Journal of Alloys and Compounds 480 (2009) 650–657

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Lattice constant of orthorhomic perovskite solids

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ARTICLE INFO

Article history:
Received 14 December 2008
Received in revised form 22 January 2009
Accepted 1 February 2009
Available online 10 February 2009

PACS:
61.50.Ah
71.15.Ap

Keywords:
Ferroelectrics
Crystal structure

ABSTRACT

In this paper, a simple lattice constants (a, b and c) prediction model based on ionic charge theory of solid is proposed. The lattice constant of orthorhomic perovskite-type oxides exhibits a linear relationship when plotted on a log–log scale against the average ionic radii r_{av} (Å), but fall on different straight lines according to the ionic charge product of the compounds. This enables us to achieve improved prediction performance of the lattice constant of structurally known perovskite-type oxides. We have applied the proposed relation to ABO_3 (A: large cation with different valence, B: transition metal, O: anion) and found a better agreement with the experimental data as compared to the values evaluated by earlier researchers.

1. Introduction

The term 'perovskite' is used to denote a category of inorganic crystalline solids with the general formula ABO_3, where A is large cation with different valence, B is transition metal and O is an anion. A large number of perovskite-type oxides have been studied because of their interesting properties, including 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. [4–7]. As the most important components in the Earth's mantle, ABO_3 (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 systems, the accurate and transparent description of the driving forces toward the high or low symmetry crystal structures is of general interest. During the last few years, many experimental and theoretical investigations were devoted to the study of perovskite solids. Oxide perovskites with general stoichiometry ABO_3 are relatively simple structures comprised of corner-linked BO_6 cation-centred octahedra with larger A cations occupying the voids within the three-dimensional framework of octahedra. 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 titling and distortion of the BO_6 octahedra [8]. The degree of distortion of these perovskites may be described by tilting of the BO_6 octahedra, and even where a structural transition is not observed the tilt angle decreases as the temperature increases. The octahedral tilting, originating from finite rotations of the BO_6 octahedra, is realized by preserving the central symmetry of the B cation, while the A cation "prefers" off-center displacements. A number of workers have used such changes to infer the presence of thermally induced phase transitions. From the crystal chemistry point of view, the two different perovskites of ABO_3 compounds 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 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 [5–12]. However, there are very few studies that have focused on the evolution of the bonding mechanism of ferroelectric perovskite materials.

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doi:10.1016/j.jallcom.2009.02.004

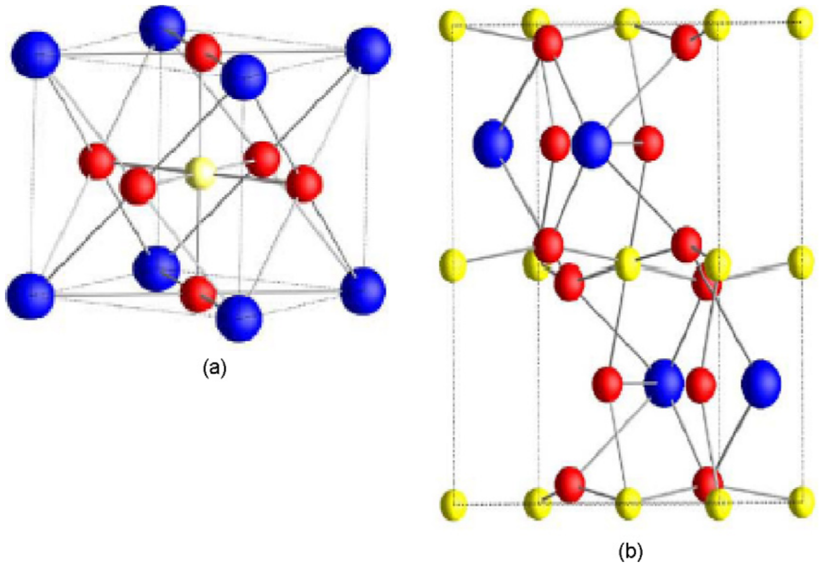
(a)
(b)

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. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Usually, both experimental as well as theoretical methods are used to determine lattice constants for identifying the crystal structure of unknown compounds. These experimental methods use X-ray, neutron or electron diffraction technique to measure the lattice constant. Experimental methods form a powerful approach for crystal structure determination but these are complicated and time consuming. Specifically, for large number of unknown compounds, these are very slow processes. On the other hand, empirical models can be used to predict lattice constants. These have the advantage that the empirical models can be used to develop software for the prediction of lattice parameters of a large number of structurally known compounds. 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 [15–19] 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

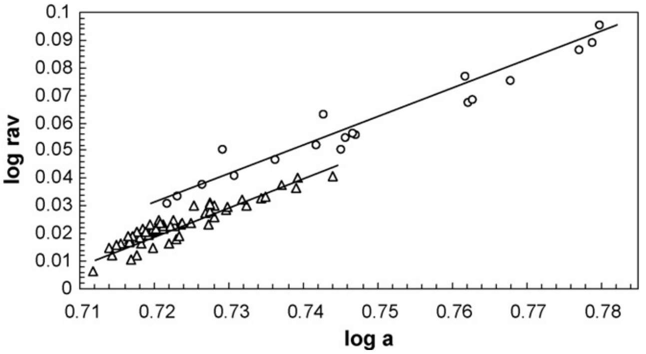

Fig. 2. Plot of log a (lattice constant in Å) against log r_{av} (average ionic radii in Å) for $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$ orthorhombic perovskites and $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$ are represented by ○ and △, respectively. In the plots of log a and log r_{av}, $A^{2+}B^{4+}O_3$ perovskites lie on lines nearly parallel to the line for $A^{3+}B^{3+}O_3$ perovskites. In this plot all experimental data (lattice constant and ionic radii) are taken from Refs. [5,21,22].

