

Prediction of lattice constant in cubic perovskites

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Abstract

Regularities of lattice constant in ideal perovskites are investigated by using a total of 132 ABX₃-type compounds, including oxides and halides. Two atomic properties; the sum of ionic radius of B and X atoms and the well known ‘tolerance factor’ (which is a function of ionic radius of A, B and X), were found very effective in reproducing the measured lattice constant through a linear combination of these two parameters ($R^2 = 0.995$). It is further indicated that these two parameters are linked to the crystal features of perovskite. The average error limits in predicting lattice constant, by using this empirical equation, are expected within 0.63%. It may be useful to design new substrates/buffer materials for compound semiconductor epitaxy, in which there is a requirement of lattice match between them and adjacent layers.

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1. Introduction

Compound semiconductors of III–V group, like GaAs, GaN and InP, attract increasing attentions because of their high carrier mobility, wide and direct bandgap [1–4]. However, it is still a challenge to fabricate large and high quality of their heteroepitaxial films, due to a considerable lattice mismatch [5] between the films and the growth substrate. For example, the lattice mismatch of GaAs, GaN and InP on Si substrate is –3.54%, 3.56% and 20.13%, respectively. Two research strategies are commonly adopted to reduce the lattice mismatch; either to select a new substrate whose lattice directly matches that of the film, or to introduce a buffer material between the substrate and the semiconductor film interface [5,6]. Therefore, it is of practical interest to derive a fast, easy and reliable solution for the prediction of lattice constant.

As one of the most abundant and widely investigated minerals, perovskite compounds are selected for this study, partly influenced by a recent success [1,6] of fabricating

large GaAs MESFETs on Si substrates using a SrTiO₃ (cubic perovskite) buffer layer. Perovskite and perovskite-related materials are also important crystal structure due to their diverse physical/chemistry properties [9,11,14] over a wide temperature range. For example, perovskites are known for their superconducting properties ((K,Ba)BiO₃), piezoelectric properties (Pb(Zr,Ti)O₃), relaxor ferroelectric properties ((Pb(Nb,Mg)O₃), dielectric properties (BaTiO₃), electro-optic properties ((Pb,Ln)(Zr,Ti)O₃), magneto-resistive properties (LaMnO₃), catalytic properties (LaCrO₃) and photonic conductivity (BaCeO₃).

In general, lattice constant can be measured using X-ray, electron or neutron diffraction techniques. However, it is usually a complicated, difficult and time-consuming process. Sometimes, it is very difficult if not impossible to prepare the form of single crystals of sufficient size and quality for conventional single-crystal X-ray diffraction studies [7]. Advances in high performance computing techniques allow materials scientists to calculate lattice constant based on first-principles quantum mechanism [8], however, it is still a computing intensive job which may not be within the reach of the majorities, due to either a lack of computing resource or computational skills. Recently,

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some empirical models were established that can predict lattice constant of perovskites from selected atomic properties of their constituent elements. On the basis of a bond–valence method, Lufaso and Woodward [9] recently developed a software package—SPuDS. The software is used to predict crystal structures of perovskites, from an input of their chemical stoichiometry. In China, Chen and his colleagues [10] used a pattern recognition/atomic parameter method to find the regularities of the formation and the lattice distortion of perovskites. Their results showed that the lattice constant of cubic perovskite oxides is linearly correlated to the ionic radius, valence electrons and electronegativities of constituent elements.

In this study, we will collect all possible lattice constant data for ideal perovskites, including oxides and halides, and determine the atomic properties that are significantly correlated to the lattice constants. Finally, we build an empirical model for the prediction of lattice constant of new compounds from the radius of ions.

