The prediction of lattice constants in orthorhombic perovskites

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ABSTRACT

The correlation between ionic radii and the lattice constants of orthorhombic perovskites is examined and new empirical formulae for the relationship are derived. As for cubic/pseudocubic perovskites, the lattice constants are largely a function of A–X and B–X bond lengths rather than ionic charge. The average absolute relative error in the predicted a, b, and c lattice constants so derived is expected to be about 0.616%, 1.089%, and 0.714%, respectively; therefore, these formulae are in better agreement with experimental data than those derived by earlier researchers.

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1. Introduction

Perovskite is a term used to describe an ABX_3 arrangement of cations and an anion (typically oxygen) that is isomorphous with $CaTiO_3$. In the ideal cubic form, the A-site is coordinated to 12 anions to form cuboctahedral coordination polyhedra. The B-site is coordinated to six anions, forming octahedra. The anions are coordinated to two B-site cations and four A-site cations about 41% further away. The anion octahedra are corner-shared, which is a key feature of all perovskites. An example of the ideal structural model is shown in Fig. 1, and others abound in the literature [1,2].

Perovskites abound both in nature and in the laboratory, and their wide compositional range renders a variety of useful properties such that perovskites are encountered in applications as disparate as electroceramics, superconductors, refractories, catalysts, magnetoresistors, and proton conductors. The design of such advanced materials requires an understanding of the relationship between chemical composition and crystal structure. Lattice constants can be measured by experimental means such as X-ray, electron, or neutron diffraction; however, these techniques are typically complicated, difficult, time-consuming, and expensive. As a consequence, predictive models based on empirical relations of easily obtainable structural parameters have gradually gained in popularity and remain an important area of solid-state chemistry research.

Due to the wide range of applications in which perovskites find uses, much effort has been expended in order to understand the stabilization and distortions of the perovskite structure. Goldschmidt [3] introduced the concept of the perovskite tolerance factor, t:

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

where r_A and r_B are the ionic radii of the A-site and B-site cations and r_X is the ionic radius of the anion. In general, the perovskite structure is stable when the value of t is close to unity, which is true for $SrTiO_3$, for which $t = 1.00$. If t is very far from unity, a rhombohedral sesquioxide forms instead, as in $MgTiO_3$ ($t = 0.81$) which adopts the ilmenite structure [4]. Reaney et al. [5] observed that $A^{1+}B^{5+}(O^{2-})_3$ perovskites with $t < \sim 0.985$ contained axes about which oxygen octahedra were tilted in an anti-phase arrangement, causing cell doubling in the three pseudocubic directions. Similarly, perovskites for which $t < \sim 0.965$ undergo a further tilt transition whereby octahedra are tilted in-phase about one or more axes as well. Perovskites for which $t > \sim 0.985$ were not observed to contain a tilt superlattice; however, many researchers have reported aluminates [6], cuprates [7], nickelates [8], and ferrites [9] with $t \sim 1$ and tilted structures. For example, $LaAlO_3$ has been reported in the $R\bar{3}c$ system [6] with octahedra tilted $5.0°$ about the $[1 1 1]_c$, yet it has a $t = 1.0166$. According to Woodward [10], the rhombohedral $a^-a^-a^-$ tilt system is stabilized by highly charged A-site cations and small tilt angles. At higher tilt angles, the orthorhombic $a^+b^-b^-$ tilt system should be preferred, as in the case of $La(Zn_{1/2}Ti_{1/2})O_3$, which has an in-phase tilt angle of $8.3°$ [11].

Historically, relationships between composition and structure have been based on the simple theory of Coulombic interactions, considering close-packing, space-filling, or symmetry arguments.

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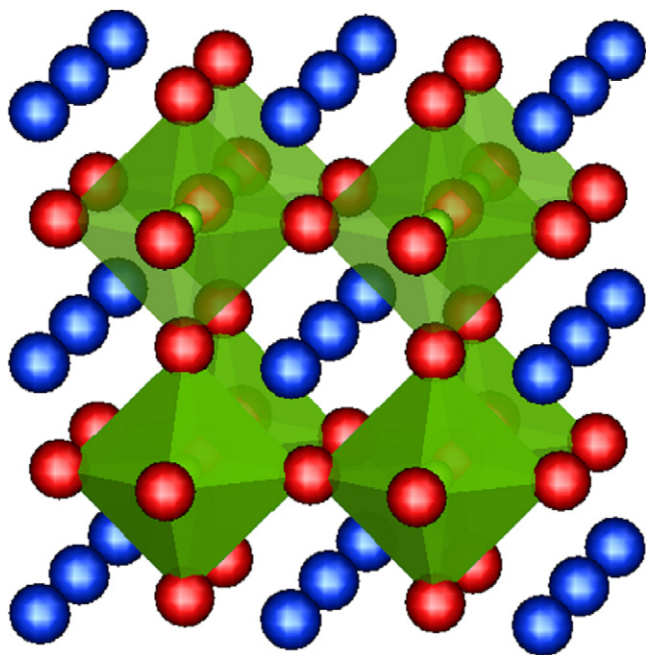
Fig. 1. Cubic perovskites (eight unit cells are shown). Atoms between octahedra are A-site cations; B-site cations are at the center of the octahedra; and atoms at the vertices of octahedra are anions.

Fig. 2. Calculated pseudocubic lattice constant, a_o, as a function of experimental lattice constant, a_{exptl}. Data from Refs. [19,20] are compared. The solid line represents a perfect fit ($a_o = a_{exptl}$).

