



Calculation Of Lattice Constant Of Orthorhombic Perovskite Solids

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Abstract:

In this paper, the relation between lattice constant of orthorhombic perovskites solids and atomic radii is examined and new empirical equations for the relationship are proposed. These enable us to achieve improved prediction performance of the lattice constant of structurally known perovskites. The average absolute relative error in the predicted 'a' lattice constant so derived is expected to be about 3.40%. We have applied the proposed relation to ABX₃ (A: large cation, B: transition metal, X: anion) and found a better agreement with the experimental data as compared to the value evaluated by earlier researchers.

Keywords: lattice constant, perovskites solids, ABX₃.

1. Introduction

The term 'Perovskites' is used to describe an ABX₃ arrangement of cations and an anion (typically oxygen) that is isomorphous with CaTiO₃. In the ideal cubic form, the A- site is coordinated to 12 anions to form cubooctahedral coordination polyhedral. The B- site is coordinated to six anions. The anions are coordinated to two B – site cations and four A-site cations about 41% further away. The anions octahedral are corner-shared, which is a essential feature of all perovskites [1].

A large number of perovskite – type oxides have been studied because of their interesting properties like superconductivity, insulator – metal transition, ionic conduction characteristics, dielectric properties and ferroelasticity [1-3]. Additionally, they have received great attention as high temperature proton conductors with the possibility of applications in fuel cells or hydrogen sensors and these solids are currently gaining considerable importance in the field of

electrical ceramics, refractories, geophysics, astrophysics, particle accelerators, fission, fusion reactors, heterogeneous catalysis, etc. [4,5,6,7]. As the most important components in the Earth's mentle, ABO₃ (orthorhombic) perovskites have been intensively studied. The understanding of the mechanisms that lead to the stabilization of the various perovskite structures has been a long-standing problem in material science. Due to the frequent occurrence of perovskites, and also to the great variety of properties presented by these system, the accurate and transparent description of the driving forces toward the high and low symmetry crystal structures is of general interest. During the last few years, many experimental and theoretical investigations were devoted to study of perovskite solids. Oxide perovskites with general stoichiometry ABO₃ are relatively simple structures comprised of corner-linked BO₆cation-centredoctahedra with larger A cations occupying the voids within the three-

dimensional framework of octahedral. In the ideal cubic perovskite structure, the A cations are surrounded by 12 equidistant oxygen ions. Many ABO_3 compounds crystallize with the orthorhombic distortion of the perovskite structure. The orthorhombic structures are derived from the ideal cubic structure via the tilting and distortion of the BO_6 octahedra [8]. From the crystal chemistry point of view, the two different perovskites of ABO_3 compound have very similar local structures, in which each B atom is octahedrally co-ordinated by O

atoms, as shown in Fig. 1 [9-12]. Orthorhombic perovskite is basically built up from the corresponding cubic perovskite. This class of materials has great potential for a variety of device applications due to their crystal structures and unique ferroelectric and dielectric properties. The structural, dielectric, optical and mechanical 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 [5, 8-12].