2. Features of perovskites

Most ABX_3 compounds have a perovskite structure, named after the mineral $CaTiO_3$. In this structure ion A has a larger size than ion B, and most of the metallic ions in the periodic table can be taken as a brick of perovskites [11]. Although majority of the perovskite compounds are oxides or fluorides, other forms like heavier halides, sulfides, hydrides, cyanides, oxyfluorides and oxynitrides are also reported [12,13]. Previously, perovskite refer to the cubic crystal structure $Pm\bar{3}m$, which is composed of a three-dimensional framework of corner-sharing BX_6 octahedron. The A-site cation fills the 12 coordinate cavities formed by the BX_3 network and is surrounded by 12 equidistant anions [12], as seen in Fig. 1.

According to Lufaso and Woodward [9], a cubic perovskite can transform into other crystal structures through tilting the octahedral BX_6 , these resulted structures are closely related to the cubic perovskite. Today, all compounds with these 15 kinds of structures (one of them is the cubic structure) belong to the ‘perovskite’ catalogue. In order to discriminate the cubic structure from the general perovskite, now the cubic perovskite is called the ideal perovskite, which is the subject of this study.

In general, the stability of perovskites is often studied in term of the ‘tolerance factor’, t , which was introduced by Goldschmidt in 1920s

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}, \quad (1)$$

where r_A , r_B and r_X are the ionic radii of cation A, B and anion X, respectively. Geometrically, for an ideal perovskite, the ratio of D_{A-X} , the bond length of A–X bond, to D_{B-X} , the bond length of B–X bond, is $\sqrt{2}:1$. Thus, if the bond length is roughly assumed to be the sum of two ionic radii, the t -value of the ideal perovskite should be equal to 1.0. However, Goldschmidt found that, as an experimental

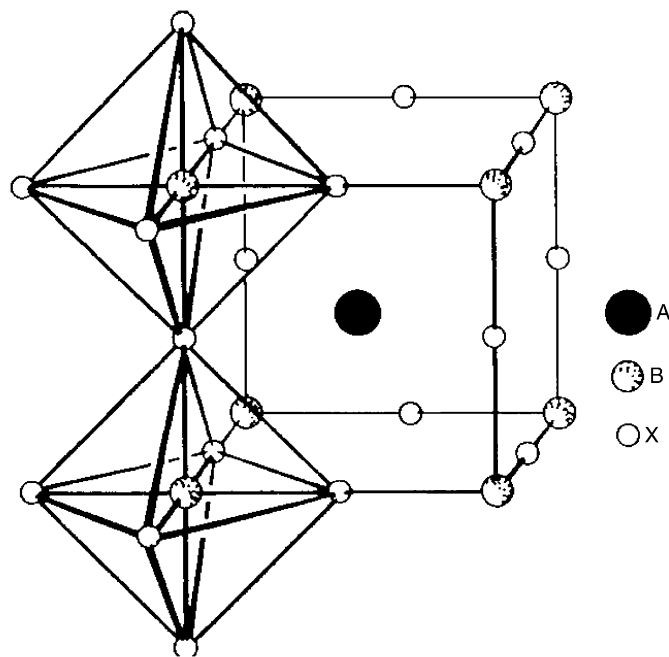


Fig. 1. Structure of an ideal perovskite ABX_3 . Note the corner-shared octahedron BX_6 , extending in three dimensions to form the framework.

fact, t values of most cubic perovskites are in the range of 0.8–0.9, and distorted perovskites occur in somewhere wider range of t . Goldschmidt’s tolerance factor t has been widely accepted as a criterion for the formation of the perovskite structure, up to now, almost all known perovskite compounds have t -values in the range of 0.75–1.00.

3. Data and results

A total of 132 ideal perovskites and their lattice constant are collected from various references: *The Major Ternary Structural Families* [12], *Inorganic Solid Fluorides* [15], *Structure and Bonding in Crystalline Materials* [16], and *Inorganic Compounds Structural Database (ICSD)* [17]. They are 77 oxides, 43 fluorides, 8 chlorides, 3 bromides and 1 iodide. Table 1 lists all these compounds with their lattice constant, a (in angstrom), tolerance factor, t , ionic radii r_A , r_B , r_X , of constituent ion A, B and X. The value of ionic radii used here is Shannon’s value with a coordination number of 6, most of them are cited from *Handbook of Chemistry and Physics* [18]. For those unavailable in this handbook, they are collected from *Elements* [19] and *Perovskites and High Tc Superconductors* [11].

