

The Lattice Constant of Anti-Perovskites

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ABSTRACT

The evaluation of structural properties of new materials, Ionic radii and quantities are useful parameters and the average ionic radii r_{av} of any compound is key parameter for calculating physical properties. In this paper I have presented the structural property (lattice constant values) for anti-perovskites with the average ionic radii r_{av} (Å). The lattice constant of these compounds exhibits a linear relationship when plotted on a scale against the average ionic radii r_{av} (Å), but fall on straight line according to the average ionic radii r_{av} of the compounds. We have applied the proposed relation $A^+_3 O^{2-}_6 X^-$ (A: is the univalent cation, O^{2-} : is oxygen, and X: is halides or a CN⁻ ion) and found a better agreement with the experimental data as compared to the values evaluated by earlier researchers. A new relationship between the lattice constant and ionic radii is proposed for the present paper.

Keywords: Lattice constants, ionic radii, anti-perovskites.

I. INTRODUCTION

In the recent years there has been an increasing attention in study of perovskites because of their use and application in the field of solar cells, superconductivity, insulator, metal-transition, ionic conduction characteristics, dielectric properties and ferro elasticity. Perovskite 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. These solids are currently gaining considerable importance in the field of electrical ceramics, refractories, geophysics, astrophysics, particle accelerators, fission, fusion reactors, heterogeneous catalysis etc [1-4].

During the last few years, many experimental and theoretical investigations were devoted to the study of perovskite solids: typically, ABX_3 (A: large cation with different valence, B: transition metal and X: oxides and halides). In perovskite structures, which is shown in figure 1(a), B cations are coordinated by six X anions, while A cations present coordination number 12(also coordinated by X anions). The X anions have coordination number 2, being coordinated by two cations, since the distance A-X is about 40% larger than the B-X bond distance. The cubic perovskite is called the ideal perovskite, which is the subject of this study. This class of materials has great potential for a variety of device applications due to their simple crystal structures and unique ferroelectric and dielectric properties. The structural, dielectric and optical properties of the perovskites are very important. The energy gap lies in the visible region of the spectrum and this is one reason why these materials are interesting [6-12]. However, there are very few studies that have focused on the evolution of the bonding mechanism of ferroelectric perovskite materials.

Ionic radii and quantities deduced from them are useful parameters for the evaluation of properties of new materials. For example, Goldschmidt's tolerance factor t serves as a discriminating parameter of classifying perovskites in terms of structure modifications and the resulting physical properties. Lattice constant of these solids may be measured by experimental process such as X-ray, electron or neutron diffraction techniques. However, these techniques are usually complicated, difficult and time-consuming. Advances in high performance computing techniques allow materials scientists to evaluate lattice constant based on empirical methods. Empirical relations have become widely recognized as the method of choice for computational solid-state studies. In modern high-speed computer techniques, they allow researchers to investigate many structural and physical properties of materials only by computation or simulation instead of by traditional experiments. 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. Empirical concepts such as valence, empirical radii, electronegativity, ionicity and plasmon energy are then useful [13,14]. 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.

Recently, the authors [15-21] have been evaluated the electronic, mechanical and optical properties of binary and complex crystals with the help of ionic charge theory of solids. 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. Therefore, we thought it would be of interest to give an alternative explanation for lattice constants of anti-perovskite solids.

THEORY, RESULTS AND DISCUSSION

The lattice constant values for anti-perovskite solids are of recognized importance, owing to the development of new solids designed for different applications, such as ferroelectric thin films, microwave and semiconductor technologies etc. Some empirical models were established that can predict lattice constants of antiperovskites from selected atomic properties of their constituent elements. Recently, the methodology developed by Jiang et. al. [6], which allows one to predict the lattice constants of cubic perovskites by using the known ionic radii of the cations and anion. According to him the lattice constant may be determine by the following relation,

$$a = 1.8836 (r_B + r_X) + 1.4898 [r_A + r_X / \sqrt{2} (r_B + r_X)] - 1.2062 \quad (1)$$

Where r_A , r_B and r_X are the ionic radii of A, B and X_3 respectively.