Such reasoning led to radius-ratio rules. Roth [12], who studied $A^{3+}B^{3+}(O^{2-})_3$ compounds, used this approach to map structural stability fields for A-M_2O_3, B-M_2O_3, bixbyite, ilmenite, corundum, orthorhombic perovskite, rhombohedral perovskite, and three different hexagonal forms; however, the regions bordering different structural types were not well defined. Newnham [13] produced a similar map for $A^{2+}B^{4+}(O^{2-})_3$ compounds, while Giaquinta and Loye [14] used a combination of ionic radii and bond ionicities to improve the accuracy of the structural plot for $A^{3+}B^{3+}(O^{2-})_3$. The concept of the global instability index (GII) was introduced by Salinas-Sanchez et al. [15] to calculate the stability of the perovskite structure and the occurrence of octahedral tilting based on differences between experimental and calculated bond valence sums. The GII is defined as:

$$GII = \left[\frac{\left\{ \sum_{i=1}^{N} (d_i^2) \right\}^{1/2}}{N} \right] \tag{2}$$

where the discrepancy factor, d_i, is the difference between the formal valence and calculated bond valence for the ith ion and N is the number of ions in the unit cell. The GII is typically <0.1 v.u. (valence units) for untilted perovskites and <0.2 v.u. for tilted perovskites. Crystal structures for which GII > 0.2 are generally unstable. Woodward [16] later developed the POTATO program, which used geometrical considerations to predict the structure of tilted perovskites but required the tilt system, tilt angles, and octahedral bond distances as inputs. Lufaso and Woodward [17] later developed an algorithm based on GII-minimization to predict the structures and lattice parameters of perovskites from composition alone and introduced the concept of a bond valence based tolerance factor. Their procedure was automated in the Structure Prediction Diagnostic Software (SPuDS).

A recent study by Jiang et al. [18] established an empirical equation relating the ionic radii (A- and B-site cations and the X-site anion) to the pseudocubic perovskite lattice constant with an aver-
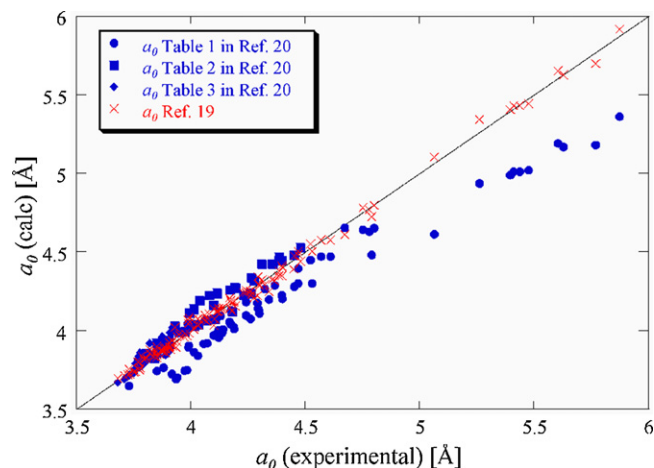
age absolute error of about 0.63%. This geometrical approach first assumes that $a_c = 2(r_B + r_X)$ and then uses the tolerance factor to account for the variation in a_c resulting from the size of the A-site species. In their work, a sixfold coordination was assumed for all ions involved. While such an error results in an underestimation of the A-site species radius and tolerance factor, it nevertheless resulted in an impressively accurate predictive formula. Ubic [19] later identified this error and used a linear regression in two variables to derive a more accurate and slightly simpler formula, also assuming sixfold coordination:

$$a_c = 0.06741 + 0.49052(r_A + r_X) + 1.29212(r_B + r_X) \tag{3}$$

A subsequent report by Verma et al. [20] attempted to relate the lattice constant of pseudocubic perovskites to a combination of ionic charge and radii; however, even after making the same corrections for inaccurate experimental lattice constants made in Ref. [19], the results were still less accurate than those calculated from Eq. (3) in 83% of cases, with an average absolute relative error of 2.52% as opposed to 0.60% for the 130 compounds analyzed. A comparison is demonstrated in Fig. 2.

Perovskites adopt a tilted structure partly to accommodate A-site species which are too small for the cuboctahedral sites which they would otherwise occupy. Octahedral tilting has the effect of reducing the coordination of the A-site cation while retaining the octahedral coordination of the B-site cation. One of the most common tilt configurations is $a^+b^-b^-$, which corresponds to in-phase tilting about one pseudocubic axis and anti-phase tilting of equal magnitude about the other two axes. This tilt system accounts for a majority of known perovskites [17]. Such a tilt system gives rise to an orthorhombic supercell in $Pbnm$ [21], although other structural details like cation ordering may further reduce the symmetry to $P2_1/n$ [11,22]. Although larger orthorhombic supercells are also possible (e.g., in $Imma$, $Cmcm$, $Pbcm$, or $Cmmm$), supercells in $Pbnm$ account for >90% of the observed orthorhombic perovskites [17]. This orthorhombic supercell is related to the cubic aristotype perovskite as shown in Fig. 3. The lattice constants are related to the cubic a_c thus: $a_o \sim 2a_c$, $b_o \sim c_o \sim \sqrt{2}a_c$.

This class of materials has useful dielectric, ferroelectric, and optical properties of their own; however, the prediction of their lattice constants is also of importance for their use as substrates or buffer layers for compound semiconductor epitaxy [23,24]. Consequently, structural prediction based on easily obtainable parameters for compounds with novel compositions remains an important problem in the area of solid-state chemistry.
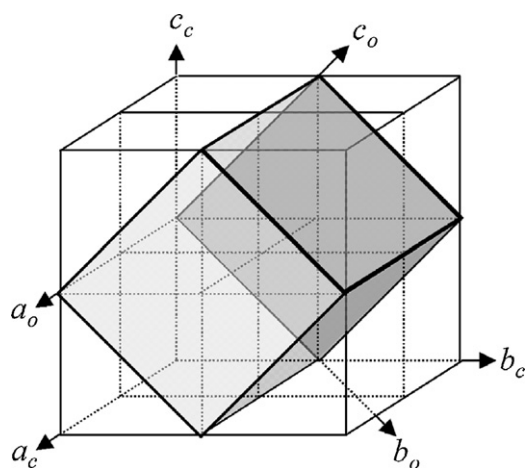
Fig. 3. The relationship between the simple cubic perovskite unit cell (eight are shown) in $Pm\bar{3}m$ and the orthorhombic $Pbnm$ supercell (shaded).