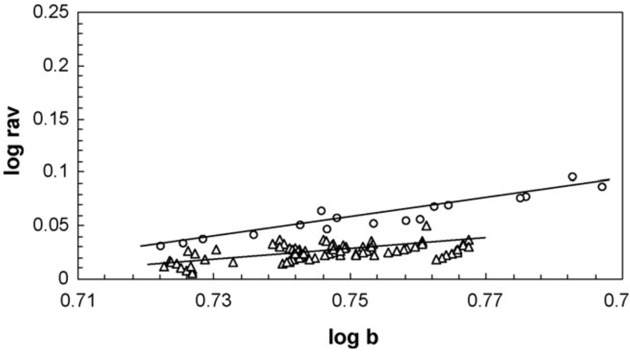

Fig. 3. Plot of log b (lattice constant in Å) against log r_{av} (average ionic radii in Å) for $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$ orthorhombic perovskites and $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$ are represented by ○ and △, respectively. In the plots of log b and log r_{av}, $A^{2+}B^{4+}O_3$ perovskites lie on lines nearly parallel to the line for $A^{3+}B^{3+}O_3$ perovskites. In this plot all experimental data (lattice constant and ionic radii) are taken from Refs. [5,21,22].

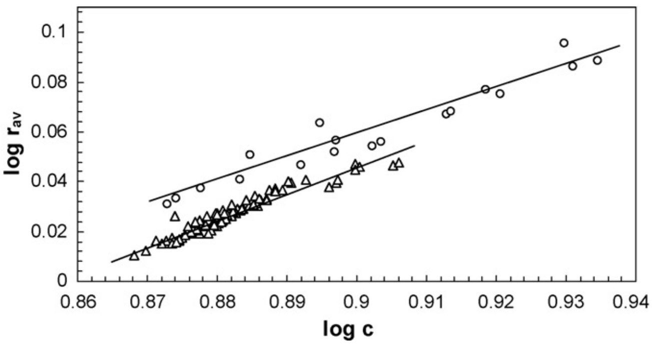

Fig. 4. Plot of log c (lattice constant in Å) against log r_{av} (average ionic radii in Å) for $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$ orthorhombic perovskites and $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$ are represented by ○ and △, respectively. In the plots of log c and log r_{av}, $A^{2+}B^{4+}O_3$ perovskites lie on lines nearly parallel to the line for $A^{3+}B^{3+}O_3$ perovskites. In this plot all experimental data (lattice constant and ionic radii) are taken from Refs. [5,21,22].

Table 1
The values of lattice constant (*a* in Å) for orthorhombic perovskite solids.

