic modulus of different types of crystal materials on the basis of the electronegativities of bonded atoms in the crystallographic frame [24]. It is interesting to note that these studies indicate that the bulk modulus is strongly influenced by the crystal structure.

Chemical hardness has long been used as one of the most useful conceptual constructs of chemistry and physics, which is a significant tool to understand the nature of chemical interactions and to predict the reactivity or stability of chemical species [25,26]. Generally, hardness, as conceived in chemistry, fundamentally offers a measure of resistance towards the deformability of atoms, ions, or molecules, and a polarization degree of electron cloud under a small perturbation generated during the process of chemical reaction [14,25]. According to Sanderson's electronegativity equalisation principle, Datta derived the geometric mean equation to calculate the chemical hardness of molecules based on the assumption that the chemical hardness is equilibrated globally [27]. Islam et al. presented an algorithm for the evaluation of the hardness of heteronuclear polyatomic molecules, and the obtained hardness data of a set of representative molecules were in good agreement with the corresponding hardness data evaluated by using quantum mechanics [26]. To further offer a practical calculation opportunity for the chemical hardness of atoms and molecules, Kaya et al. proposed a new equation for calculating chemical hardness atoms by using the charges, ionisation energy, and electron affinity of atoms [14]. In addition, chemical hardness is an important parameter that is closely related to lattice energy [18]. Kaya et al. developed a facile technique for the estimation of the lattice energy of inorganic ionic compounds via chemical hardness [18]. Such a method allows for the easy evaluation of the lattice energy of inorganic ionic crystals without the need for ab initio techniques and complex calculations.

Electronic polarizability, which governs non-linear optical responses, is one of the most important parameters in the field of electro-optic devices [28–30]. Meanwhile, electronic polarizability is also crucial to the study of doping and defect behaviours of functional materials [31]. Dimitrov et al. attempted to calculate the average electronic oxide polarizability of numerous single component oxides based on the linear refractive index and energy gap, and also searched for a suitable relationship between polarizability and the non-linear properties of simple oxide materials [32]. Xue's group presented a new method for estimating the electronic polarizability of binary and ternary chalcopyrite semiconductors by using electronegativity and the principal quantum number as calculation parameters [33]. Based on a thermodynamic approach, an important link between electronic polarizability and the lattice energy of crystalline silicates has been quantitatively established by Duffy [34], and the value of lattice energy has been estimated by means of the enthalpies of formation. Petrov et al. successfully calculated the lattice energy of complex lanthanide compounds, and their correlations between electronic polarizability and lattice energy have been investigated [35–37]. In the previous study, we have searched for a systematic relationship between lattice energy density and electronic polarizability, and the empirical expressions were found for $A^{N}B^{8\text{-}N}$ crystal systems, including rock salt (group I–VII, II–VI) and tetrahedral coordinated crystals (group II–VI, III–V) [38]. These empirical methods provide a convenient condition for studying the relationship between lattice energy and electronic polarizability.

Relying upon the commonality of the basic philosophy of the origin and development of the abovementioned physicochemical parameters, more theoretical approaches have been attempted to further explore intrinsic relationships based on the mathematic fitting equation. However, they are too complex to be used by most researchers due to containing many fitting parameters or involving some important theory. Especially, the rationalization of these density functional theory (DFT) calculations often requires a profound understanding of quantum mechanical theory and complex structure parameters. It is, therefore, of scientific and practical interest to develop a simple and suitable method to explore the systematic relationship between lattice energy, bulk modulus, chemical hardness, electronic polarizability, and chemical bond length for binary $A^{N}B^{8\text{-}N}$ crystals, and to gain a deeper understanding of these significative physicochemical parameters.

As technologically important materials, binary $A^{N}B^{8\text{-}N}$ inorganic crystals have been widely investigated because of their potential applications in modern industry areas, such as microelectronic devices, light-emitting diodes, non-linear optics, catalysts, and superhard materials [39–43]. For example, the BN with zinc blende and orthorhombic structure can be widely used for cutting and polishing tools or scratch-resistant coatings, which have been considered to be promising materials for superhard material in the place of costly diamonds [39]. Group II–VI semiconductors, especially CdTe, have gained a great deal of research interest in optoelectronic devices and catalysts [40–42]. On the other hand, second harmonic generation has been observed from nanoarchitecture ZnS under linearly polarized and circularly polarized femtosecond laser excitations due to its remarkably large non-linear optical coefficient [43]. All these applications indicate that an understanding of the relevant chemical and physical parameters for describing their performance in the system of $A^{N}B^{8\text{-}N}$ type crystals is crucial to purposely designing new functional materials with tunable intrinsic properties. To search for the link between macro-performance and micro-structure, significant theoretical work has been conducted in this direction for inorganic crystals in recent years [44–47]. For this purpose, the present work is an attempt to find a mathematic correlation between lattice energy, bulk modulus, chemical hardness, electronic polarizability, and chemical bond length based on the empirical curve fitting model with the use of only a few numerical constants.

To the best of our knowledge, such relations have not yet been well revealed for the comprehensive estimation of multiple physicochemical parameters, just by using a simple mathematical formula with the same one parameter of chemical bond length. In the present paper, the main aim of this study is an attempt to present a systematic relationship between lattice energy, bulk modulus, chemical hardness, electronic polarizability, and chemical bond length in a lot of data analysis on the abovementioned physicochemical parameters from the reported literature. Moreover, the empirical expressions obtained by means of the curve fitting method can be used to calculate the value of lattice energy, bulk modulus, chemical hardness, and electronic polarizability for binary $A^{N}B^{8\text{-}N}$ type crystals. The results show that, within the systems studied, the calculated values agree well with the reported data in the previous literature. The present work provides a useful guide for researchers to predict lattice energy, bulk modulus, chemical hardness, and electronic polarizability by means of a simple crystal structure parameter, which are easily understandable and accessible, and thus could give us useful information for designing novel functional materials.