In order to study the regularities of lattice constant in an ideal perovskite, its crystal structure is first examined, as in Fig. 1. For this structure the lattice constant, a , equals to the theoretical distance between two nearest neighbor B ions, D_{B-B} . This distance is two times the bond length between ion B and anion X, D_{B-X} . Assuming a bond length between two ions is the radius summation of the two ions,

Table 1
A total of 132 ideal perovskites and their lattice constants

No.	Compound	$a(\text{\AA})$	Citation	$r_A(\text{\AA})$	$r_B(\text{\AA})$	$r_X(\text{\AA})$	t	$2(r_B + r_X)$	$2(r_B + r_X) - a$	a_{pre}	error(%)
1	CsIO ₃	4.674	Ref. [12]	1.67	0.95	1.4	0.924	4.700	0.026	4.596	1.659
2	RbUO ₃	4.323	Ref. [12]	1.52	0.76	1.4	0.956	4.320	−0.003	4.286	0.845
3	KUO ₃	4.290	Ref. [12]	1.38	0.76	1.4	0.910	4.320	0.030	4.218	1.674
4	RbPaO ₃	4.368	Ref. [12]	1.52	0.78	1.4	0.947	4.360	−0.008	4.311	1.303
5	KPaO ₃	4.341	Ref. [12]	1.38	0.78	1.4	0.902	4.360	0.019	4.243	2.248
6	KTaO ₃	3.988	Ref. [12]	1.38	0.64	1.4	0.964	4.080	0.092	4.072	2.104
7	BaFeO ₃	3.994	Ref. [12]	1.35	0.59	1.4	0.977	3.980	−0.014	3.998	0.098
8	BaMoO ₃	4.040	Ref. [12]	1.35	0.65	1.4	0.949	4.100	0.060	4.068	0.702
9	BaNbO ₃	4.080	Ref. [12]	1.35	0.68	1.4	0.935	4.160	0.080	4.104	0.600
10	BaSnO ₃	4.116	Ref. [12]	1.35	0.69	1.4	0.930	4.180	0.064	4.117	0.016
11	BaHfO ₃	4.171	Ref. [12]	1.35	0.71	1.4	0.922	4.220	0.049	4.141	0.715
12	BaZrO ₃	4.193	Ref. [12]	1.35	0.72	1.4	0.917	4.240	0.047	4.154	0.941
13	BaIrO ₃	4.100	Ref. [17]	1.35	0.63	1.4	0.958	4.060	−0.040	4.045	1.351
14	EuTiO ₃	3.905	Ref. [17]	0.95	0.67	1.4	0.803	4.140	0.235	3.889	0.415
15	NaWO ₃	3.850	Ref. [17]	1.02	0.62	1.4	0.847	4.040	0.190	3.861	0.279
16	SnTaO ₃	3.880	Ref. [17]	0.93	0.68	1.4	0.792	4.160	0.280	3.892	0.303