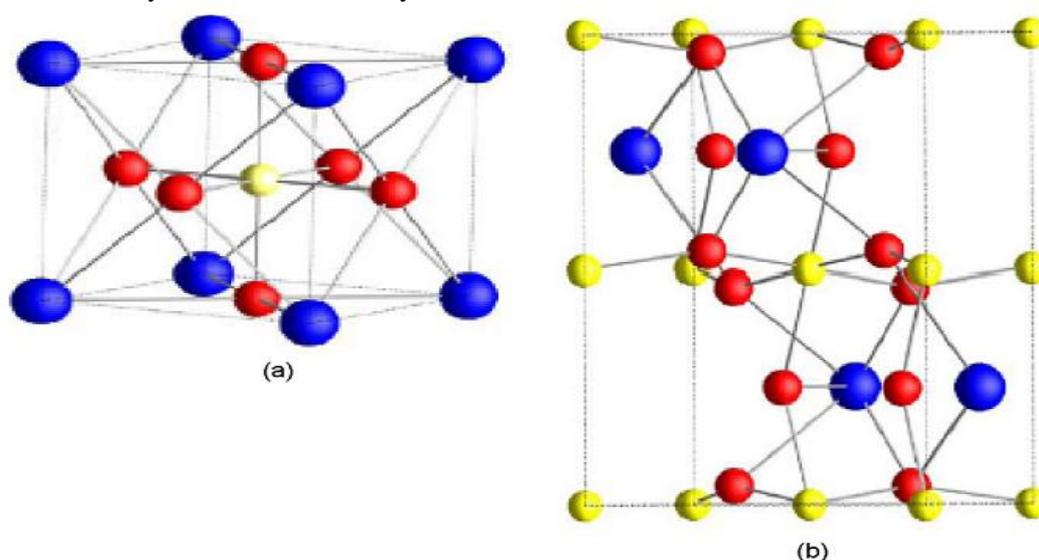


Fig. 1. Schematic structures of cubic perovskite (a), orthorhombic perovskite (b) of ABO_3 compounds. Large filled blue circles represent A, small yellow B and small red O atoms.

Perovskite oxides exhibit a wide range of physical properties, such as high dielectric, piezoelectric, pyroelectric, ferroelectric/multiferroic, non-linear optical, ferromagnetic, colossal/giant magnetic resistant and high-temperature superconducting properties [13]. Because of the wide spectrum of electronic, optical, magnetic and structural properties of perovskite oxides, these oxides and their hetero-structures / super-lattices will be core elements of next generation functional devices for sensors, signal processing, electric/optical circuits and energy conversion [14-17]. In this study, we

will collect all possible lattice constant data for orthorhombic perovskite oxides and determine the atomic properties that are significantly correlated to the lattice constants. At the last, we build an empirical model for the prediction of lattice constants of compounds from the radius of ions.

2. Theory, Results and Discussion

The correct values of lattice constants for perovskite solids is of recognized important for analyzing the structure and properties of materials, such as ferroelectric thin films, microwave and semiconductor technologies etc. [5]. Some empirical models were established that can predict lattice

constant of perovskites from selected atomic properties of their constituent elements. Recently, the methodology developed by Jiang et al. [6] which allows one to predict the lattice constant of cubic perovskites by using the known ionic radii of the cations and anion. According to them, the lattice constant may be determine by the following relation,

$$a = 1.8836(r_B + r_X) + [(r_A + r_X)/\sqrt{3}(r_B + r_X)] - 1.2062 \quad (1)$$

where r_A , r_B , and r_X are the ionic radii of A, B and X_3 ($X = O, F, Cl, Br$ and I), respectively.

According to Ye et al. [18], the lattice constant of the idea perovskite oxides (ABO_3) can be linearly correlated to some atomic parameters as,

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

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.

Recently, a methodology developed by Ubic and Subodh [19] to predict the lattice constant of orthorhombic perovskites by using the two variables ($r_A + r_O$) and ($r_B + r_O$) where r_A , r_B and r_O are the ionic radii of A, B and O_3 . According to them, the lattice constant may be determine by the following relation,

$$a = 1.514921(r_A + r_O) + 1.310215(r_B + r_O) - 0.86631 \quad (3)$$

$$b = 0.082623(r_A + r_O) + 2.101275(r_B + r_O) - 1.114993 \quad (4)$$

$$c = 1.625883(r_A + r_O) + 2.470594(r_B + r_O) - 1.20754 \quad (5)$$

Now in this work, the authors also give an empirical relation which is based on only one variable. According to authors,

$$a = [r_A + r_B + (r_O)^{3.9}] \quad (6)$$

Where r_A , r_B and r_O are the ionic radii of A, B and O_3 .

Table for the value of lattice constant ‘a’ orthorhombic perovskites solids.