S. No.	Solids	r_A (Å) [5]	r_B (Å) [5]	*a* (Å) [22]	*a* (Å) [this work]	% error
1	$NaUO_3$	1.39	0.76	5.775	5.607	2.9
2	$NaTaO_3$	1.39	0.64	5.494	5.415	1.4
3	$NaNbO_3$	1.39	0.64	5.51	5.415	1.7
4	$NaPaO_3$	1.39	0.78	5.82	5.639	3.1
5	$CaMnO_3$	1.34	0.53	5.27	5.292	0.4
6	$CaCrO_3$	1.34	0.55	5.287	5.324	0.7
7	$CaVO_3$	1.34	0.58	5.326	5.374	0.9
8	$CaTiO_3$	1.34	0.605	5.381	5.415	0.6
9	$CaRuO_3$	1.34	0.68	5.36	5.538	3.3
10	$CaMoO_3$	1.34	0.65	5.45	5.489	0.7
11	$CaNbO_3$	1.34	0.68	5.56	5.538	0.4
12	$CaSnO_3$	1.34	0.69	5.519	5.554	0.6
13	$CaHfO_3$	1.34	0.71	5.568	5.587	0.3
14	$CaZrO_3$	1.34	0.72	5.587	5.604	0.3
15	$CaUO_3$	1.34	0.89	5.78	5.883	1.8
16	$BaPbO_3$	1.61	0.775	6.024	6.138	1.9
17	$SrRuO_3$	1.44	0.68	5.53, 5.567[e]	5.702	3.1
18	$SrUO_3$	1.44	0.89	6.01	6.047	0.6
19	$SrIrO_3$	1.44	0.625	5.58	5.612	0.6
20	$SrHfO_3$	1.44	0.71	5.785	5.752	0.6
21	$SrZrO_3$	1.44	0.72	5.792, 5.796[d]	5.768	0.4
22	$SrPbO_3$	1.44	0.775	5.86	5.858	0
23	$SrCeO_3$	1.44	0.87	5.986	6.015	0.5
24	$LaCrO_3$	1.36	0.615	5.515	5.498	0.3
25	$LaGaO_3$	1.36	0.62	5.526, 5.527[a]	5.507	0.3
26	$LaFeO_3$	1.36	0.645	5.556	5.548	0.1
27	$LaVO_3$	1.36	0.64	5.54	5.54	0
28	$LaMnO_3$	1.36	0.645	5.529, 5.582[a]	5.548	0.3
29	$LaRhO_3$	1.36	0.665	5.524	5.581	1
30	$LaTiO_3$	1.36	0.67	5.546	5.589	0.8
31	$LaScO_3$	1.36	0.745	5.678	5.713	0.6
32	$LaInO_3$	1.36	0.8	5.723	5.804	1.4
33	$LaYO_3$	1.36	0.645	5.877, 6.086[a]	5.548	5.6
34	$CeCrO_3$	1.34	0.615	5.475	5.465	0.2
35	$CeFeO_3$	1.34	0.645	5.519	5.515	0.1
36	$CeVO_3$	1.34	0.64	5.486	5.507	0.4
37	$CeMnO_3$	1.3	0.645	5.532	5.449	1.5
38	$CeTiO_3$	1.34	0.67	5.513	5.556	0.8
39	$PrCrO_3$	1.3	0.615	5.484	5.399	1.5
40	$PrGaO_3$	1.3	0.62	5.458	5.407	0.9
41	$PrFeO_3$	1.3	0.645	5.495	5.449	0.8
42	$PrVO_3$	1.3	0.64	5.487	5.441	0.8
43	$PrMnO_3$	1.3	0.645	5.545	5.449	1.7
44	$PrRhO_3$	1.3	0.665	5.414	5.482	1.3
45	$PrTiO_3$	1.3	0.67	5.499	5.49	0.2
46	$PrCoO_3$	1.3	0.545	5.331	5.283	0.9
47	$PrScO_3$	1.3	0.745	5.615	5.614	0
48	$PrAlO_3$	1.3	0.535	5.347	5.267	1.5
49	$NdCrO_3$	1.27	0.615	5.425	5.35	1.4
50	$NdGaO_3$	1.27	0.62	5.431	5.358	1.3
51	$NdFeO_3$	1.27	0.645	5.441	5.399	0.8
52	$NdVO_3$	1.27	0.64	5.451	5.391	1.1
53	$NdMnO_3$	1.27	0.645	5.38	5.399	0.4
54	$NdRhO_3$	1.27	0.665	5.378	5.432	1
55	$NdTiO_3$	1.27	0.67	5.487	5.441	0.8
56	$NdCoO_3$	1.27	0.545	5.336	5.234	1.9
57	$NdScO_3$	1.27	0.745	5.574	5.565	0.2
58	$NdInO_3$	1.27	0.8	5.627	5.656	0.5
59	PmCrO3	1.25	0.615	5.4	5.317	1.5
60	PmScO3	1.25	0.745	5.56	5.532	0.5
61	PmInO3	1.25	0.8	5.7	5.622	1.4
62	$SmAlO_3$	1.24	0.535	5.285, 5.286 [c]	5.168	2.2
63	$SmCrO_3$	1.24	0.615	5.367	5.3	1.2
64	$SmGaO_3$	1.24	0.62	5.369	5.308	1.1
65	$SmFeO_3$	1.24	0.645	5.394	5.35	0.8
66	$SmVO_3$	1.24	0.64	5.393	5.341	1
67	$SmMnO_3$	1.24	0.645	5.359	5.35	0.2
68	$SmRhO_3$	1.24	0.665	5.321	5.383	1.2
69	$SmTiO_3$	1.24	0.67	5.468	5.391	1.4
70	$SmCoO_3$	1.24	0.545	5.289	5.184	2
71	$SmScO_3$	1.24	0.745	5.53	5.515	0.3
72	$SmInO_3$	1.24	0.8	5.589	5.606	0.3
73	$EuAlO_3$	1.23	0.535	5.271[f]	5.151	2.3
74	$EuCrO_3$	1.23	0.615	5.34	5.283	1.1
75	$EuGaO_3$	1.23	0.62	5.351	5.292	1.1

Table 1 (*Continued*)