17	SrMnO ₃	3.806	Ref. [12]	1.18	0.53	1.4	0.945	3.860	0.054	3.837	0.825
18	SrVO ₃	3.890	Ref. [16]	1.18	0.61	1.4	0.908	4.020	0.130	3.932	1.080
19	SrFeO ₃	3.850	Ref. [12]	1.18	0.59	1.4	0.917	3.980	0.130	3.908	1.505
20	SrTiO ₃	3.905	Ref. [12]	1.18	0.61	1.4	0.908	4.020	0.115	3.932	0.692
21	SrTcO ₃	3.949	Ref. [12]	1.18	0.65	1.4	0.890	4.100	0.151	3.981	0.810
22	SrMoO ₃	3.975	Ref. [12]	1.18	0.65	1.4	0.890	4.100	0.125	3.981	0.151
23	SrNbO ₃	4.016	Ref. [12]	1.18	0.68	1.4	0.877	4.160	0.144	4.018	0.059
24	SrSnO ₃	4.034	Ref. [12]	1.18	0.69	1.4	0.873	4.180	0.146	4.031	0.076
25	SrHfO ₃	4.069	Ref. [12]	1.18	0.71	1.4	0.865	4.220	0.151	4.056	0.312
26	CaVO ₃	3.767	Ref. [12]	1	0.61	1.4	0.844	4.020	0.253	3.838	1.876
27	BaPbO ₃	4.265	Ref. [12]	1.35	0.78	1.4	0.892	4.360	0.095	4.229	0.846
28	BaTbO ₃	4.285	Ref. [12]	1.35	0.76	1.4	0.900	4.320	0.035	4.204	1.900
29	BaPrO ₃	4.354	Ref. [12]	1.35	0.85	1.4	0.864	4.500	0.146	4.319	0.794
30	BaCeO ₃	4.397	Ref. [12]	1.35	0.87	1.4	0.857	4.540	0.143	4.346	1.165
31	BaAmO ₃	4.357	Ref. [12]	1.35	0.85	1.4	0.864	4.500	0.143	4.319	0.862
32	BaNpO ₃	4.384	Ref. [12]	1.35	0.87	1.4	0.857	4.540	0.156	4.346	0.872
33	BaUO ₃	4.387	Ref. [12]	1.35	0.89	1.4	0.849	4.580	0.193	4.372	0.335
34	BaPaO ₃	4.450	Ref. [12]	1.35	0.9	1.4	0.845	4.600	0.150	4.386	1.446
35	BaThO ₃	4.480	Ref. [12]	1.35	0.94	1.4	0.831	4.680	0.200	4.439	0.905
36	SrTbO ₃	4.180	Ref. [12]	1.18	0.76	1.4	0.845	4.320	0.140	4.121	1.420
37	SrAmO ₃	4.230	Ref. [12]	1.18	0.85	1.4	0.811	4.500	0.270	4.240	0.233
38	SrPuO ₃	4.280	Ref. [12]	1.18	0.86	1.4	0.807	4.520	0.240	4.253	0.623
39	SrCoO ₃	3.850	Ref. [12]	1.18	0.53	1.4	0.945	3.860	0.010	3.837	0.328
40	BaTiO ₃	4.012	Ref. [16]	1.35	0.61	1.4	0.967	4.020	0.008	4.021	0.227
41	CaTiO ₃	3.840	Ref. [16]	1	0.61	1.4	0.844	4.020	0.180	3.838	0.060