2. Theoretical Method

As was mentioned above, lattice energy is one of the most important quantities in understanding and predicting the structure, character, and behaviour of inorganic solid materials from the point of view of thermodynamics [12]. Recently, an empirical methodology to calculate the lattice energy of inorganic ionic crystals was proposed by Zhang and coworkers based on the dielectric theory of chemical bond [12,19]. In this method, the total lattice energy, U_{all}, of inorganic crystals with one type of chemical bond can be divided into bond-dependent terms, ionic part U_i and covalent part U_c, as follows:

$$U_{all} = U_i + U_c, \tag{1}$$

We suppose that the formula of a simple crystal is A_mB_n (A and B represent cation and anion, respectively), so then lattice energy U_i and U_c of a binary crystal can be expressed by the following relations:

$$U_i = \frac{1270(m+n)Z_AZ_B}{d}\left(1 - \frac{0.4}{d}\right)f_i, \tag{2}$$

$$U_c = 2100\frac{{Z_A}^{1.64}}{d^{0.75}}f_c, \tag{3}$$

where Z_A and Z_B are the valences of A and B ions, respectively; f_i and f_c are the fractional ionicity and fractional covalency of the chemical bond in crystals. For the binary inorganic crystals, the detailed structural data on the calculation of ionicity and covalency and other chemical bond properties are taken from the literature [48]. The estimated values of lattice energy are in good agreement with the available experimental data. Subsequently, the bulk modulus was calculated by introducing the concept of lattice energy density, U_d, and the mathematic equation is expressed as follows:

$$B = \delta + \frac{U_d}{-1.445 + 1.8185e^{1.54\gamma}}, \tag{4}$$

In this equation, B represents the bulk modulus, and γ and δ are the empirical parameters, which are relating to the valence and coordination number of the cation [19]. For the rock salt crystals of group I–VII, rock salt crystals of group II–VI, the tetrahedral coordinated crystals of group II–VI, and the tetrahedral coordinated crystals of group III–V, the parameters, γ, are 0.2917, 0.375, 0.5625, and 0.6875, respectively. According to the valence and coordination number of the cation, the value of empirical parameter, δ, is equal to $18/Z_AN_{CA}$ for $N_{CA} > 4$, the values of are equal to $18/Z_AN_{CA}$ for the $N_{CA} \leq 4$ [19].

It is important to note that chemical hardness is a useful theoretical parameter in many experimental and theoretical studies, and this concept has several important applications in multiple topics including complex stability, chemical reactivity, estimation of formed products in a reaction, and solubility of molecules [14,18]. In order to accurately describe such a parameter, Kaya et al. presented a mathematic equation for the estimation of the chemical hardness of both neutral and charged moleculars according to the hardness equalization principle [14], as follows:

$$\eta_M = \frac{2\sum_{i=1}^{N}\frac{b_i}{a_i} + q}{\sum_{i=1}^{N}\frac{1}{a_i}}, \tag{5}$$

where N represents the total number of atoms in the molecule, q stands for charge of molecule, and a_i and b_i are parameters based on the ionization energy (I) and electron affinity (A) of atoms, respectively, which can be obtained by using the following mathematical expressions:

$$a_i = \frac{I + A}{2}, \tag{6}$$

$$b_i = \frac{I - A}{2}, \tag{7}$$

Polarizability of inorganic crystals is a basic property of materials and has been studied for a long time, both in experiments and theory in the field of optics and electronics, which is related to many macro and microscopic physicochemical properties, such as dielectric properties, ferroelectricity, optical non-linearity, and chemical stability [15,26,27]. Hence, it is extremely important to quantitatively evaluate the electronic polarizability of crystals. One of the most effective and reasonable methods for calculating electronic polarizability, α, is to apply the Clausius–Mossotti equation based on the concept of dielectric susceptibility, ε, and molar volume, V_m, of substance, and the relevant relation was written as

$$\alpha = \frac{1}{b}\frac{\varepsilon - 1}{\varepsilon + 2}V_m, \tag{8}$$

where the parameter of b is defined as $b = 4\pi N_A/3$, and N is Avogadro's number [49]. According to P-V dielectric theory [50,51], the following empirical equation is proposed for the calculation of dielectric constant ε

$$\varepsilon = 1 + Ad^{s'}, \tag{9}$$

The corresponding constants A and s' are collected in Ref. [48].

3. Results and Discussion

Firstly, according to the crystal structure type and properties, we calculated lattice energy, U, value based on Equations (1)–(3), which are listed in Tables 1–4 (column 4). For the same cation in binary ionic crystals, we can see that the lattice energy decreases with an increasing atomic number of anions. Meanwhile, it can be seen that, in general, there is a decreasing trend in the lattice energy along with the chemical bond length. Furthermore, we also calculated the bulk modulus, B, of binary crystals by means of Equation (4). The calculated bulk modulus values of binary crystals are given in Tables 1–4 (column 6), which have the same trend as lattice energy. On the basis of Equations (5)–(7), we calculated the chemical hardness, η, which are listed in Tables 1–4 (column 8). The dielectric constant, ε, values obtained from Equation (9) by using the chemical bond length are substituted in Equation (8), and the electronic polarizability, α, values can be evaluated as shown in Tables 1–4 (column 10). As can be seen from Tables 1–4, it is obvious that the electronic polarizability trends in binary $A^NB^{8\text{-}N}$ crystals increases with an increasing chemical bond length for the same cation.