Sr. No.	Solids	r_A (Å) [5]	r_B (Å) [5]	r_X (Å) [6]	a (Å) Expt. [20]	a (Å) [this work]	% error of a
1	NaUO ₃	1.39	0.76	1.4	5.775	5.86	1.5
2	NaTaO ₃	1.39	0.64	1.4	5.494	5.74	4.6
3	NaNbO ₃	1.39	0.64	1.4	5.51	5.74	4.3
4	NaPaO ₃	1.39	0.78	1.4	5.82	5.88	1.1
5	CaMoO ₃	1.34	0.65	1.4	5.45	5.70	4.7
6	CaNbO ₃	1.34	0.68	1.4	5.56	5.73	3.1
7	CaSnO ₃	1.34	0.69	1.4	5.519	5.74	4.1
8	CaHfO ₃	1.34	0.71	1.4	5.568	5.76	3.5
9	CaZrO ₃	1.34	0.72	1.4	5.587	5.77	3.4

10	CaUO ₃	1.34	0.89	1.4	5.78	5.94	2.8
11	BaPbO ₃	1.61	0.78	1.4	6.024	6.10	1.3
Sr. No.	Solids	r_A (Å) [5]	r_B (Å) [5]	r_X (Å) [6]	a (Å) Expt. [20]	a (Å) [this work]	% error of a
12	SrUO ₃	1.44	0.89	1.4	6.01	6.04	0.6
13	SrIrO ₃	1.44	0.63	1.4	5.58	5.78	3.6
14	SrHfO ₃	1.44	0.71	1.4	5.785	5.86	1.4
15	SrZrO ₃	1.44	0.72	1.4	5.792	5.87	1.4
16	SrPbO ₃	1.44	0.78	1.4	5.86	5.93	1.2
17	SrCeO ₃	1.44	0.87	1.4	5.986	6.02	0.6
18	LaCrO ₃	1.36	0.62	1.4	5.515	5.69	3.2
19	LaGaO ₃	1.36	0.62	1.4	5.526	5.69	3.0
20	LaFeO ₃	1.36	0.65	1.4	5.556	5.72	2.9
21	LaVO ₃	1.36	0.64	1.4	5.54	5.71	3.1
22	LaMnO ₃	1.36	0.65	1.4	5.529	5.72	3.4
23	LaRhO ₃	1.36	0.67	1.4	5.524	5.74	3.9
24	LaTiO ₃	1.36	0.67	1.4	5.546	5.74	3.6
25	LaScO ₃	1.36	0.75	1.4	5.678	5.82	2.5
26	LaInO ₃	1.36	0.80	1.4	5.723	5.87	2.6
27	LaYO ₃	1.36	0.65	1.4	5.877	5.72	2.7
28	CeCrO ₃	1.34	0.62	1.4	5.475	5.67	3.6
29	CeFeO ₃	1.34	0.65	1.4	5.519	5.70	3.3
30	CeVO ₃	1.34	0.64	1.4	5.486	5.69	3.8
31	CeMnO ₃	1.3	0.65	1.4	5.532	5.66	2.3
32	CeTiO ₃	1.34	0.67	1.4	5.513	5.72	3.8