Kumar and Verma [25] recently reported equations describing the relationship between composition and lattice constants based on a combination of ionic charge and radii. Unfortunately, their list of orthorhombic perovskites contains only oxides, so it is unclear if their approach would work for the more generic case of ABX_3; and the errors reported in lattice constants were up to 10% in some cases. While such an approach may be worthwhile phenomenologically, simpler geometrical models have proven more effective as predictive tools.

Based on the results of Ref. [19] and the geometrical relationship of the orthorhombic supercell to the aristotype cubic perovskite illustrated in Fig. 3, a predictive tool more accurate than any reported previously has now been developed for the lattice constants of orthorhombic ($Pbnm$) perovskites.

2. Theory, results, and discussion

Ideally, A-site cations and anions are packed along $\langle 1\,1\,0 \rangle$ pseudocubic directions in perovskite. The pseudocubic lattice constant, a', can therefore be derived from the equation:

$$a' = \sqrt{2}(r_A + r_X) \tag{4}$$

In addition, B-site cations and anions are packed along $\langle 1\,0\,0 \rangle$ pseudocubic directions. The lattice constant, a'', can therefore alter-
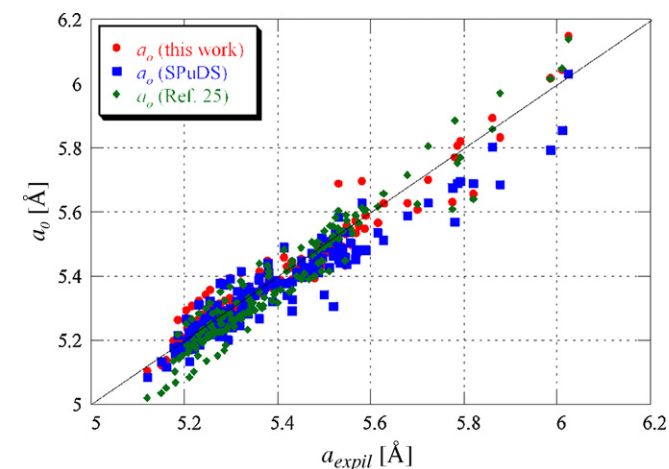

Fig. 4. Calculated lattice constant, a_o, as a function of measured lattice constant, a_{exptl}. The solid line represents a perfect fit ($a_o = a_{exptl}$). The fit parameter for the data from this work is $R^2 = 0.93403$, and the average absolute relative error is 0.617%.
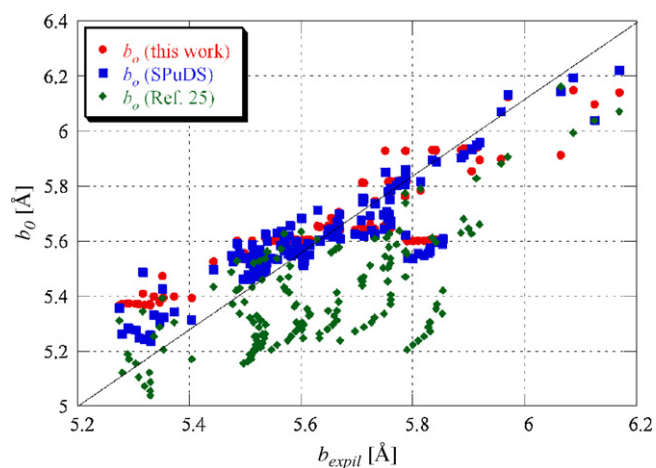

Fig. 5. Calculated lattice constant, b_o, as a function of measured lattice constant, b_{exptl}. The solid line represents a perfect fit ($b_o = b_{exptl}$). The linear fit parameter for the data from this work is $R^2 = 0.77138$, and the average absolute relative error is 1.089%.

natively be defined thus:

$$a'' = 2(r_B + r_X) \tag{5}$$

The ratio of a'/a'' is the tolerance factor, t. It is a very well-demonstrated fact that, in general, $a' \neq a''$ and so $t \neq 1$. At low values of t, a' tends to be underestimated and a'' overestimated; whereas at high values of t, the reverse is true. This discrepancy implies stretching/compressing of the A–X and B–X bonds, which has been demonstrated in bond valence (BV) calculations [19]. It is only around $t \sim 1.0$ that errors in both a' and a'' approach zero and the pseudocubic lattice constant, $a_c \approx a' \approx a''$. Ubic's formula [19], which is a linear regression of a' and a'', achieves an average absolute relative error in predicted values of a_c of only 0.60%, better than values obtained using the equation of Jiang et al. [18] in 64% of cases. It can easily be modified to predict the three lattice parameters of orthorhombic ($Pbnm$) perovskites.

To obtain a good first approximation of the three orthorhombic lattice constants, it is only necessary to consider the geometry in Fig. 3 and assume $a_o \sim 2a_c$, $b_o \sim c_o \sim \sqrt{2}a_c$. One can then define the average absolute errors $|\Delta\bar{a}_o|, |\Delta\bar{b}_o|, |\Delta\bar{c}_o|$ as well as a generalized error parameter which combines errors in a_o, b_o, and c_o. As error parameters which involve the products of Δa_o, Δb_o, and/or Δc_o, such as errors in cell volume, can be underestimated when one of the errors is very small while one or both of the others can be arbitrarily large, such parameters are not appropriate measures of error in the orthorhombic system. A more reliable diagnostic is the sum of absolute errors $|\Delta a_o| + |\Delta b_o| + |\Delta c_o| = |error|$. Based on Table 1 from Ref. [25], which contains the structural details of 152 orthorhombic oxide perovskites, $|\Delta\bar{a}_o|, |\Delta\bar{b}_o|, |\Delta\bar{c}_o|$, and $|error|$ are equal to 0.915%, 4.185%, 3.181%, and 8.281%, respectively; however, simply modifying the results from Ref. [19] as above one obtains better overall results: 1.880%, 2.576%, 1.087%, and 5.543.