S. No.	Solids	r_A (Å) [5]	r_B (Å) [5]	a (Å) [22]	a (Å) [this work]	% error
76	$EuFeO_3$	1.23	0.645	5.371	5.333	0.7
77	$EuMnO_3$	1.23	0.645	5.338	5.333	0.1
78	$EuRhO_3$	1.23	0.665	5.298	5.366	1.3
79	$EuScO_3$	1.23	0.745	5.51	5.498	0.2
80	$EuInO_3$	1.23	0.8	5.567	5.589	0.4
81	$GdAlO_3$	1.22	0.535	5.247, 5.253[b]	5.135	2.1
82	$GdCrO_3$	1.22	0.615	5.312	5.267	0.8
83	$GdGaO_3$	1.22	0.62	5.322	5.275	0.9
84	$GdFeO_3$	1.22	0.645	5.346, 5.351[b]	5.317	0.6
85	$GdVO_3$	1.22	0.64	5.343	5.308	0.7
86	$GdMnO_3$	1.22	0.645	5.313	5.317	0.1
87	$GdRhO_3$	1.22	0.665	5.277	5.35	1.4
88	$GdTiO_3$	1.22	0.67	5.407	5.358	0.9
89	$GdCoO_3$	1.22	0.545	5.228	5.151	1.5
90	$GdScO_3$	1.22	0.745	5.487	5.482	0.1
91	$GdInO_3$	1.22	0.8	5.548	5.573	0.4
92	$TbAlO_3$	1.2	0.535	5.22	5.102	2.3
93	$TbCrO_3$	1.2	0.615	5.291	5.234	1.1
94	$TbGaO_3$	1.2	0.62	5.307	5.242	1.2
95	$TbFeO_3$	1.2	0.645	5.326	5.283	0.8
96	$TbMnO_3$	1.2	0.645	5.297	5.283	0.3
97	$TbRhO_3$	1.2	0.665	5.254	5.317	1.2
98	$TbTiO_3$	1.2	0.67	5.388	5.325	1.2
99	$DyAlO_3$	1.19	0.535	5.21	5.085	2.4
100	$DyCrO_3$	1.19	0.615	5.263	5.217	0.9
101	$DyGaO_3$	1.19	0.62	5.282	5.226	1.1
102	$DyFeO_3$	1.19	0.645	5.302	5.267	0.7
103	$DyVO_3$	1.19	0.64	5.302	5.259	0.8
104	$DyMnO_3$	1.19	0.645	5.275	5.267	0.2
105	$DyRhO_3$	1.19	0.665	5.245	5.3	1
106	$DyTiO_3$	1.19	0.67	5.361	5.308	1
107	$DyScO_3$	1.19	0.745	5.43	5.432	0
108	$DyInO_3$	1.19	0.8	5.519	5.523	0.1
109	$HoAlO_3$	1.18	0.535	5.18	5.068	2.2
110	$HoCrO_3$	1.18	0.615	5.243	5.201	0.8
111	$HoGaO_3$	1.18	0.62	5.251	5.209	0.8
112	$HoFeO_3$	1.18	0.645	5.278	5.25	0.5
113	$HoMnO_3$	1.18	0.645	5.255	5.25	0.1
114	$HoRhO_3$	1.18	0.665	5.23	5.283	1
115	$HoTiO_3$	1.18	0.67	5.339	5.292	0.9
116	$HoScO_3$	1.18	0.745	5.42	5.416	0.1
117	$ErAlO_3$	1.17	0.535	5.16	5.052	2.1
118	$ErCrO_3$	1.17	0.615	5.223	5.184	0.7
119	$ErGaO_3$	1.17	0.62	5.239	5.193	0.9
120	$ErFeO_3$	1.17	0.645	5.263	5.234	0.6
121	$ErVO_3$	1.17	0.64	5.262	5.226	0.7
122	$ErMnO_3$	1.17	0.645	5.24	5.234	0.1
123	$ErRhO_3$	1.17	0.665	5.216	5.267	1
124	$ErTiO_3$	1.17	0.67	5.318	5.275	0.8
125	$TmAlO_3$	1.16	0.535	5.15	5.035	2.2
126	$TmCrO_3$	1.16	0.615	5.209	5.168	0.8
127	$TmGaO_3$	1.16	0.62	5.224	5.176	0.9
128	$TmFeO_3$	1.16	0.645	5.251	5.217	0.6
129	$TmMnO_3$	1.16	0.645	5.23	5.217	0.2
130	$TmRhO_3$	1.16	0.665	5.203	5.25	0.9
131	$TmTiO_3$	1.16	0.67	5.306	5.259	0.9
132	$YbAlO_3$	1.15	0.535	5.12	5.019	2
133	$YbCrO_3$	1.15	0.615	5.195	5.151	0.8
134	$YbGaO_3$	1.15	0.62	5.208	5.159	0.9
135	$YbFeO_3$	1.15	0.645	5.233	5.201	0.6
136	$YbMnO_3$	1.15	0.645	5.22	5.201	0.4
137	$YbTiO_3$	1.15	0.67	5.293	5.242	1
138	$LuCrO_3$	1.14	0.615	5.176	5.135	0.8
139	$LuGaO_3$	1.14	0.62	5.188	5.143	0.9
140	$LuFeO_3$	1.14	0.645	5.213	5.184	0.6
141	$LuMnO_3$	1.14	0.645	5.205	5.184	0.4
142	$LuRhO_3$	1.14	0.665	5.186	5.217	0.6
143	$LuTiO_3$	1.14	0.67	5.274	5.226	0.9
144	$YAlO_3$	1.2	0.535	5.179	5.102	1.5
145	$YCrO_3$	1.2	0.615	5.241	5.234	0.1
146	$YGaO_3$	1.2	0.62	5.257	5.242	0.3
147	$YFeO_3$	1.2	0.645	5.283	5.283	0
148	YVO_3	1.2	0.64	5.284	5.275	0.2
149	$YMnO_3$	1.2	0.645	5.26	5.283	0.4
150	$YTiO_3$	1.2	0.67	5.34	5.325	0.3

Table 1 (*Continued*)

S. No.	Solids	r_A (Å) [5]	r_B (Å) [5]	*a* (Å) [22]	*a* (Å) [this work]	% error
151	$\mathrm{YScO_3}$	1.2	0.745	5.431	5.449	0.3
152	$\mathrm{YInO_3}$	1.2	0.8	5.5	5.54	0.7

[a] Ref. [28].
[b] Ref. [29].
[c] Ref. [23].
[d] Ref. [12].
[e] Ref. [30].
[f] Ref. [31].