During the last few decades, the extensive theoretical research based on the curve fitting model was devoted to understanding basic structural properties and the relation between the physics and chemistry of solids, which led to great advances in the rational design synthetic route of novel functional materials [4–19,28–38]. Although those methods are not supported by present fundamental theory, much important information about materials have been acquired, which has gradually become an essential part of materials research. In particular, the simplicity of these approaches allows a broader class of researchers to calculate useful properties, and often trends become more evident. With the help of the empirical fitting model and relevant chemical theories, chemists can achieve the goal of predicting chemical reactions and design a feasible synthetic route. Hence, numerous attempts have been made to establish links between macroscopic properties of solids and their atomic-scale microparameters.

Table 1. Chemical bond length d, molar volume V_m, lattice energy U, calculated lattice energy U_{cal}, bulk modulus B and calculated bulk modulus B_{cal}, chemical hardness η, calculated chemical hardness η_{cal}, electronic polarizability α, calculated electronic polarizability α_{cal} of rock salt crystals of group I–VII.

Crystal	d (Å)	V_m (Å^3)	U (kJ·mol^{-1})	U_{cal} (kJ·mol^{-1})	B (GPa)	B_{cal} (GPa)	η (eV)	η_{cal} (eV)	α (Å^3)	α_{cal} (Å^3)
LiF	2.01	16.2	1032	1038	76.4	76.4	6.85	6.91	0.855	0.956
LiCl	2.57	34.0	854	846	32.9	32.8	5.99	6.00	3.026	3.016
LiBr	2.75	41.6	809	800	26.0	26.0	5.82	5.76	4.184	4.150
LiI	3.02	55.1	750	741	19.3	18.8	5.58	5.45	6.461	6.440
NaF	2.31	24.7	921	925	47.1	47.3	6.61	6.39	1.168	1.246
NaCl	2.81	44.4	788	786	23.9	24.1	5.81	5.68	3.259	3.281
NaBr	2.98	52.9	751	749	19.6	19.7	5.64	5.48	4.379	4.390
NaI	3.23	67.4	702	700	14.9	15.0	5.42	5.23	6.481	6.530
KF	2.67	38.1	818	820	28.7	28.8	5.76	5.86	1.762	1.954
KCl	3.14	61.9	715	717	16.5	16.5	5.09	5.32	4.424	4.283
KBr	3.29	71.2	687	690	13.9	14.0	4.96	5.17	5.280	5.366
KI	3.53	88.0	647	651	11.1	11.0	4.78	4.96	7.520	7.536
RbF	2.82	44.9	782	784	24.1	23.8	5.58	5.68	2.169	2.254
RbCl	3.29	71.2	686	690	14.0	14.0	4.93	5.17	4.890	4.948
RbBr	3.43	80.7	662	666	12.0	12.2	4.81	5.05	6.046	6.116
RbI	3.66	98.1	626	631	9.6	9.7	4.64	4.86	8.383	8.506

Table 2. Chemical bond length d, molar volume V_m, lattice energy U, calculated lattice energy U_{cal}, bulk modulus B and calculated bulk modulus B_{cal}, chemical hardness η, calculated chemical hardness η_{cal}, electronic polarizability α, calculated electronic polarizability α_{cal} of rock salt crystals of group II–VI.

Crystal	d (Å)	V_m (Å^3)	U (kJ·mol^{-1})	U_{cal} (kJ·mol^{-1})	B (GPa)	B_{cal} (GPa)	η (eV)	η_{cal} (eV)	α (Å^3)	α_{cal} (Å^3)
MgO	2.105	18.7	3883	3901	193.6	193.1	8.88	8.87	1.876	1.941
MgS	2.602	35.2	3281	3285	85.9	86.9	7.57	7.43	4.857	4.816
MgSe	2.731	40.5	3155	3158	71.4	72.4	7.36	7.11	5.932	5.951
CaO	2.405	27.8	3510	3501	116.6	116.9	7.84	7.93	2.833	2.957
CaS	2.846	46.1	3062	3055	61.5	62.0	6.81	6.92	6.076	6.019
CaSe	2.962	51.6	2960	2957	52.5	53.3	6.65	6.65	7.164	7.177
CaTe	3.179	63.9	2789	2792	40.5	40.8	6.43	6.29	9.642	9.659
SrO	2.580	34.4	3319	3308	89.7	89.7	7.44	7.51	3.550	4.416
SrS	3.010	54.5	2922	2919	53.9	50.2	6.48	6.60	7.131	6.986
SrSe	3.122	60.5	2833	2834	43.0	43.7	6.33	6.38	8.305	7.824
SrTe	3.331	67.7	2681	2689	37.2	34.2	6.12	5.57	10.05	10.288
BaO	2.770	42.1	3132	3122	68.5	68.6	6.93	7.00	4.333	4.549
BaS	3.194	65.2	2780	2782	40.0	40.1	6.04	6.30	8.379	8.274
BaSe	3.302	71.9	2702	2708	34.4	35.4	5.90	6.12	9.657	9.556
BaTe	3.500	85.2	2570	2583	27.8	28.4	5.71	5.81	12.313	12.316

Table 3. Chemical bond length d, molar volume V_m, lattice energy U, calculated lattice energy U_{cal}, bulk modulus B and calculated bulk modulus B_{cal}, chemical hardness η, calculated chemical hardness η_{cal}, electronic polarizability α, calculated electronic polarizability α_{cal} of tetrahedral coordinated crystals of group II–VI.