42	CeAlO ₃	3.772	Ref. [16]	1.01	0.54	1.4	0.878	3.880	0.108	3.757	0.407
43	EuAlO ₃	3.725	Ref. [16]	0.95	0.54	1.4	0.857	3.880	0.155	3.724	0.025
44	EuCrO ₃	3.803	Ref. [16]	0.95	0.62	1.4	0.823	4.040	0.237	3.824	0.558
45	EuFeO ₃	3.836	Ref. [16]	0.95	0.645	1.4	0.813	4.090	0.254	3.856	0.530
46	GdAlO ₃	3.710	Ref. [16]	0.94	0.54	1.4	0.853	3.880	0.170	3.719	0.233
47	GdCrO ₃	3.795	Ref. [16]	0.94	0.62	1.4	0.819	4.040	0.245	3.819	0.632
48	GdFeO ₃	3.820	Ref. [16]	0.94	0.645	1.4	0.809	4.090	0.270	3.851	0.816
49	KNbO ₃	4.007	Ref. [16]	1.38	0.64	1.4	0.964	4.080	0.073	4.072	1.620
50	LaAlO ₃	3.778	Ref. [16]	1.03	0.54	1.4	0.886	3.880	0.102	3.768	0.278
51	LaCrO ₃	3.874	Ref. [16]	1.03	0.62	1.4	0.851	4.040	0.166	3.866	0.208
52	LaFeO ₃	3.920	Ref. [16]	1.03	0.645	1.4	0.840	4.090	0.170	3.898	0.573
53	LaGaO ₃	3.874	Ref. [16]	1.03	0.62	1.4	0.851	4.040	0.166	3.866	0.208
54	LaRhO ₃	3.940	Ref. [16]	1.03	0.67	1.4	0.830	4.140	0.200	3.930	0.266
55	LaTiO ₃	3.920	Ref. [16]	1.03	0.67	1.4	0.830	4.140	0.220	3.930	0.243
56	LaVO ₃	3.910	Ref. [16]	1.03	0.64	1.4	0.842	4.080	0.170	3.891	0.481
57	NaAlO ₃	3.730	Ref. [16]	1.02	0.54	1.4	0.882	3.880	0.150	3.762	0.860
58	NaTaO ₃	3.881	Ref. [16]	1.02	0.64	1.4	0.839	4.080	0.199	3.886	0.129
59	NdAlO ₃	3.752	Ref. [16]	0.98	0.54	1.4	0.867	3.880	0.128	3.740	0.310
60	NdCoO ₃	3.777	Ref. [16]	0.98	0.55	1.4	0.863	3.900	0.123	3.753	0.647
61	NdCrO ₃	3.835	Ref. [16]	0.98	0.62	1.4	0.833	4.040	0.205	3.840	0.127
62	NdFeO ₃	3.870	Ref. [16]	0.98	0.645	1.4	0.823	4.090	0.220	3.872	0.046
63	NdMnO ₃	3.800	Ref. [16]	0.98	0.645	1.4	0.823	4.090	0.290	3.872	1.889
64	PrAlO ₃	3.757	Ref. [16]	0.99	0.54	1.4	0.871	3.880	0.123	3.746	0.298
65	PrCrO ₃	3.852	Ref. [16]	0.99	0.62	1.4	0.837	4.040	0.188	3.845	0.180
66	PrFeO ₃	3.887	Ref. [16]	0.99	0.645	1.4	0.826	4.090	0.203	3.877	0.259