In compiling these data, it becomes immediately obvious that the large error for $LaYO_3$ ($|error| = 449$) is the result of an incorrect ionic radius for Y_{VI}^{3+} ($r = 0.9$ Å not 0.645 Å) [26] used in Ref. [25]. Similarly, correcting the errors in the ionic radius of Ru_{VI}^{4+} ($r = 0.62$ Å not 0.68 Å) [26] as well as the c parameter of $DyCrO_3$ ($c = 5.520$ Å not 5.2 Å) [27] improves the fit overall. Finally, there are several inconsistencies in the table compiled by Kumar and Verma [25]. While the lattice constants of most compounds are listed assuming a $Pbnm$ model, several are listed in $Pnam$ ($CaVO_3$, $SrRuO_3$, $SrCeO_3$, $LaCrO_3$, $LaGaO_3$, $LaTiO_3$, and $SmAlO_3$). When the unit cells are re-oriented such that they can all be described in $Pbnm$, the fit improves such that $|\Delta\bar{a}_o|, |\Delta\bar{b}_o|, |\Delta\bar{c}_o|$, and $|error|$ are equal to 1.832%, 2.506%,

Table 1
Experimental and calculated values of lattice constants for orthorhombic perovskites.

Compound	r_A^{VI}	r_B^{VI}	a_{exptl} (Å)	b_{exptl} (Å)	c_{exptl} (Å)	a_o (Å)	$|\Delta a_o|$ (%)	b_o (Å)	$|\Delta b_o|$ (%)	c_o (Å)	$|\Delta c_o|$ (%)	|Error|
NaUO$_3$	1.02	0.76	5.775	5.905	8.25	5.630	2.513	5.854	0.869	8.064	2.260	5.642
NaTaO$_3$	1.02	0.64	5.494	5.513	7.751	5.473	0.389	5.602	1.606	7.767	0.208	2.203
NaNbO$_3$	1.02	0.64	5.51	5.57	7.77	5.473	0.678	5.602	0.566	7.767	0.037	1.282
NaPaO$_3$	1.02	0.78	5.82	5.92	8.36	5.656	2.817	5.896	0.410	8.113	2.955	6.181
CaMnO$_3$	1	0.53	5.27	5.275	7.464	5.298	0.535	5.369	1.777	7.463	0.016	2.328
CaCrO$_3$	1	0.55	5.287	5.316	7.486	5.324	0.708	5.411	1.783	7.512	0.350	2.841
CaVO$_3$	1	0.58	5.326	5.352	7.547	5.364	0.708	5.474	2.276	7.586	0.521	3.506
CaTiO$_3$	1	0.605	5.381	5.443	7.645	5.396	0.288	5.526	1.531	7.648	0.041	1.860
CaRuO$_3$	1	0.62	5.36	5.53	7.67	5.416	1.047	5.558	0.504	7.685	0.198	1.749
CaMoO$_3$	1	0.65	5.45	5.58	7.8	5.455	0.100	5.621	0.733	7.759	0.522	1.355
CaNbO$_3$	1	0.68	5.5338	5.6541	7.9131	5.495	0.706	5.684	0.528	7.833	1.007	2.240
CaSnO$_3$	1	0.69	5.519	5.668	7.885	5.508	0.202	5.705	0.652	7.858	0.341	1.195
CaHfO$_3$	1	0.71	5.568	5.732	7.984	5.534	0.610	5.747	0.261	7.908	0.958	1.829
CaZrO$_3$	1	0.72	5.587	5.758	8.008	5.547	0.713	5.768	0.174	7.932	0.946	1.833
CaUO$_3$	1	0.89	5.78	5.97	8.29	5.770	0.175	6.125	2.600	8.352	0.751	3.525
BaPbO$_3$	1.35	0.775	6.024	6.065	8.506	6.149	2.082	5.912	2.515	8.637	1.542	6.139
SrRuO$_3$	1.18	0.62	5.53	5.57	7.847	5.689	2.872	5.573	0.049	7.978	1.667	4.588
SrUO$_3$	1.18	0.89	6.01	6.17	8.6	6.043	0.542	6.140	0.485	8.645	0.522	1.549
SrIrO$_3$	1.18	0.625	5.58	5.6	7.89	5.695	2.068	5.583	0.299	7.990	1.270	3.637
SrHfO$_3$	1.18	0.71	5.785	5.786	8.182	5.807	0.376	5.762	0.417	8.200	0.222	1.016
SrZrO$_3$	1.18	0.72	5.792	5.814	8.196	5.820	0.481	5.783	0.536	8.225	0.353	1.369
SrPbO$_3$	1.18	0.775	5.86	5.958	8.331	5.892	0.544	5.898	1.000	8.361	0.357	1.902
SrCeO$_3$	1.18	0.87	5.986	6.125	8.531	6.016	0.507	6.098	0.440	8.595	0.756	1.703
LaCrO$_3$	1.032	0.615	5.479	5.515	7.753	5.458	0.382	5.550	0.635	7.725	0.363	1.380
LaGaO$_3$	1.032	0.62	5.473	5.526	7.767	5.465	0.153	5.561	0.624	7.737	0.384	1.161
LaFeO$_3$	1.032	0.645	5.556	5.565	7.862	5.497	1.055	5.613	0.863	7.799	0.802	2.720
LaVO$_3$	1.032	0.64	5.54	5.54	7.83	5.491	0.888	5.603	1.129	7.787	0.554	2.571
LaMnO$_3$	1.032	0.645	5.529	5.662	7.715	5.497	0.572	5.613	0.865	7.799	1.088	2.525
LaRhO$_3$	1.032	0.665	5.524	5.629	7.9	5.524	0.008	5.655	0.463	7.848	0.653	1.124
LaTiO$_3$	1.032	0.67	5.546	5.753	7.832	5.530	0.286	5.666	1.520	7.861	0.367	2.173