Crystal	d (Å)	V_m (Å^3)	U (kJ·mol^{-1})	U_{cal} (kJ·mol^{-1})	B (GPa)	B_{cal} (GPa)	η (eV)	η_{cal} (eV)	α (Å^3)	α_{cal} (Å^3)
BeS	2.105	28.5	3846	3849	93.2	93.6	8.70	8.81	3.526	3.452
BeSe	2.225	32.6	3686	3685	81.7	80.0	8.45	8.48	4.353	4.422
BeTe	2.436	42.5	3433	3434	63.1	61.8	8.10	8.35	6.343	6.331
ZnS	2.340	39.6	3544	3543	67.0	69.3	9.21	8.81	5.558	5.570
ZnSe	2.450	45.5	3417	3418	60.3	60.8	8.96	8.78	6.744	6.733
ZnTe	2.630	56.4	3225	3234	49.3	49.7	8.61	8.73	9.015	9.018
CdS	2.530	49.2	3341	3334	55.6	55.5	8.86	8.59	7.104	7.197
CdSe	2.630	56.2	3240	3234	49.8	49.7	8.61	8.70	8.486	8.377
CdTe	2.800	68.0	3077	3080	42.1	41.6	8.28	8.67	10.957	10.971

As can be seen in all investigated systems of Tables 1–4, we can find a general trend in the lattice energy, bulk modulus, chemical hardness, and electronic polarizability with chemical bond length. Therefore, to search for a detailed and precise relation between these physicochemical parameters and the chemical bond length of binary $A^NB^{8\text{-}N}$ crystals, we plotted the data of the lattice energy, bulk modulus, chemical hardness, and electronic polarizability in Tables 1–4 as a function of chemical bond length in Figures 1–4. Furthermore, for the estimation of chemical hardness and polarizability, we introduced a parameter of molar volume of inorganic materials that can be easily obtained by means of their chemical formulas and densities in their curve fitting assessment. According to pioneering studies on the concept of lattice energy density by Zhang's group, we defined η_V ($\eta_V = \eta/V_m$) as chemical hardness density [19]. Meanwhile, $\alpha_{\mathrm{v}*}$ ($\alpha_{\mathrm{v}*} = \alpha \cdot V_m$) is defined as a product of electronic polarizability and molar volume learned from Qi's ideas [29]. As can be seen from Figures 1–4, it is worth noting that a very good agreement exists between these physicochemical parameters and the chemical bond length of binary $A^NB^{8\text{-}N}$ crystals, and the correlation coefficient R^2 values are larger than 0.9 (most correlation R^2 values are 0.99), indicating that least squares fittings and calculations are effective and reliable for the present binary $A^NB^{8\text{-}N}$ crystal systems. The corresponding trend lines, correlation equations, and the values of squares of correlation coefficient are given in Figures 1–4. The normal mathematical expression between the abovementioned parameters and the chemical bond length is $P = a{\cdot}d^b$ (P represents these parameters, d is chemical bond length). The detailed data on constant, a and b, are listed in Figures 1–4. As can be seen from Figure 1a–c, Figure 2a–c, Figures 3a–c and 4a–c, there is a clear decreasing trend in the lattice energy, bulk modulus, and chemical hardness along with the chemical bond length. However, different trends can be seen in Figures 1d, 2d, 3d and 4d, where we plotted the data on electronic polarizability as a function of chemical bond length for binary $A^NB^{8\text{-}N}$ crystals.

Table 4. Chemical bond length d, molar volume V_m, lattice energy U, calculated lattice energy U_{cal}, bulk modulus B and calculated bulk modulus B_{cal}, chemical hardness η, calculated chemical hardness η_{cal}, electronic polarizability α, calculated electronic polarizability α_{cal} of tetrahedral coordinated crystals of group III–V.

Crystal	d (Å)	V_m (Å^3)	U (kJ·mol^{-1})	U_{cal} (kJ·mol^{-1})	B (GPa)	B_{cal} (GPa)	η (eV)	η_{cal} (eV)	α (Å^3)	α_{cal} (Å^3)
BN	1.568	11.8	9560	9449	367.0	366.9	10.40	10.51	1.388	1.387
BP	1.966	21.0	7758	8076	165.0	165.8	8.76	7.83	3.321	3.319
AlP	2.365	40.5	7212	7104	86.0	86.7	7.08	7.42	6.957	6.951
AlAs	2.442	44.4	7082	6948	77.0	77.4	6.84	7.19	8.051	8.051
AlSb	2.646	57.7	6634	6572	58.2	58.4	6.36	6.86	11.274	11.269
GaP	2.359	40.5	7132	7117	88.7	87.4	7.09	7.49	6.952	6.907
GaAs	2.456	45.2	6915	6920	74.8	75.9	6.85	7.16	8.213	8.247
GaSb	2.650	57.3	6444	6565	57.0	58.1	6.37	6.77	11.200	11.184
InP	2.542	51.3	6850	6757	71.0	67.3	6.98	7.12	9.067	8.977
InAs	2.619	55.0	6627	6619	60.0	60.6	6.76	6.80	10.212	10.306
InSb	2.806	68.0	6237	6309	47.4	47.5	6.29	6.45	13.488	13.471