33	PrCrO3	1.3	0.62	1.4	5.484	5.63	2.7
Sr. No.	Solids	r_A(Å) [5]	r_B (Å) [5]	r_X (Å) [6]	a (Å)Expt. [20]	a(Å) [this work]	% error of a
34	PrGaO3	1.3	0.62	1.4	5.458	5.63	3.2
35	PrFeO3	1.3	0.65	1.4	5.495	5.66	3.0
36	PrVO3	1.3	0.64	1.4	5.487	5.65	3.1
37	PrMnO3	1.3	0.65	1.4	5.545	5.66	2.1
38	PrTiO3	1.3	0.67	1.4	5.499	5.68	3.4
39	PrCoO3	1.3	0.55	1.4	5.331	5.56	4.3
40	PrScO3	1.3	0.75	1.4	5.615	5.76	2.6
41	PrAlO3	1.3	0.54	1.4	5.347	5.55	3.8
42	NdCrO3	1.27	0.62	1.4	5.425	5.60	3.2
43	NdGaO3	1.27	0.62	1.4	5.431	5.60	3.2
44	NdFeO3	1.27	0.65	1.4	5.441	5.63	3.5
45	NdVO3	1.27	0.64	1.4	5.451	5.62	3.2
46	NdTiO3	1.27	0.67	1.4	5.487	5.65	3.1
47	NdCoO3	1.27	0.55	1.4	5.336	5.53	3.6
48	NdScO3	1.27	0.75	1.4	5.574	5.73	2.8
49	NdInO3	1.27	0.80	1.4	5.627	5.78	2.8
50	PmCrO3	1.25	0.62	1.4	5.4	5.58	3.3
51	PmScO3	1.25	0.75	1.4	5.56	5.71	2.7
52	PmInO3	1.25	0.80	1.4	5.7	5.76	1.1
53	SmAlO3	1.24	0.54	1.4	5.285	5.49	3.9
54	SmCrO3	1.24	0.62	1.4	5.367	5.57	3.8
55	SmGaO3	1.24	0.62	1.4	5.369	5.57	3.8

Sr. No.	Solids	r_A (Å) [5]	r_B (Å) [5]	r_X (Å) [6]	a (Å) Expt. [20]	a (Å) [this work]	% error of a
56	SmFeO3	1.24	0.65	1.4	5.394	5.60	3.8
57	SmVO3	1.24	0.64	1.4	5.393	5.59	3.7
58	SmMnO3	1.24	0.65	1.4	5.359	5.60	4.5
59	SmTiO3	1.24	0.67	1.4	5.468	5.62	2.9
60	SmCoO3	1.24	0.55	1.4	5.289	5.50	4.0
61	SmScO3	1.24	0.75	1.4	5.53	5.70	3.1
62	SmInO3	1.24	0.80	1.4	5.589	5.75	3.0
63	EuAlO3	1.23	0.54	1.4	5.271	5.48	4.0
64	EuCrO3	1.23	0.62	1.4	5.34	5.56	4.1
65	EuGaO3	1.23	0.62	1.4	5.351	5.56	4.0
66	EuFeO3	1.23	0.65	1.4	5.371	5.59	4.1
67	EuScO3	1.23	0.75	1.4	5.51	5.69	3.3
68	EuInO3	1.23	0.80	1.4	5.567	5.74	3.2
69	GdAlO3	1.22	0.54	1.4	5.253	5.47	4.1
70	GdCrO3	1.22	0.62	1.4	5.312	5.55	4.5
71	GdGaO3	1.22	0.62	1.4	5.322	5.55	4.4
72	GdFeO3	1.22	0.65	1.4	5.351	5.58	4.3
73	GdVO3	1.22	0.64	1.4	5.343	5.57	4.3
74	GdTiO3	1.22	0.67	1.4	5.407	5.60	3.7
75	GdScO3	1.22	0.75	1.4	5.487	5.68	3.5
76	GdInO3	1.22	0.80	1.4	5.548	5.73	3.4
77	TbAlO3	1.2	0.54	1.4	5.22	5.45	4.4
Sr. No.	Solids	r_A (Å) [5]	r_B (Å) [5]	r_X (Å) [6]	a (Å) Expt. [20]	a (Å) [this work]	% error of a