LaScO$_3$	1.032	0.745	5.678	5.787	8.098	5.628	0.874	5.823	0.625	8.046	0.642	2.140
LaInO$_3$	1.032	0.8	5.723	5.914	8.207	5.700	0.394	5.939	0.418	8.182	0.306	1.118
LaYO$_3$	1.032	0.9	5.877	6.087	8.493	5.831	0.775	6.149	1.016	8.429	0.754	2.545
CeCrO$_3$	1.01	0.615	5.475	5.475	7.74	5.425	0.918	5.548	1.337	7.689	0.658	2.913
CeFeO$_3$	1.01	0.645	5.519	5.536	7.819	5.464	0.996	5.611	1.359	7.763	0.714	3.068
CeVO$_3$	1.01	0.64	5.486	5.486	7.74	5.457	0.520	5.601	2.091	7.751	0.140	2.751
CeMnO$_3$	1.01	0.645	5.532	5.557	7.812	5.464	1.229	5.611	0.976	7.763	0.625	2.829
CeTiO$_3$	1.01	0.67	5.513	5.757	7.801	5.497	0.294	5.664	1.620	7.825	0.307	2.221
PrCrO$_3$	0.99	0.615	5.479	5.484	7.718	5.394	1.543	5.547	1.140	7.657	0.796	3.480
PrGaO$_3$	0.99	0.62	5.458	5.49	7.733	5.401	1.045	5.557	1.221	7.669	0.829	3.094
PrFeO$_3$	0.99	0.645	5.495	5.578	7.81	5.434	1.115	5.610	0.566	7.731	1.016	2.696
PrVO$_3$	0.99	0.64	5.487	5.562	7.751	5.427	1.090	5.599	0.666	7.718	0.421	2.178
PrMnO$_3$	0.99	0.645	5.545	5.787	7.575	5.434	2.006	5.610	3.066	7.731	2.055	7.128
PrRhO$_3$	0.99	0.665	5.414	5.747	7.803	5.460	0.849	5.652	1.660	7.780	0.294	2.802
PrTiO$_3$	0.99	0.67	5.499	5.724	7.798	5.466	0.591	5.662	1.081	7.792	0.071	1.744
PrCoO$_3$	0.99	0.545	5.331	5.373	7.587	5.303	0.530	5.399	0.492	7.484	1.363	2.385
PrScO$_3$	0.99	0.745	5.615	5.776	8.027	5.565	0.895	5.820	0.757	7.978	0.614	2.265
PrAlO$_3$	0.99	0.535	5.322	5.347	7.481	5.290	0.608	5.378	0.588	7.459	0.295	1.491
NdCrO$_3$	0.983	0.615	5.425	5.478	7.694	5.384	0.759	5.546	1.240	7.645	0.634	2.634
NdGaO$_3$	0.983	0.62	5.431	5.499	7.71	5.390	0.748	5.556	1.045	7.658	0.680	2.473
NdFeO$_3$	0.983	0.645	5.441	5.573	7.753	5.423	0.328	5.609	0.646	7.719	0.435	1.409
NdVO$_3$	0.983	0.64	5.451	5.579	7.734	5.417	0.631	5.598	0.349	7.707	0.350	1.330
NdMnO$_3$	0.983	0.645	5.38	5.854	7.557	5.423	0.802	5.609	4.185	7.719	2.148	7.135
NdRhO$_3$	0.983	0.665	5.378	5.755	7.775	5.449	1.327	5.651	1.807	7.769	0.081	3.214
NdTiO$_3$	0.983	0.67	5.487	5.707	7.765	5.456	0.567	5.662	0.797	7.781	0.207	1.571
NdCoO$_3$	0.983	0.545	5.336	5.336	7.547	5.292	0.822	5.399	1.178	7.472	0.991	2.991
NdScO$_3$	0.983	0.745	5.574	5.771	7.998	5.554	0.356	5.819	0.834	7.966	0.396	1.585
NdInO$_3$	0.983	0.8	5.627	5.891	8.121	5.626	0.014	5.935	0.742	8.102	0.231	0.986
PmCrO$_3$	0.97	0.615	5.4	5.49	7.69	5.364	0.664	5.545	1.000	7.624	0.858	2.521
PmScO$_3$	0.97	0.745	5.56	5.79	7.94	5.534	0.459	5.818	0.484	7.945	0.066	1.009
PmInO$_3$	0.97	0.8	5.7	5.9	8.2	5.607	1.640	5.934	0.570	8.081	1.450	3.660
SmAlO$_3$	0.958	0.535	5.285	5.29	7.473	5.241	0.830	5.376	1.622	7.407	0.885	3.336
SmCrO$_3$	0.958	0.615	5.367	5.508	7.643	5.346	0.392	5.544	0.652	7.605	0.503	1.547
SmGaO$_3$	0.958	0.62	5.369	5.52	7.65	5.353	0.307	5.554	0.623	7.617	0.433	1.363
SmFeO$_3$	0.958	0.645	5.394	5.592	7.711	5.385	0.162	5.607	0.267	7.679	0.419	0.848
SmVO$_3$	0.958	0.64	5.393	5.588	7.672	5.379	0.265	5.596	0.151	7.666	0.074	0.490
SmMnO$_3$	0.958	0.645	5.359	5.843	7.482	5.385	0.490	5.607	4.040	7.679	2.628	7.159
SmRhO$_3$	0.958	0.665	5.321	5.761	7.708	5.411	1.700	5.649	1.945	7.728	0.260	3.906
SmTiO$_3$	0.958	0.67	5.468	5.665	7.737	5.418	0.914	5.659	0.098	7.740	0.044	1.056
SmCoO$_3$	0.958	0.545	5.289	5.354	7.541	5.254	0.657	5.397	0.799	7.432	1.451	2.907
SmScO$_3$	0.958	0.745	5.53	5.76	7.95	5.516	0.248	5.817	0.991	7.926	0.305	1.544
SmInO$_3$	0.958	0.8	5.589	5.886	8.082	5.588	0.012	5.933	0.792	8.062	0.252	1.056
EuAlO$_3$	0.947	0.535	5.271	5.292	7.458	5.224	0.883	5.375	1.566	7.389	0.925	3.374
EuCrO$_3$	0.947	0.615	5.34	5.515	7.622	5.329	0.201	5.543	0.507	7.587	0.464	1.172