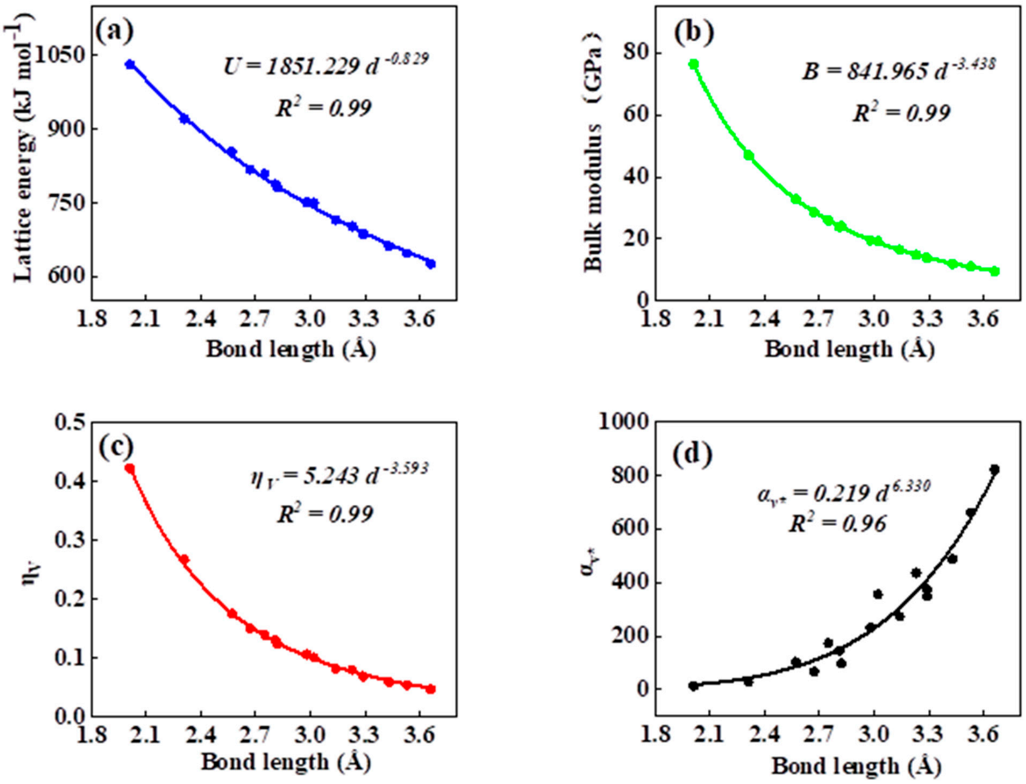

Figure 1. Plot of correlation between the lattice energy, (**a**) bulk modulus, (**b**) chemical hardness density, (**c**) product of electronic polarizability and molar volume, (**d**) and chemical bond length of rock salt crystals of group I–VII.