No.	Compound	$a(\text{\AA})$	Citation	$r_A(\text{\AA})$	$r_B(\text{\AA})$	$r_X(\text{\AA})$	t	$2(r_B + r_X)$	$2(r_B + r_X) - a$	a_{pre}	error(%)
67	PrGaO ₃	3.863	Ref. [16]	0.99	0.62	1.4	0.837	4.040	0.177	3.845	0.464
68	PrMnO ₃	3.820	Ref. [16]	0.99	0.645	1.4	0.826	4.090	0.270	3.877	1.490
69	PrVO ₃	3.890	Ref. [16]	0.99	0.64	1.4	0.828	4.080	0.190	3.871	0.501
70	SmAlO ₃	3.734	Ref. [16]	0.96	0.54	1.4	0.860	3.880	0.146	3.729	0.121
71	SmCoO ₃	3.750	Ref. [16]	0.96	0.55	1.4	0.856	3.900	0.150	3.742	0.220
72	SmVO ₃	3.890	Ref. [16]	0.96	0.64	1.4	0.818	4.080	0.190	3.855	0.899
73	SmFeO ₃	3.845	Ref. [16]	0.96	0.645	1.4	0.816	4.090	0.245	3.861	0.429
74	SrZrO ₃	4.101	Ref. [16]	1.18	0.72	1.4	0.861	4.240	0.139	4.069	0.779
75	YAlO ₃	3.680	Ref. [16]	0.9	0.54	1.4	0.838	3.880	0.200	3.697	0.460
76	YCrO ₃	3.768	Ref. [16]	0.9	0.62	1.4	0.805	4.040	0.272	3.798	0.800
77	YFeO ₃	3.785	Ref. [16]	0.9	0.645	1.4	0.795	4.090	0.305	3.831	1.204
78	CsCdF ₃	4.470	Ref. [12]	1.67	0.95	1.33	0.930	4.560	0.090	4.475	0.101
79	CsCaF ₃	4.523	Ref. [12]	1.67	1	1.33	0.910	4.660	0.137	4.539	0.353
80	CsHgF ₃	4.570	Ref. [12]	1.67	1.02	1.33	0.903	4.700	0.130	4.565	0.108
81	CsSrF ₃	4.750	Ref. [12]	1.67	1.18	1.33	0.845	5.020	0.270	4.781	0.647
82	TiCoF ₃	4.138	Ref. [12]	1.5	0.74	1.33	0.967	4.140	0.002	4.133	0.119
83	TiFeF ₃	4.188	Ref. [12]	1.5	0.78	1.33	0.948	4.220	0.032	4.181	0.164
84	TiMnF ₃	4.260	Ref. [12]	1.5	0.83	1.33	0.926	4.320	0.060	4.243	0.409
85	TiCdF ₃	4.400	Ref. [12]	1.5	0.95	1.33	0.878	4.560	0.160	4.396	0.091
86	NH ₄ ZnF ₃	4.115	Ref. [12]	1.49	0.74	1.33	0.963	4.140	0.025	4.128	0.316
87	NH ₄ CoF ₃	4.129	Ref. [12]	1.49	0.74	1.33	0.963	4.140	0.011	4.128	0.025
88	NH ₄ FeF ₃	4.177	Ref. [12]	1.49	0.78	1.33	0.945	4.220	0.043	4.176	0.021
89	NH ₄ MnF ₃	4.241	Ref. [12]	1.49	0.83	1.33	0.923	4.320	0.079	4.238	0.078
90	RbZnF ₃	4.122	Ref. [12]	1.52	0.74	1.33	0.974	4.140	0.018	4.143	0.516
91	RbCoF ₃	4.141	Ref. [12]	1.52	0.74	1.33	0.974	4.140	-0.001	4.143	0.054
92	RbVF ₃	4.170	Ref. [12]	1.52	0.79	1.33	0.951	4.240	0.070	4.203	0.797
93	RbFeF ₃	4.174	Ref. [12]	1.52	0.78	1.33	0.955	4.220	0.046	4.191	0.410
94	RbMnF ₃	4.240	Ref. [12]	1.52	0.83	1.33	0.933	4.320	0.080	4.252	0.291
95	RbCdF ₃	4.398	Ref. [12]	1.52	0.95	1.33	0.884	4.560	0.162	4.405	0.164
96	RbCaF ₃	4.452	Ref. [12]	1.52	1	1.33	0.865	4.660	0.208	4.471	0.430
97	RbHgF ₃	4.470	Ref. [12]	1.52	1.02	1.33	0.858	4.700	0.230	4.498	0.623
98	KCdF ₃	4.293	Ref. [16]	1.38	0.95	1.33	0.840	4.560	0.267	4.341	1.107
99	KMgF ₃	3.989	Ref. [