According to C. Z. Ye et al [22], the lattice constant of the ideal perovskite oxides (ABO_3) can be linearly correlated to some atomic parameters as,

$$a = 0.3166 r_A + 1.422 r_B - 0.1708 X_A + 0.0562 X_B - 0.0066 (Z_B - Z_A) + 2.706 \quad (2)$$

where r_A , r_B , X_A , X_B , Z_A and Z_B are the ionic radii, electronegativity and valence number of ion A and B, respectively. Any change in the crystallographic environment of an atom is related to core electrons via the valence electrons. The change in wave function that occurs for the outer electrons usually means a displacement of electric charge in the valence shell so that the interaction between valence, shell and core electrons is changed. This leads to a change in binding energy of the inner electron and to a shift in the position of the absorption edge. Because, equation (2), depends on the number of valence electrons and ionic charge also depends on the number of valence electrons, which changes when a metal forms a compound. Therefore, we thought it would be of interest to give an alternative explanation for lattice constants of cubic perovskite solids in terms of ionic charge. The lattice constants of perovskite solids exhibit a linear relationship when plotted against average ionic radii r_{av} (Å), but fall on different straight lines according to the ionic charge product of the compounds, which is presented in figure 1. In figure 1, we observe that in the plot of experimental lattice constants and average ionic radii, the perovskite oxides lie on lines nearly parallel to the line for perovskite halides. From the figure 1, it is quite obvious that the lattice constant trends in these compounds increases with increases average ionic radii and fall on straight lines according to the ionic charge product of the solids.

For calculation of the unit lattice constants in the cubic halide perovskites of ABX_3 composition, the following formula was derived.[5]

$$a_{calc} = 0.481R_A + 1.228R_B + 1.802R_X, \quad (3)$$

R_A , R_B , and R_X are the radii of the A, B, and X ions from the Shannon system for 52 known cubic halide perovskites, Using this idea to get better agreement with experimental and theoretical data for the lattice constant of perovskite solids equations (1), (2) and (3) may be extended as

$$a = k. r_{av} \quad (4)$$

Where k is the constant these values for cubic anti-perovskite solids is 3.25, r_{av} is the average ionic radii of antiperovskites in Å and it can be calculated by $r_{av} = (r_A + r_B + r_X) / 3$. In perovskite structures, which is shown in figure (a), B cations are coordinates by six X anions, while A cations present coordination number 12 (also

coordinated by X anions). The X anions have coordination number 2, being coordinated by two B cations, since the distance A—X is about 40% larger than the B—X bond distance.

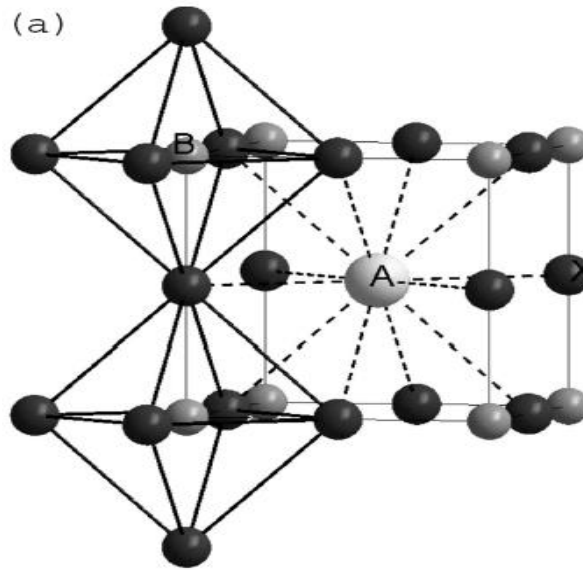


Figure (a). Perovskite Structure

Basically, in the proposed relation we have been used the average of cation A, B and anion X. The values so obtained are presented in the following tables 1. The main advantage of equation (4) is the simplicity of the formula, which does not require any experimental data except the ionic radii of perovskite solids. We note that the evaluated values are in close agreement with the experimental and theoretical data as compared to the values reported by previous researchers so far. These results show that our current method is quite reasonable and can give us a useful guide in calculating and predicting of the more complex class of antiperovskites solids.