Table 1 (*Continued*)

Compound	r_A^{VI}	r_B^{VI}	a_{exptl} (Å)	b_{exptl} (Å)	c_{exptl} (Å)	a_o (Å)	$|\Delta a_o|$ (%)	b_o (Å)	$|\Delta b_o|$ (%)	c_o (Å)	$|\Delta c_o|$ (%)	$|Error|$
EuGaO$_3$	0.947	0.62	5.351	5.528	7.628	5.336	0.283	5.553	0.461	7.599	0.380	1.124
EuFeO$_3$	0.947	0.645	5.371	5.611	7.686	5.369	0.045	5.606	0.089	7.661	0.328	0.462
EuMnO$_3$	0.947	0.645	5.338	5.842	7.453	5.369	0.573	5.606	4.039	7.661	2.788	7.400
EuRhO$_3$	0.947	0.665	5.298	5.761	7.68	5.395	1.827	5.648	1.961	7.710	0.393	4.181
EuScO$_3$	0.947	0.745	5.51	5.76	7.94	5.500	0.188	5.816	0.975	7.908	0.405	1.568
EuInO$_3$	0.947	0.8	5.567	5.835	8.078	5.572	0.084	5.932	1.657	8.044	0.424	2.166
GdAlO$_3$	0.938	0.535	5.247	5.304	7.447	5.211	0.689	5.374	1.322	7.374	0.975	2.987
GdCrO$_3$	0.938	0.615	5.312	5.525	7.606	5.316	0.069	5.542	0.312	7.572	0.447	0.828
GdGaO$_3$	0.938	0.62	5.322	5.537	7.606	5.322	0.004	5.553	0.284	7.584	0.284	0.573
GdFeO$_3$	0.938	0.645	5.346	5.616	7.668	5.355	0.168	5.605	0.191	7.646	0.285	0.644
GdVO$_3$	0.938	0.64	5.343	5.614	7.637	5.348	0.101	5.595	0.343	7.634	0.042	0.486
GdMnO$_3$	0.938	0.645	5.313	5.853	7.432	5.355	0.790	5.605	4.232	7.646	2.881	7.904
GdRhO$_3$	0.938	0.665	5.277	5.761	7.658	5.381	1.974	5.647	1.974	7.696	0.490	4.438
GdTiO$_3$	0.938	0.67	5.407	5.667	7.692	5.388	0.357	5.658	0.162	7.708	0.207	0.726
GdCoO$_3$	0.938	0.545	5.228	5.404	7.436	5.224	0.078	5.395	0.164	7.399	0.497	0.738
GdScO$_3$	0.938	0.745	5.487	5.756	7.925	5.486	0.018	5.815	1.032	7.893	0.401	1.452
GdInO$_3$	0.938	0.8	5.548	5.842	8.071	5.558	0.181	5.931	1.523	8.029	0.519	2.223
TbAlO$_3$	0.923	0.535	5.22	5.28	7.41	5.188	0.611	5.373	1.759	7.350	0.810	3.180
TbCrO$_3$	0.923	0.615	5.291	5.518	7.576	5.293	0.037	5.541	0.417	7.548	0.374	0.828
TbGaO$_3$	0.923	0.62	5.307	5.531	7.578	5.299	0.142	5.552	0.371	7.560	0.238	0.750
TbFeO$_3$	0.923	0.645	5.326	5.602	7.635	5.332	0.117	5.604	0.036	7.622	0.174	0.327
TbMnO$_3$	0.923	0.645	5.297	5.831	7.403	5.332	0.665	5.604	3.892	7.622	2.955	7.513
TbRhO$_3$	0.923	0.665	5.254	5.749	7.623	5.358	1.988	5.646	1.791	7.671	0.632	4.410
TbTiO$_3$	0.923	0.67	5.388	5.648	7.676	5.365	0.427	5.657	0.152	7.684	0.098	0.677
DyAlO$_3$	0.912	0.535	5.21	5.31	7.38	5.171	0.740	5.372	1.167	7.332	0.649	2.556
DyCrO$_3$	0.912	0.615	5.263	5.52	7.552	5.276	0.252	5.540	0.364	7.530	0.295	0.911
DyGaO$_3$	0.912	0.62	5.282	5.534	7.556	5.283	0.016	5.551	0.300	7.542	0.184	0.499
DyFeO$_3$	0.912	0.645	5.302	5.598	7.623	5.316	0.256	5.603	0.092	7.604	0.251	0.599
DyVO$_3$	0.912	0.64	5.302	5.602	7.601	5.309	0.133	5.593	0.167	7.592	0.125	0.425
DyMnO$_3$	0.912	0.645	5.275	5.828	7.375	5.316	0.769	5.603	3.859	7.604	3.103	7.731
DyRhO$_3$	0.912	0.665	5.245	5.731	7.6	5.342	1.845	5.645	1.498	7.653	0.701	4.044
DyTiO$_3$	0.912	0.67	5.361	5.659	7.647	5.348	0.236	5.656	0.059	7.666	0.244	0.539
DyScO$_3$	0.912	0.745	5.43	5.71	7.89	5.447	0.306	5.813	1.808	7.851	0.495	2.609
DyInO$_3$	0.912	0.8	5.519	5.751	8.041	5.519	0.006	5.929	3.092	7.987	0.674	3.772
HoAlO$_3$	0.901	0.535	5.18	5.33	7.36	5.155	0.487	5.371	0.771	7.314	0.622	1.879
HoCrO$_3$	0.901	0.615	5.243	5.519	7.538	5.260	0.317	5.539	0.366	7.512	0.347	1.029