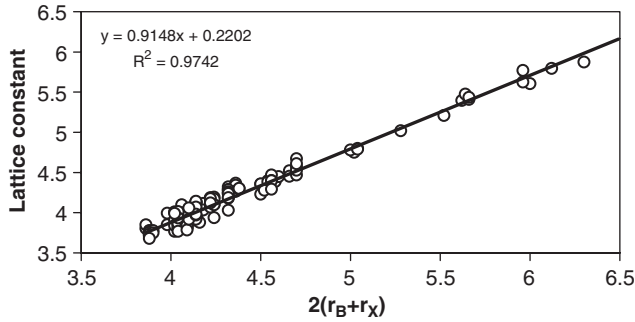


Fig. 2. Linear correlation of the lattice constant of the ideal perovskite to the theoretical distance between two nearest neighbour B ions, $2(r_B + r_X)$ (Å).

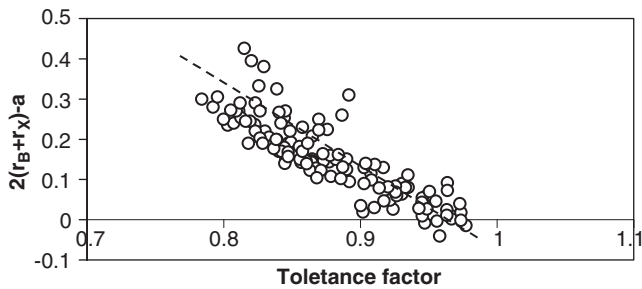


Fig. 3. Trend of decreasing of the $2(r_B + r_X) - a$ (in Å) with increasing the tolerance factor.

the lattice constant can be further obtained by

$$\alpha = D_{B-B} = 2(r_B + r_X). \quad (2)$$

The theoretical distance between two nearest neighbor B ions, $2(r_B + r_X)$, and the difference between a and $2(r_B + r_X)$, which is $(2(r_B + r_X) - a)$, are given in Table 1. It is shown that the lattice constants of the compounds are smaller than $2(r_B + r_X)$, except for those of four compounds (RbUO_3 , RbPaO_3 , BaFeO_3 and BaIrO_3) with a tolerance factors close to 1.

Although the lattice constant does not equal to $2(r_B + r_X)$, a rough linear correlation between them is still observed as in Fig. 2. The size effect of ionic A may be included to further improve the accuracy of the model. As mentioned earlier, the tolerance factor is a key index to characterize the stability of perovskites, it may also affect the lattice constant to some extent. As shown in Fig. 3, a general trend between $(2(r_B + r_X) - a)$ and the tolerance factor is observed, and $(2(r_B + r_X) - a)$ roughly decrease when increasing the tolerance factors.

So it may be necessary to include both the estimate of the distance between two nearest neighbor B ions; $(2(r_B + r_X))$, and the tolerance factor, in order to build an accurate model. By using all 132 ideal perovskites, a linear regression model is obtained ($R^2 = 0.995$):

$$\alpha = 0.9148 \times 2(r_B + r_X) + 1.4898t - 1.2062 \quad (3)$$

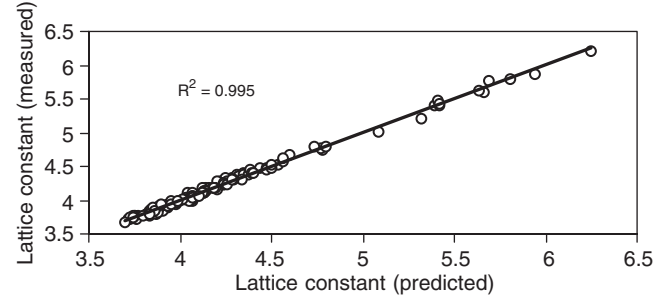


Fig. 4. Comparison between measured lattice constants and predicted values by our empirical model for 132 ABX_3 -type ideal perovskites (in Å).

by substituting Eq. (2), it becomes

$$\alpha = 1.8836(r_B + r_X) + 1.4898 \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} - 1.2062. \quad (4)$$

The lattice constants predicted by using Eq. (4), α_{pre} , together with their error limits are listed in Table 1 for all 132 compounds. The lattice constants predicted by this model are in good agreement with the experiments as in Fig. 4, with an average error of 0.63%. This empirical model is further tested by a recently reported compound [20] (KBiO_3), which is not used in the model development. Its predicted lattice constant, 4.218 Å, is in an excellent agreement with the measured value of 4.233 Å, and also in a good agreement with the calculated value of 4.104 Å (at 0K) by first principles quantum mechanics [21].