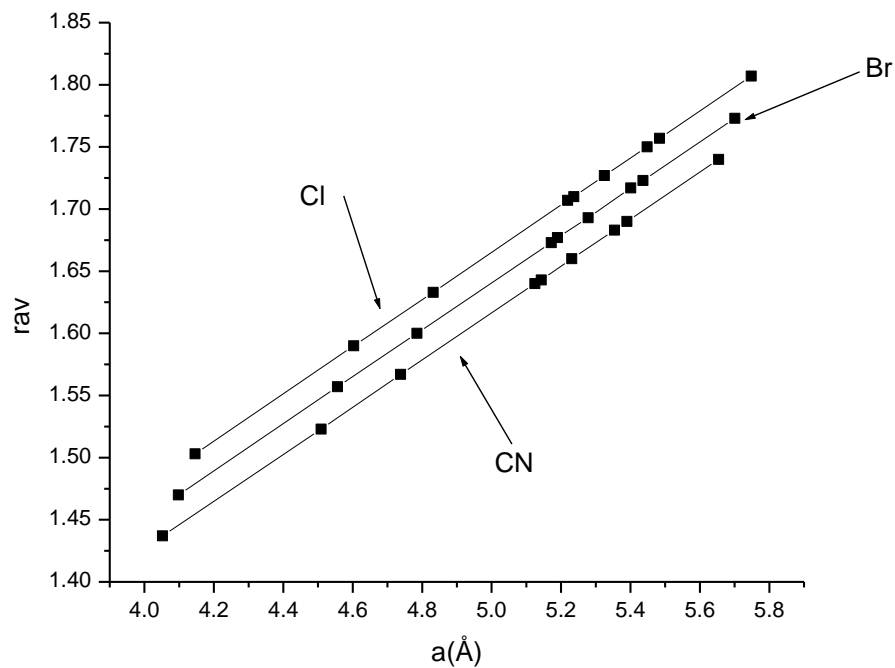


Figure 1. Plot of a (lattice constant in Å) against r_{av} (average ionic radii in Å) for antiperovskites. In the plots of a and r_{av} , antiperovskites lie on lines nearly parallel to the line for anti-perovskite. In this plot all experimental data (lattice constant and ionic radii) are taken from reference [5].

Table no 1 In this table I have presented the values of lattice constant (in Å) for anti-perovskite solids.