HoGaO$_3$	0.901	0.62	5.251	5.531	7.536	5.266	0.289	5.550	0.338	7.524	0.156	0.783
HoFeO$_3$	0.901	0.645	5.278	5.591	7.602	5.299	0.396	5.602	0.201	7.586	0.211	0.808
HoMnO$_3$	0.901	0.645	5.255	5.831	7.354	5.299	0.836	5.602	3.924	7.586	3.154	7.914
HoRhO$_3$	0.901	0.665	5.23	5.726	7.582	5.325	1.819	5.644	1.428	7.635	0.704	3.951
HoTiO$_3$	0.901	0.67	5.339	5.665	7.626	5.332	0.137	5.655	0.181	7.648	0.285	0.603
HoScO$_3$	0.901	0.745	5.42	5.71	7.87	5.430	0.183	5.812	1.792	7.833	0.470	2.445
ErAlO$_3$	0.89	0.535	5.16	5.32	7.33	5.138	0.424	5.370	0.943	7.296	0.459	1.826
ErCrO$_3$	0.89	0.615	5.223	5.516	7.519	5.243	0.382	5.538	0.404	7.494	0.333	1.118
ErGaO$_3$	0.89	0.62	5.239	5.527	7.522	5.249	0.200	5.549	0.394	7.506	0.208	0.803
ErFeO$_3$	0.89	0.645	5.263	5.582	7.591	5.282	0.366	5.601	0.346	7.568	0.302	1.013
ErVO$_3$	0.89	0.64	5.262	5.604	7.578	5.276	0.260	5.591	0.236	7.556	0.294	0.790
ErMnO$_3$	0.89	0.645	5.24	5.82	7.335	5.282	0.806	5.601	3.758	7.568	3.178	7.742
ErRhO$_3$	0.89	0.665	5.216	5.712	7.561	5.308	1.772	5.643	1.202	7.618	0.747	3.722
ErTiO$_3$	0.89	0.67	5.318	5.657	7.613	5.315	0.056	5.654	0.056	7.630	0.221	0.334
TmAlO$_3$	0.88	0.535	5.15	5.33	7.29	5.123	0.525	5.369	0.738	7.280	0.136	1.399
TmCrO$_3$	0.88	0.615	5.209	5.508	7.5	5.228	0.361	5.537	0.535	7.478	0.297	1.192
TmGaO$_3$	0.88	0.62	5.224	5.515	7.505	5.234	0.198	5.548	0.597	7.490	0.199	0.994
TmFeO$_3$	0.88	0.645	5.251	5.576	7.584	5.267	0.307	5.600	0.439	7.552	0.424	1.170
TmMnO$_3$	0.88	0.645	5.23	5.81	7.32	5.267	0.709	5.600	3.606	7.552	3.167	7.483
TmRhO$_3$	0.88	0.665	5.203	5.697	7.543	5.293	1.736	5.643	0.957	7.601	0.772	3.464
TmTiO$_3$	0.88	0.67	5.306	5.647	7.607	5.300	0.116	5.653	0.106	7.614	0.087	0.309
YbAlO$_3$	0.868	0.535	5.12	5.33	7.31	5.105	0.297	5.368	0.719	7.261	0.676	1.693
YbCrO$_3$	0.868	0.615	5.195	5.51	7.49	5.210	0.281	5.536	0.480	7.458	0.424	1.186
YbGaO$_3$	0.868	0.62	5.208	5.51	7.49	5.216	0.157	5.547	0.671	7.471	0.260	1.087
YbFeO$_3$	0.868	0.645	5.233	5.557	7.57	5.249	0.304	5.599	0.765	7.532	0.498	1.566
YbMnO$_3$	0.868	0.645	5.22	5.8	7.3	5.249	0.554	5.599	3.457	7.532	3.183	7.194
YbTiO$_3$	0.868	0.67	5.293	5.633	7.598	5.282	0.214	5.652	0.338	7.594	0.051	0.603
LuCrO$_3$	0.861	0.615	5.176	5.497	7.475	5.199	0.445	5.536	0.707	7.447	0.377	1.529
LuGaO$_3$	0.861	0.62	5.188	5.505	7.484	5.206	0.338	5.546	0.752	7.459	0.332	1.422
LuFeO$_3$	0.861	0.645	5.213	5.547	7.565	5.238	0.486	5.599	0.936	7.521	0.582	2.004
LuMnO$_3$	0.861	0.645	5.205	5.79	7.31	5.238	0.640	5.599	3.300	7.521	2.886	6.826
LuRhO$_3$	0.861	0.665	5.186	5.67	7.512	5.265	1.514	5.641	0.513	7.570	0.777	2.804
LuTiO$_3$	0.861	0.67	5.274	5.633	7.58	5.271	0.056	5.651	0.327	7.583	0.036	0.419
YAlO$_3$	0.9	0.535	5.179	5.329	7.37	5.153	0.497	5.371	0.788	7.313	0.779	2.064
YCrO$_3$	0.9	0.615	5.241	5.521	7.532	5.258	0.326	5.539	0.328	7.510	0.289	0.943
YGaO$_3$	0.9	0.62	5.257	5.536	7.533	5.265	0.145	5.550	0.246	7.523	0.138	0.529
YFeO$_3$	0.9	0.645	5.283	5.592	7.603	5.297	0.273	5.602	0.181	7.584	0.245	0.699
YVO$_3$	0.9	0.64	5.284	5.605	7.587	5.291	0.130	5.592	0.239	7.572	0.198	0.566