Table 2
The values of lattice constants (*b* and *c* in Å) for orthorhombic perovskite solids.

S. No.	Solids	*b* (Å) [22]	*c* (Å) [22]	*b* (Å) [this work]	*c* (Å) [this work]	% error of *b*	% error of *c*
1	$\mathrm{NaUO_3}$	5.905	8.25	5.627	8.02	4.7	2.8
2	$\mathrm{NaTaO_3}$	5.513	7.751	5.434	7.745	1.4	0.1
3	$\mathrm{NaNbO_3}$	5.57	7.77	5.434	7.745	2.4	0.3
4	$\mathrm{NaPaO_3}$	5.92	8.36	5.659	8.065	4.4	3.5
5	$\mathrm{CaMnO_3}$	5.275	7.464	5.312	7.519	0.7	0.7
6	$\mathrm{CaCrO_3}$	5.316	7.486	5.345	7.565	0.5	1.1
7	$\mathrm{CaVO_3}$	5.352	7.547	5.394	7.635	0.8	1.2
8	$\mathrm{CaTiO_3}$	5.443	7.645	5.436	7.694	0.1	0.6
9	$\mathrm{CaRuO_3}$	5.53	7.67	5.559	7.869	0.5	2.6
10	$\mathrm{CaMoO_3}$	5.58	7.8	5.51	7.799	1.3	0
11	$\mathrm{CaNbO_3}$	5.77	8.016	5.559	7.869	3.7	1.8
12	$\mathrm{CaSnO_3}$	5.668	7.885	5.576	7.892	1.6	0.1
13	$\mathrm{CaHfO_3}$	5.732	7.984	5.609	7.939	2.1	0.6
14	$\mathrm{CaZrO_3}$	5.758	8.008	5.625	7.962	2.3	0.6
15	$\mathrm{CaUO_3}$	5.97	8.29	5.906	8.359	1.1	0.8
16	$\mathrm{BaPbO_3}$	6.065	8.506	6.162	8.721	1.6	2.5
17	$\mathrm{SrRuO_3}$	5.57, 5.53[e]	7.847, 7.845[e]	5.724	8.102	2.8	3.3
18	$\mathrm{SrUO_3}$	6.17	8.6	6.071	8.593	1.6	0.1
19	$\mathrm{SrIrO_3}$	5.6	7.89	5.634	7.974	0.6	1.1
20	$\mathrm{SrHfO_3}$	5.786	8.182	5.774	8.173	0.2	0.1
21	$\mathrm{SrZrO_3}$	5.814, 5.82[d]	8.196, 8.205[d]	5.79	8.196	0.4	0
22	$\mathrm{SrPbO_3}$	5.958	8.331	5.881	8.324	1.3	0.1
23	$\mathrm{SrCeO_3}$	6.125	8.531	6.038	8.546	1.4	0.2
24	$\mathrm{LaCrO_3}$	5.479	7.753	5.521	7.794	0.8	0.5
25	$\mathrm{LaGaO_3}$	5.473, 5.5[a]	7.767, 7.781[a]	5.529	7.806	1	0.5
26	$\mathrm{LaFeO_3}$	5.565	7.862	5.57	7.864	0.1	0
27	$\mathrm{LaVO_3}$	5.54	7.83	5.562	7.852	0.4	0.3
28	$\mathrm{LaMnO_3}$	5.662, 5.58[a]	7.715, 7.89[a]	5.57	7.864	1.6	
29	$\mathrm{LaRhO_3}$	5.629	7.9	5.604	7.911	0.5	0.1
30	$\mathrm{LaTiO_3}$	5.753	7.832	5.612	7.923	2.5	1.2
31	$\mathrm{LaScO_3}$	5.787	8.098	5.736	8.099	0.9	0
32	$\mathrm{LaInO_3}$	5.914	8.207	5.828	8.227	1.5	0.2
33	$\mathrm{LaYO_3}$	6.087, 5.89[a]	8.493, 8.511[a]	5.57	7.864	8.5	7.4
34	$\mathrm{CeCrO_3}$	5.475	7.74	5.487	7.747	0.2	0.1
35	$\mathrm{CeFeO_3}$	5.536	7.819	5.537	7.817	0	0
36	$\mathrm{CeVO_3}$	5.486	7.74	5.529	7.806	0.8	0.8
37	$\mathrm{CeMnO_3}$	5.557	7.812	5.471	7.723	1.6	1.1
38	$\mathrm{CeTiO_3}$	5.757	7.801	5.579	7.876	3.1	1
39	$\mathrm{PrCrO_3}$	5.479	7.718	5.421	7.653	1.1	0.8
40	$\mathrm{PrGaO_3}$	5.49	7.733	5.429	7.665	1.1	0.9
41	$\mathrm{PrFeO_3}$	5.578	7.81	5.471	7.723	1.9	1.1
42	$\mathrm{PrVO_3}$	5.562	7.751	5.462	7.712	1.8	0.5
43	$\mathrm{PrMnO_3}$	5.787	7.575	5.471	7.723	5.5	2
44	$\mathrm{PrRhO_3}$	5.747	7.803	5.504	7.77	4.2	0.4
45	$\mathrm{PrTiO_3}$	5.724	7.798	5.512	7.782	3.7	0.2
46	$\mathrm{PrCoO_3}$	5.373	7.587	5.305	7.489	1.3	1.3
47	$\mathrm{PrScO_3}$	5.776	8.027	5.637	7.958	2.4	0.9
48	$\mathrm{PrAlO_3}$	5.322	7.481	5.288	7.466	0.6	0.2
49	$\mathrm{NdCrO_3}$	5.478	7.694	5.371	7.583	2	1.4
50	$\mathrm{NdGaO_3}$	5.499	7.71	5.379	7.595	2.2	1.5
51	$\mathrm{NdFeO_3}$	5.573	7.753	5.421	7.653	2.7	1.3
52	$\mathrm{NdVO_3}$	5.579	7.734	5.413	7.641	3	1.2
53	$\mathrm{NdMnO_3}$	5.854	7.557	5.421	7.653	7.4	1.3
54	$\mathrm{NdRhO_3}$	5.755	7.775	5.454	7.7	5.2	1
55	$\mathrm{NdTiO_3}$	5.707	7.765	5.462	7.712	4.3	0.7
56	$\mathrm{NdCoO_3}$	5.336	7.547	5.255	7.419	1.5	1.7
57	$\mathrm{NdScO_3}$	5.771	7.998	5.587	7.888	3.2	1.4
58	$\mathrm{NdInO_3}$	5.891	8.121	5.678	8.016	3.6	1.3
59	$\mathrm{PmCrO_3}$	5.49	7.69	5.338	7.536	2.8	2
60	$\mathrm{PmScO_3}$	5.79	7.94	5.554	7.841	4.1	1.3
61	$\mathrm{PmInO_3}$	5.9	8.2	5.645	7.97	4.3	2.8
62	$\mathrm{SmAlO_3}$	5.29, 5.28[c]	7.473, 7.46[c]	5.189	7.325	1.9	2