Solids	r_A (Å) [5]	r_B (Å) [5]	r_X (Å) [5]	a (Å) cal. [5]	a (Å) [This work]	% error
Cs ₃ OCl	1.67	1.35	2.2	5.654	5.66	-0.02
Rb ₃ OCl	1.52	1.35	2.2	5.39	5.49	-1.90
Tl ₃ OCl	1.50	1.35	2.2	5.354	5.47	-2.18
(NH ₄) ₃ OCl	1.43	1.35	2.2	5.231	5.40	-3.14
K ₃ OCl	1.38	1.35	2.2	5.143	5.34	-3.85
Au ₃ OCl	1.37	1.35	2.2	5.125	5.33	-4.00
Ag ₃ OCl	1.15	1.35	2.2	4.738	5.09	-7.46
Na ₃ OCl	1.02	1.35	2.2	4.509	4.95	-9.80
Li ₃ OCl	0.76	1.35	2.2	4.052	4.67	-15.23
Cs ₃ OBr	1.67	1.35	2.3	5.701	5.76	-1.09
Rb ₃ OBr	1.52	1.35	2.3	5.436	5.60	-3.03
Tl ₃ OBr	1.50	1.35	2.3	5.401	5.58	-3.30
(NH ₄) ₃ OBr	1.43	1.35	2.3	5.278	5.50	-4.27
K ₃ OBr	1.38	1.35	2.3	5.19	5.45	-4.99
Au ₃ OBr	1.37	1.35	2.3	5.172	5.44	-5.15
Ag ₃ OBr	1.15	1.35	2.3	4.785	5.20	-8.67
Na ₃ OBr	1.02	1.35	2.3	4.556	5.06	-11.04
Li ₃ OBr	0.76	1.35	2.3	4.098	4.78	-16.58
Cs ₃ O(CN)	1.67	1.35	2.3	5.701	5.76	-1.09
Rb ₃ (CN)	1.52	1.35	2.3	5.436	5.60	-3.03
Tl ₃ (CN)	1.50	1.35	2.3	5.401	5.58	-3.30
(NH ₄) ₃ (CN)	1.43	1.35	2.3	5.278	5.50	-4.27
K ₃ (CN)	1.38	1.35	2.3	5.19	5.45	-4.99
Au ₃ (CN)	1.37	1.35	2.3	5.172	5.44	-5.15
Ag ₃ (CN)	1.15	1.35	2.3	4.785	5.20	-8.67
Na ₃ (CN)	1.02	1.35	2.3	4.556	5.06	-11.04
Li ₃ (CN)	0.76	1.35	2.3	4.098	4.78	-16.58
Cs ₃ OI	1.67	1.35	2.4	5.748	5.87	-2.15
Rb ₃ OI	1.52	1.35	2.4	5.484	5.71	-4.11
Tl ₃ OI	1.50	1.35	2.4	5.448	5.69	-4.40
(NH ₄) ₃ OI	1.43	1.35	2.4	5.325	5.61	-5.38
K ₃ OI	1.38	1.35	2.4	5.237	5.56	-6.12
Au ₃ OI	1.37	1.35	2.4	5.219	5.55	-6.28
Au ₃ OI	1.15	1.35	2.4	4.832	5.31	-9.86
Na ₃ OI	1.02	1.35	2.4	4.603	5.17	-12.26
Li ₃ OI	0.76	1.35	2.4	4.146	4.89	-17.84

CONCLUSIONS

The conclusion is that the average ionic radii r_{av} of any compound is key parameter for calculating physical properties. Furthermore, we found that in the compounds investigated here, the lattice constant exhibits a linear relationship when plotted graph against the average ionic radii r_{av} (Å), but fall on four straight lines, which is presented in figure 1. We observe that in the plot of lattice constant and ionic radii, the halides and CN^- anti-perovskite oxides lie on lines nearly parallel to the line for the halides antiperovskites and the CN^- anti-perovskites lie on lines nearly parallel to the line for the perovskite halides. From the results and discussion obtained by using the proposed empirical relation, it is quite obvious that the lattice constant reflecting the structural property can be expressed in terms of the ionic radii of these materials. The calculated values are presented in tables 1. According to this idea we may evaluate all-important properties of anti-perovskite solids using their average ionic radii, which are basic parameters. An excellent agreement between the author's calculated values of lattice constant and the values reported by different researchers has been found. It is also to be noteworthy that proposed empirical relation is simpler, widely applicable and values obtained are in better agreement with experiment data as compared to the empirical relations proposed by previous researchers [5]. I have been reasonably successful in calculating lattice constant using the ionic radii of the materials for anti-perovskite solids. It is natural to say that this model can easily be extended to rock-salt, zinc blende and chalcopyrite crystals, for which the work is in progress and will be appearing in forthcoming paper. Hence it is possible to predict the order of physical properties of binary and complex structured solids from their average ionic radii. The method presented in this work will be helpful to material scientists for finding new materials with desired lattice constant among a series of structurally similar materials.

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