4. Discussion

It is of interest to discuss the size effects on lattice constant among different ions in the ideal perovskites ABX_3 , especially for cation A and B. By Eq. (4), the coefficient of r_B (1.8836) is much larger than the greatest coefficient of r_A in all 132 compounds (0.46, obtained by replacing the $r_B + r_X$ with 2.3, the typical value in all 132 compounds). This may imply that the lattice constant is predominated by the size effect of ion B over ion A, which may be further explained by the crystal structure of an ideal perovskite. Cubic perovskite structure can be considered as a variant of oxide BO_3 with ReO_3 structure. This structure can be thought of as a three-dimensional network of corner-sharing octahedral unit BO_6 . The shortest possible O–B bond length of such a BO_3 network is $(r_B + r_O)$, assuming a close contacted atomic shell model. When ion A is introduced and occupies the cavity formed by the BO_3 network, this structure transforms into perovskite structure [12,16], seen in Fig. 1. So the lattice constant is mainly decided by the three-dimensional network of corner-sharing octahedral unit BO_6 , in other words, the radius of cation B and anion O primarily determine the lattice constant of the ideal perovskite ABO_3 . In all 132 ideal perovskites except 4 in Table 1, their measured lattice constants are shorter than two times of the possible shortest X–B bonds in the BX_3 network. The introduction of A to the cavity of the network, therefore, may cause a shrink of the

network along the B–B bond direction, so the effect of radius A on lattice constant is, therefore, of secondary importance.

When selecting the ionic radius data, especially for the ions with ferromagnetism, more precaution is needed. It is noticed that the values of ionic radius of high spin state (HS) should be used for Fe^{2+} (0.78 Å), Fe^{3+} (0.645 Å), Co^{2+} (0.74 Å), Mn^{2+} (0.83 Å), and Mn^{3+} (0.645 Å) for the prediction of lattice constants of perovskites. These results are consistent with previous reports [11,13]. Comparing to other halides, LiBaF_3 is somewhat special. For perovskites, in general cation A of lower valence is larger than cation B of higher valence, so the cation B and anion X form the octahedron BX_6 and these octahedrons share the vertex t to form the framework. And ion A fills the cavity formed by these octahedrons. In fluoride LiBaF_3 , the Ba^{2+} (1.35 Å) is larger than Li^+ (0.68 Å). And the octahedron is in the form of LiF_6 not BaF_6 , where Ba^{2+} fills the hole, so ion A is Ba^{2+} and ion B is Li^+ . This structure is confirmed by a recent report [17].

In a similar approach [10] the lattice constant of the ideal perovskites ABO_3 can be linearly correlated to some atomic parameters as

$$\alpha = 0.3166r_A + 1.422r_B - 0.1708X_A + 0.0562X_B - 0.0066(Z_B - Z_A) + 2.706, \quad (5)$$

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. Comparing to Eq. (5), our model is much simpler with clear physical support. In addition, not only oxide, this model works for halide perovskites as well.

5. Conclusion

In this study, a total of 132 ABX_3 -type ideal perovskites and their lattice constants are collected, regularities governing lattice constant are investigated by a statistical regress method. It is found that, although the lattice constant do not simply equal to two times the ionic radius summation of cation B and anion X, it can be precisely determined by the size of the 3 constituent ions. The following conclusions are obtained:

- (1) The lattice constant of an ideal perovskite is predominately determined by the size of cation B and anion X (strictly say, by the bond length between ion B and anion X), and less by that of ion A.
- (2) A good correlation among lattice constant, the estimated bond length between ion B and ion X, ($r_B + r_X$), and the tolerance factor, t , exists with a regress coefficient $R^2 = 0.995$ as

$$\alpha = 0.9418 \cdot 2(r_B + r_X) + 1.4898t - 1.2062 \quad (3)$$

or expressed by the ionic radii of constituent ions A, B and X

$$\alpha = 1.8836(r_B + r_X) + 1.4898 \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} - 1.2062. \quad (4)$$

- (3) The lattice constant of an ideal perovskite can be predicted by this empirical model (Eq. (4)) with an average error of 0.63%. A recent reported perovskite (KBiO_3) is used to validate this model. The predicting is merely 0.12%. This model may be useful in the design of new substrates or buffer materials for compound semiconductor epitaxy.

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