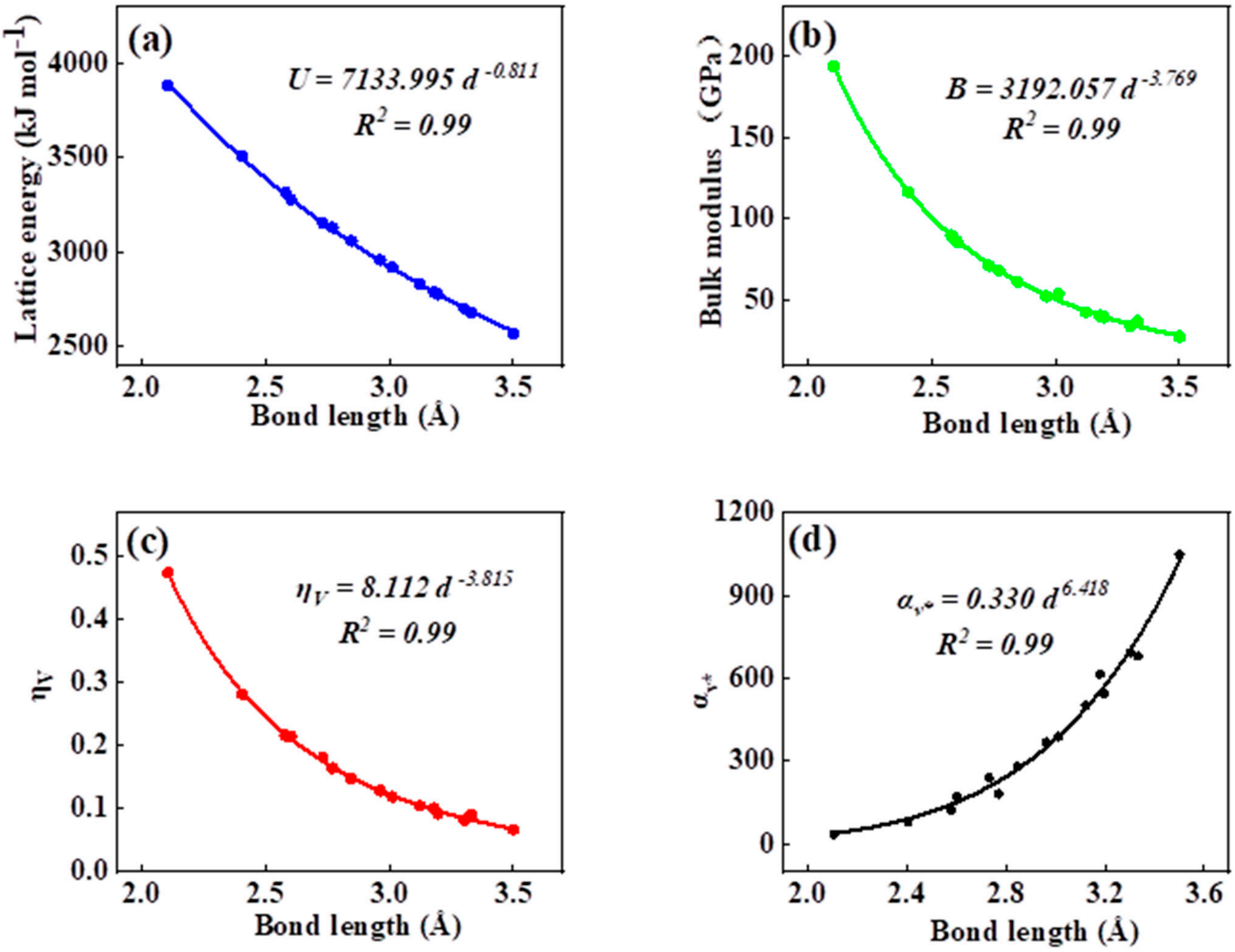

Figure 2. Plot of correlation between the lattice energy, (**a**) bulk modulus, (**b**) chemical hardness density, (**c**) product of electronic polarizability and molar volume, (**d**) and chemical bond length of rock salt crystals of group II–VI.

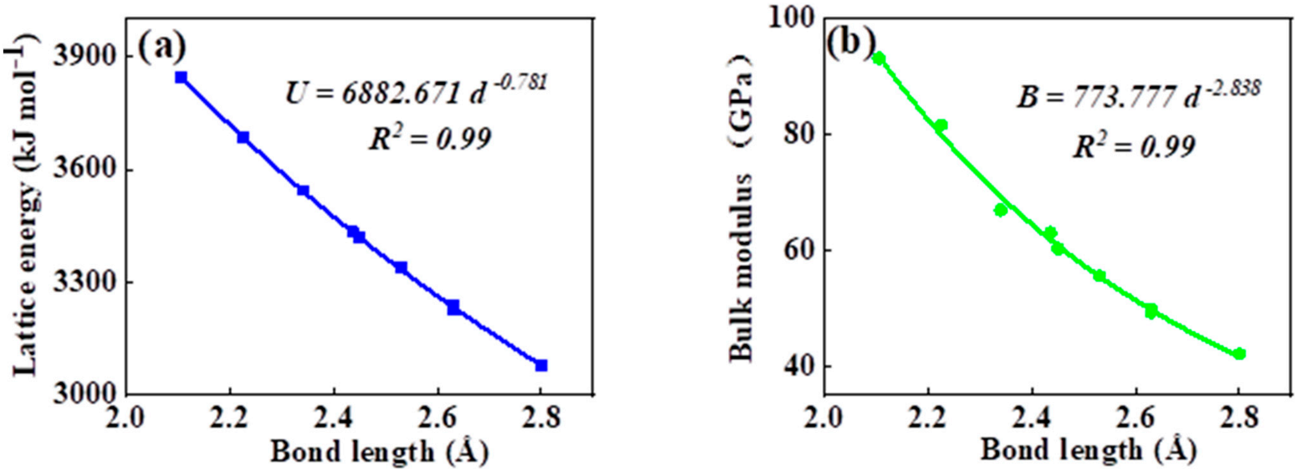

Figure 3. *Cont.*

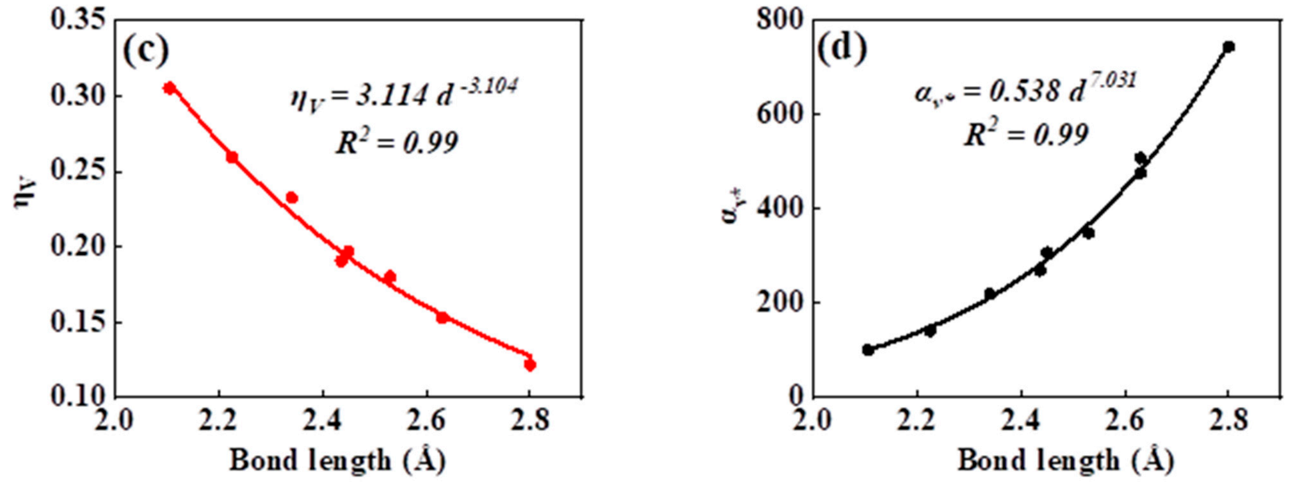

Figure 3. Plot of correlation between the lattice energy, (**a**) bulk modulus, (**b**) chemical hardness density, (**c**) product of electronic polarizability and molar volume, (**d**) and chemical bond length of tetrahedral coordinated crystals of group II–VI.