78	TbGaO ₃	1.2	0.62	1.4	5.307	5.53	4.3
79	TbFeO ₃	1.2	0.65	1.4	5.326	5.56	4.4
80	TbTiO ₃	1.2	0.67	1.4	5.388	5.58	3.6
81	DyAlO ₃	1.19	0.54	1.4	5.21	5.44	4.4
82	DyGaO ₃	1.19	0.62	1.4	5.282	5.52	4.6
83	DyVO ₃	1.19	0.64	1.4	5.302	5.54	4.6
84	DyTiO ₃	1.19	0.67	1.4	5.361	5.57	4.0
85	DyScO ₃	1.19	0.75	1.4	5.43	5.65	4.0
86	DyInO ₃	1.19	0.80	1.4	5.519	5.70	3.4
87	HoTiO ₃	1.18	0.67	1.4	5.339	5.56	4.2
88	HoScO ₃	1.18	0.75	1.4	5.42	5.64	4.0
89	ErTiO ₃	1.17	0.67	1.4	5.318	5.55	4.4
90	TmTiO ₃	1.16	0.67	1.4	5.306	5.54	4.5
91	YbTiO ₃	1.15	0.67	1.4	5.293	5.53	4.6
92	LuTiO ₃	1.14	0.67	1.4	5.274	5.52	4.7
93	YTlO ₃	1.2	0.67	1.4	5.34	5.58	4.6
94	YScO ₃	1.2	0.75	1.4	5.431	5.66	4.2
95	YInO ₃	1.2	0.80	1.4	5.5	5.71	3.9

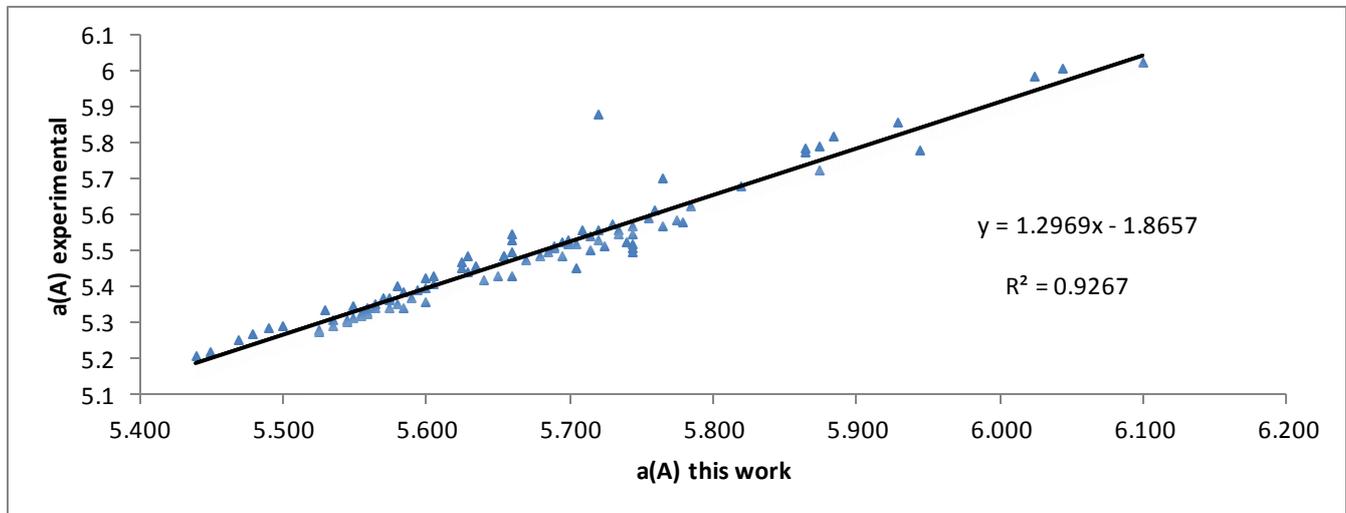


Fig. 2: Calculated lattice constant, $a(\text{\AA})$ this work, as a function of measured lattice constant, $a(\text{\AA})$ experimental. The solid line represents a perfect fit. The fit parameter for the data from this work is $R^2 = 0.9267$.

The main advantage of Eq. (6) is the simplicity of the formula, which does not require any experimental data except ionic radii of orthorhombic 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 orthorhombic perovskite solids.

3. Conclusions

New empirical relations (6) describing the relationship between ionic radii and orthorhombic lattice constant for perovskites have been derived. The results are illustrated graphically in Fig. 2. These formulae can be used to predict the lattice constants of orthorhombic perovskites with more accuracy than any other method yet reported.

4. References

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