Table 2 (*Continued*)

S. No.	Solids	*b* (Å) [22]	*c* (Å) [22]	*b* (Å) [this work]	*c* (Å) [this work]	% error of *b*	% error of *c*
63	$SmCrO_3$	5.508	7.643	5.321	7.513	3.4	1.7
64	$SmGaO_3$	5.52	7.65	5.33	7.524	3.4	1.6
65	$SmFeO_3$	5.592	7.711	5.371	7.583	3.9	1.7
66	$SmVO_3$	5.588	7.672	5.363	7.571	4	1.3
67	$SmMnO_3$	5.843	7.482	5.371	7.583	8.1	1.3
68	$SmRhO_3$	5.761	7.708	5.404	7.63	6.2	1
69	$SmTiO_3$	5.665	7.737	5.413	7.641	4.5	1.2
70	$SmCoO_3$	5.354	7.541	5.205	7.348	2.8	2.6
71	$SmScO_3$	5.76	7.95	5.537	7.817	3.9	1.7
72	$SmInO_3$	5.886	8.082	5.629	7.946	4.4	1.7
73	$EuAlO_3$	5.292[f]	7.458[f]	5.172	7.302	2.3	2.1
74	$EuCrO_3$	5.515	7.622	5.305	7.489	3.8	1.7
75	$EuGaO_3$	5.528	7.628	5.313	7.501	3.9	1.7
76	$EuFeO_3$	5.611	7.686	5.355	7.559	4.6	1.6
77	$EuMnO_3$	5.842	7.453	5.355	7.559	8.3	1.4
78	$EuRhO_3$	5.761	7.68	5.388	7.606	6.5	1
79	$EuScO_3$	5.76	7.94	5.521	7.794	4.2	1.8
80	$EuInO_3$	5.835	8.078	5.612	7.923	3.8	1.9
81	$GdAlO_3$	5.304, 5.30[b]	7.447, 7.44[b]	5.155	7.278	2.8	2.3
82	$GdCrO_3$	5.525	7.606	5.288	7.466	4.3	1.8
83	$GdGaO_3$	5.537	7.606	5.296	7.477	4.3	1.7
84	$GdFeO_3$	5.616, 5.61[b]	7.668, 7.67[b]	5.338	7.536	5	1.7
85	$GdVO_3$	5.614	7.637	5.33	7.524	5.1	1.5
86	$GdMnO_3$	5.853	7.432	5.338	7.536	8.8	1.4
87	$GdRhO_3$	5.761	7.658	5.371	7.583	6.8	1
88	$GdTiO_3$	5.667	7.692	5.379	7.595	5.1	1.3
89	$GdCoO_3$	5.404	7.436	5.172	7.302	4.3	1.8
90	$GdScO_3$	5.756	7.925	5.504	7.77	4.4	2
91	$GdInO_3$	5.842	8.071	5.595	7.899	4.2	2.1
92	$TbAlO_3$	5.28	7.41	5.122	7.231	3	2.4
93	$TbCrO_3$	5.518	7.576	5.255	7.419	4.8	2.1
94	$TbGaO_3$	5.531	7.578	5.263	7.43	4.8	1.9
95	$TbFeO_3$	5.602	7.635	5.305	7.489	5.3	1.9
96	$TbMnO_3$	5.831	7.403	5.305	7.489	9	1.2
97	$TbRhO_3$	5.749	7.623	5.338	7.536	7.1	1.1
98	$TbTiO_3$	5.648	7.676	5.346	7.548	5.3	1.7
99	$DyAlO_3$	5.31	7.38	5.106	7.208	3.9	2.3
100	$DyCrO_3$	5.2	7.552	5.238	7.395	0.7	2.1
101	$DyGaO_3$	5.534	7.556	5.247	7.407	5.2	2
102	$DyFeO_3$	5.598	7.623	5.288	7.466	5.5	2.1
103	$DyVO_3$	5.602	7.601	5.28	7.454	5.8	1.9
104	$DyMnO_3$	5.828	7.375	5.288	7.466	9.3	1.2
105	$DyRhO_3$	5.731	7.6	5.321	7.513	7.1	1.2
106	$DyTiO_3$	5.659	7.647	5.33	7.524	5.8	1.6
107	$DyScO_3$	5.71	7.89	5.454	7.7	4.5	2.4
108	$DyInO_3$	5.751	8.041	5.546	7.829	3.6	2.6
109	$HoAlO_3$	5.33	7.36	5.089	7.184	4.5	2.4
110	$HoCrO_3$	5.519	7.538	5.222	7.372	5.4	2.2
111	$HoGaO_3$	5.531	7.536	5.23	7.384	5.4	2
112	$HoFeO_3$	5.591	7.602	5.272	7.442	5.7	2.1
113	$HoMnO_3$	5.831	7.354	5.272	7.442	9.6	1.2
114	$HoRhO_3$	5.726	7.582	5.305	7.489	7.4	1.2
115	$HoTiO_3$	5.665	7.626	5.313	7.501	6.2	1.6
116	$HoScO_3$	5.71	7.87	5.438	7.677	4.8	2.5
117	$ErAlO_3$	5.32	7.33	5.072	7.161	4.7	2.3
118	$ErCrO_3$	5.516	7.519	5.205	7.348	5.6	2.3
119	$ErGaO_3$	5.527	7.522	5.213	7.36	5.7	2.2
120	$ErFeO_3$	5.582	7.591	5.255	7.419	5.9	2.3
121	$ErVO_3$	5.604	7.578	5.247	7.407	6.4	2.3
122	$ErMnO_3$	5.82	7.335	5.255	7.419	9.7	1.1
123	$ErRhO_3$	5.712	7.561	5.288	7.466	7.4	1.3
124	$ErTiO_3$	5.657	7.613	5.296	7.477	6.4	1.8
125	$TmAlO_3$	5.33	7.29	5.056	7.137	5.1	2.1
126	$TmCrO_3$	5.508	7.5	5.189	7.325	5.8	2.3
127	$TmGaO_3$	5.515	7.505	5.197	7.337	5.8	2.2
128	$TmFeO_3$	5.576	7.584	5.238	7.395	6.1	2.5
129	$TmMnO_3$	5.81	7.32	5.238	7.395	9.8	1
130	$TmRhO_3$	5.697	7.543	5.272	7.442	7.5	1.3
131	$TmTiO_3$	5.647	7.607	5.28	7.454	6.5	2
132	$YbAlO_3$	5.33	7.31	5.039	7.114	5.5	2.7
133	$YbCrO_3$	5.51	7.49	5.172	7.302	6.1	2.5
134	$YbGaO_3$	5.51	7.49	5.18	7.313	6	2.4
135	$YbFeO_3$	5.557	7.57	5.222	7.372	6	2.6
136	$YbMnO_3$	5.8	7.3	5.222	7.372	10	1
137	$YbTiO_3$	5.633	7.598	5.263	7.43	6.6	2.2
138	$LuCrO_3$	5.497	7.475	5.155	7.278	6.2	2.6