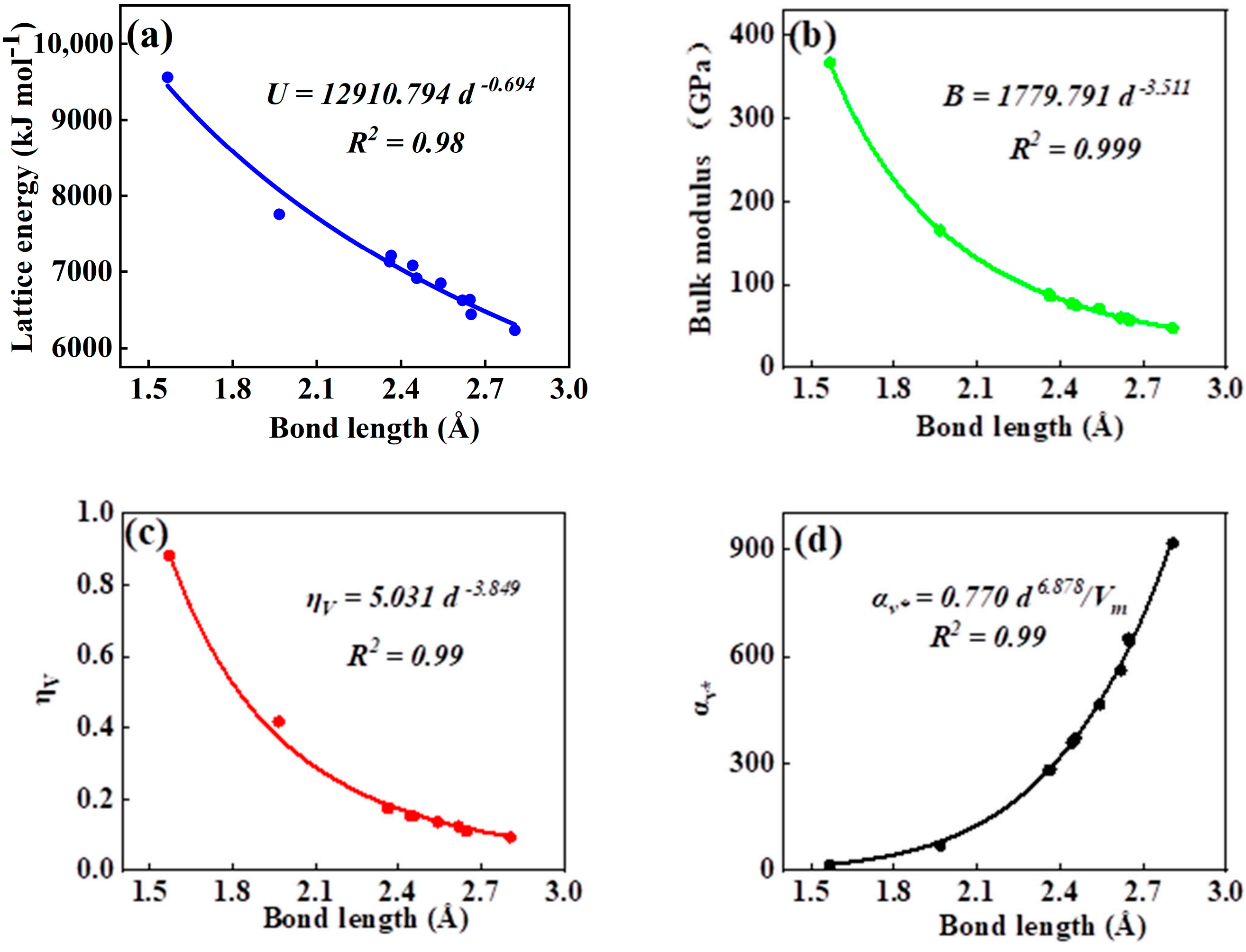

Figure 4. Plot of correlation between the lattice energy, (**a**) bulk modulus, (**b**) chemical hardness density, (**c**) product of electronic polarizability and molar volume, (**d**) and chemical bond length of tetrahedral coordinated crystals of group II–VI.

As was mentioned in the introduction, so far, many theoretical methods have been proposed for the estimation of the lattice energy, bulk modulus, chemical hardness, and electronic polarizability of inorganic ionic crystals. In order to show the practical significance of the present curve fitting model, we introduced such a mathematic equation into calculating the lattice energy, bulk modulus, chemical hardness, and electronic polarizability values of binary A^NB^{8-N} crystals. The calculated results of lattice energy, bulk modulus, and electronic polarizability of A^NB^{8-N} crystals by means of the abovementioned empirical equation $P = a{\cdot}d^b$ have been compared with the reported values in the literature, which are plotted and presented in Figure 5a–d. As shown in Figure 5, we can see that a remarkable linear correlation between the estimated values and the corresponding data evaluated in the literature is found ($R^2 > 0.9$). Hence, it is obvious that the calculation of these physicochemical parameters, such as lattice energy, bulk modulus, and electronic polarizability, can be expressed in terms of the chemical bond length of A^NB^{8-N} crystals on the basis of empirical fitting relation $P = a{\cdot}d^b$.