Table 2 (*Continued*)

S. No.	Solids	b (Å) [22]	c (Å) [22]	b (Å) [this work]	c (Å) [this work]	% error of b	% error of c
139	$LuGaO_3$	5.505	7.484	5.164	7.29	6.2	2.6
140	$LuFeO_3$	5.547	7.565	5.205	7.348	6.2	2.9
141	$LuMnO_3$	5.79	7.31	5.205	7.348	10	0.5
142	$LuRhO_3$	5.67	7.512	5.238	7.395	7.6	1.6
143	$LuTiO_3$	5.633	7.58	5.247	7.407	6.9	2.3
144	$YAlO_3$	5.329	7.37	5.122	7.231	3.9	1.9
145	$YCrO_3$	5.521	7.532	5.255	7.419	4.8	1.5
146	$YGaO_3$	5.536	7.533	5.263	7.43	4.9	1.4
147	$YFeO_3$	5.592	7.603	5.305	7.489	5.1	1.5
148	YVO_3	5.605	7.587	5.296	7.477	5.5	1.4
149	$YMnO_3$	5.83	7.36	5.305	7.489	9	1.8
150	$YTiO_3$	5.665	7.624	5.346	7.548	5.6	1
151	$YScO_3$	5.712	7.894	5.471	7.723	4.2	2.2
152	$YInO_3$	5.787	8.053	5.562	7.852	3.9	2.5

[a] Ref. [28].
[b] Ref. [29].
[c] Ref. [23].
[d] Ref. [12].
[e] Ref. [30].
[f] Ref. [31].

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 orthorhombic perovskite solids.