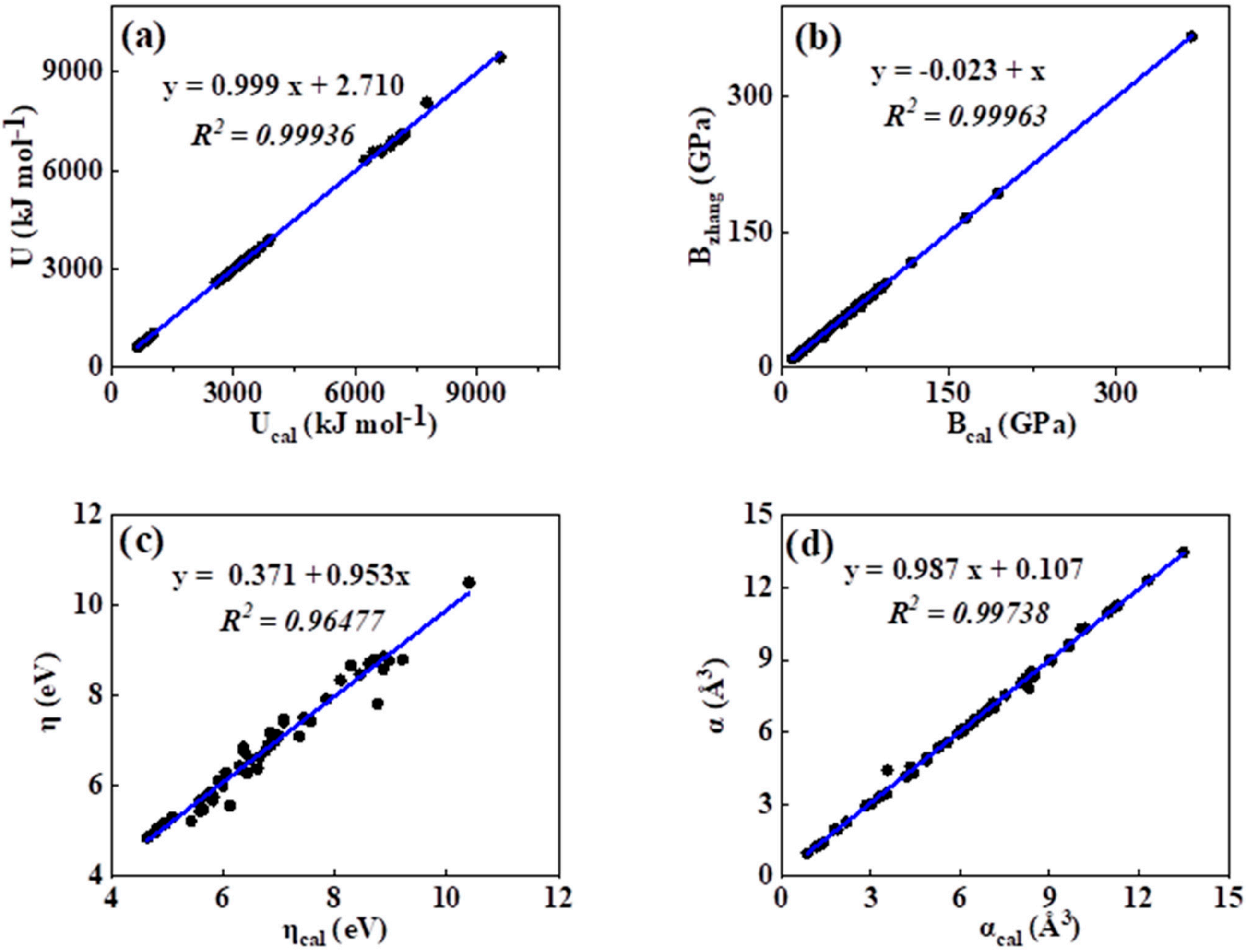

Figure 5. Plot of correlation between the present calculated values and the date reported in the literature. (**a**) lattice energy, (**b**) bulk modulus, (**c**) chemical hardness, (**d**) electronic polarizability).

4. Conclusions

In summary, the purpose of the present paper is to propose a facile method for the comprehensive estimation of the lattice energy, bulk modulus, electronic polarizability, and chemical hardness of inorganic crystals based on simple structure parameters for exploring the intrinsic relationships between the structure and property of solid matters. This new method demonstrates that there is a good mathematical relationship between the lattice energy, bulk modulus, electronic polarizability, chemical hardness, and chemical bond length of binary $A^N B^{8\text{-}N}$ crystals. The normal mathematical expression between these physicochemical parameters and chemical bond length is $P = a \cdot d^b$; a and b depend on the type of crystals and the relevant squares of the correlation coefficient R^2 have been given to measure the effectiveness of the least squares fitting. The new data on lattice energy, bulk modulus, and electronic polarizability were calculated by using empirical equations. The calculated results are in good agreement with the values reported in the previous literature. It is clear from the obtained results that the present method allows for easy evaluation of the lattice energy, bulk modulus, electronic polarizability, and chemical hardness of binary $A^N B^{8\text{-}N}$ crystals using a mathematic fitting model without the need for ab initio calculations and complex structure parameters. Finally, it should be noted that further studies about the correlation among lattice energy, bulk modulus, electronic polarizability, and chemical bond length are still necessary for complex crystals. Furthermore, we will search for other physicochemical parameters that are closely related to chemical bond length.

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