2. Theory, results and discussion

The correct knowledge of lattice constants of unknown compounds is necessary for analyzing the structure and properties of materials. This helps in the selection of an appropriate material in many industries related problems [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 him the lattice constant may be determine by the following relation,

$$a = 1.8836(r_B + r_X) + 1.4898\left[\frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}\right] - 1.2062 \qquad (1)$$

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. [20], the lattice constant of the ideal perovskite oxides (ABO_3) can be linearly correlated to some atomic parameters as,

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

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 the binding energy of the inner electron and to a shift in the position of the absorption edge. Because, Eq. (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. Furthermore, perovskite oxide solids can be defined in different systems like as $A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$. Therefore, we thought it would be of interest to give an alternative explanation for lattice constants of orthorhombic perovskite solids in terms of ionic charge. The lattice constants of orthorhombic 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 are presented in Figs. 2–4. In these figures, we observe that in the plot of experimental lattice constants and average ionic radii, the $A^{2+}B^{4+}O_3$ orthorhombic perovskite oxides lie on lines nearly parallel to the line for $A^{3+}B^{3+}O_3$ orthorhombic perovskite oxides. From these figures, 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.

In the previous work, [15–19], we proposed simple expressions for the electronic, optical and mechanical properties such as heteropolar energy gaps (E_c), average energy gaps (E_g), crystal ionicity (f_i), dielectric constant (ε_∞), electronic susceptibility (χ), cohesive energy (E_{coh}), bulk modulus (B) and microhardness (H) of rocksalt, zinc blende and chalcopyrite structured solids in terms of the product of ionic charges of cation and anion by the following relations,

$$\text{bulk modulus}\,(B\text{ in GPa}) = C(Z_1Z_2)^D\,d^{-3} \qquad (3)$$

$$\text{lattice energy}\,(U\text{ in kcal/mol}) = \frac{C(Z_1Z_2)^D}{\sqrt{d}} \qquad (4)$$

$$\text{dielectric constant}\ (\varepsilon_\infty) = C(Z_1Z_2)^D d^2 \qquad (5)$$

where C and D are constants, which depend upon crystal structures and d is the nearest-neighbour distance in Å. Z_1 and Z_2 are the ionic charges on the cation and anion, respectively. The Krishnan–Roy theory [21], Jayaraman et al. [22] and Sirdeshmukh and Subhadra [23] found that substantially reduced ionic charges must be used to get better agreement with experimental values. Similarly, based on the above expressions and discussion, we are of the view that lattice constant of orthorhombic perovskite-type crystal structure compounds can be evaluated using their ionic charge by following relations,

$$\text{lattice constant}\ (a\text{ in Å}) = 4(Z_1Z_2Z_3)^{0.054}\ r_{av} \qquad (6a)$$

$$\text{lattice constant}\,(b\text{ in Å}) = 4(Z_1Z_2Z_3)^{0.055}\,r_{av} \qquad (6b)$$

$$\text{lattice constant}\,(c\text{ in Å}) = 6(Z_1Z_2Z_3)^{0.04}\ r_{av} \qquad (6c)$$

where Z_1, Z_2 and Z_3 are the ionic charge on the A, B and O_3, respectively, r_{av} is the average ionic radii of ABO_3 in Å and it can be calculated by $r_{av} = \{(r_A + r_B + r_O)/3\}$. The correct ionic radii (r_a, r_b and r_o) are taken from Shanon's work [24] and other Ref. [5]. The value of product of ionic charge $(Z_1Z_2Z_3) = 30$ for $A^{1+}B^{5+}O_3$, $(Z_1Z_2Z_3) = 48$ for $A^{2+}B^{4+}O_3$ and $(Z_1Z_2Z_3) = 54$ for $A^{3+}B^{3+}O_3$ orthorhombic perovskites and ionic radii of oxide (r_o) is 1.35 [5]. A total of 152 orthorhombic perovskites and their lattice constants are collected from *The Major Ternary Structural Families* [25] and other Refs. [4–12,26–31]. The values so obtained are presented in Tables 1 and 2. The main advantage of Eqs. (6a)–(6c) is the simplicity of the formula, which does not require any experimental data expect the 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. Conclusion

We come to the conclusion that the product of ionic charges of any compound is the key parameter for calculating physical properties of solids. Furthermore, we found that in the compounds investigated here, the lattice constant exhibit a linear relationship when plotted on a log–log scale against the average ionic radii r_{av} (Å), but fall on straight lines according to the ionic charge product of the compounds, which are presented in Figs. 2–4. We observe that in the plot of lattice constant and ionic radii, the divalent perovskite-type oxides lie on line nearly parallel to the line for the trivalent perovskite oxides. 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 product of ionic charges and ionic radii of these materials. The calculated values are presented in Tables 1 and 2. An excellent agreement between the author's calculated values of lattice constant and the experimental values reported by different researchers has been found. The lattice constants evaluated in this work hardly deviates 0–10% from experimental data. The values evaluated show a systematic trend and are consistent with the available data reported so far, which proves the validity of the approach. According to this idea we may evaluate the all-important properties of orthorhombic perovskite solids using their ionic charge and average ionic radii, which are basic parameters. It is also to be note worthy 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. We have been reasonably successful in calculating lattice constant using the product of ionic charges and ionic radii of the materials for orthorhombic perovskite solids. It is natural to say that the ionic charge theory of solids can easily be extended to other physical properties like as bulk modulus, dielectric constant, etc. of perovskite structured solids, for which the work is in progress and will be appearing in forthcoming paper. 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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