Table 1 (*Continued*)

Compound	r_A^{VI}	r_B^{VI}	a_{exptl} (Å)	b_{exptl} (Å)	c_{exptl} (Å)	a_o (Å)	$|\Delta a_o|$ (%)	b_o (Å)	$|\Delta b_o|$ (%)	c_o (Å)	$|\Delta c_o|$ (%)	$|Error|$
YMnO$_3$	0.9	0.645	5.26	5.83	7.36	5.297	0.711	5.602	3.909	7.584	3.048	7.668
YTiO$_3$	0.9	0.67	5.34	5.665	7.624	5.330	0.184	5.655	0.182	7.646	0.290	0.657
YScO$_3$	0.9	0.745	5.431	5.712	7.894	5.428	0.048	5.812	1.755	7.831	0.793	2.596
YInO$_3$	0.9	0.8	5.5	5.787	8.053	5.500	0.009	5.928	2.434	7.967	1.064	3.507
					Averages:		0.617		1.089		0.714	2.420

$|Error| = |\Delta a_o| + |\Delta b_o| + |\Delta c_o|$. $r_O^{VI} = 1.4$ Å [25].
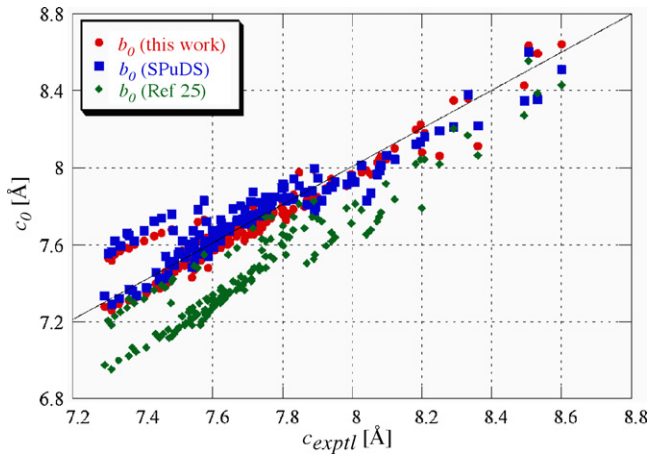
Fig. 6. Calculated lattice constant, c_o, as a function of measured lattice constant, c_{exptl}. The solid line represents a perfect fit ($c_o = c_{exptl}$). The linear fit parameter for the data from this work is $R^2 = 0.90936$, and the average absolute relative error is 0.714%.

1.009%, and 5.348, respectively. One of the compounds with a large error remaining is CaNbO$_3$ ($|error| = 5.530$); however, when the unit cell reported by Hervieu et al. [28] (PDF 47-1668) is substituted for the one used in Ref. [25], the value of $|error|$ decreases to just 2.752.

A great improvement to the fits can be made now by calculating a linear regression in two variables, $(r_A + r_O)$ and $(r_B + r_O)$, for each parameter a_o, b_o, and c_o instead of simply assuming $a_o \sim 2a_c$, $b_o \sim c_o \sim \sqrt{2}a_c$. A still better fit is obtained if, like Jiang et al. [18] and Ubic [19], a sixfold coordination for all ions is assumed. The fact that neither A-site cations nor oxygen anions are coordinated in this way is irrelevant. As a predictive tool it turns out to be more accurate to use the sixfold radii, probably because these values are known with greater certainty than the 12-fold radii. The result is a set of three equations (one each for a_o, b_o, and c_o) with $|\Delta \bar{a}_o|$, $|\Delta \bar{b}_o|$, $|\Delta \bar{c}_o|$, and $|error|$ equal to 0.631%, 1.104%, 0.714%, and 2.449, respectively. A further slight improvement can be achieved by again re-orienting unit cells such that the rule $a_o < b_o < c_o$ is always obeyed, even when it means altering the setting of the space group accordingly. The final fits yield results with $|\Delta \bar{a}_o|$, $|\Delta \bar{b}_o|$, $|\Delta \bar{c}_o|$, and $|error|$ equal to 0.617%, 1.089%, 0.714%, and 2.420, respectively. The equations are listed below:

$$a_o = 1.514921(r_A + r_O) + 1.310215(r_B + r_O) - 0.86631 \quad (6)$$

$$b_o = 0.082623(r_A + r_O) + 2.101275(r_B + r_O) + 1.114993 \quad (7)$$

$$c_o = 1.625883(r_A + r_O) + 2.470594(r_B + r_O) - 1.20754 \quad (8)$$

The results are shown in Table 1, which is based on Table 1 from Ref. [25]. The results are slightly better even than those calculated from the SPuDS program [17]. The average errors ($|\Delta \bar{a}_o|$, $|\Delta \bar{b}_o|$, $|\Delta \bar{c}_o|$, and $|error|$) as calculated by SPuDS are 0.889%, 1.132%, 0.999%, and 3.020 (excluding the three Pm^{3+}-containing compounds – PmCrO$_3$, PmScO$_3$, and PmInO$_3$ – as SPuDS does not support the Pm^{3+} cation). While not quite as accurate as Eqs. (5)–(7), SPuDS nevertheless produces far more accurate results than the

equations published by Kumar and Verma [25]; however, in almost all cases it predicts a structure in $R\bar{3}c$ rather than $Pbnm$ as the most stable perovskite structure by *GII*-minimization.

These results are illustrated graphically in Figs. 4–6. From Fig. 4 it can be seen that Eq. (6) produces generally more accurate results for a_o than that of Kumar and Verma [25], especially at lower values of a_{exptl}, or SPuDS [17], especially at higher values of a_{exptl}. Fig. 5 reveals the comparatively very poor fit of the equation for b_o given in Ref. [25]. Both SPuDS [17] and Eq. (7) yield far more accurate results. According to Fig. 6, there is some overestimation in values of c_o as predicted by either Eq. (8) or SPuDS [17] at lower values of c_{exptl}; however, the values obtained from Ref. [25] are almost always underestimated.

According to Eq. (6), a_o is a function of both $(r_A + r_O)$ and $(r_B + r_O)$ in fairly equal measure; however, Eq. (7) shows that b_o is almost independent of $(r_A + r_O)$ and is far more sensitive to $(r_B + r_O)$. Likewise, Eq. (8) indicates that, while c_o is a function of both $(r_A + r_O)$ and $(r_B + r_O)$, it is influenced more strongly by changes in $(r_B + r_O)$.

3. Conclusions

New empirical formulations describing the relationship between ionic radii and orthorhombic lattice constants for perovskites in space group $Pbnm$ have been derived. These formulae can be used to predict the lattice constants of orthorhombic perovskites with more accuracy than any other method yet reported.

References

[1] H.D. Megaw, Proc. Phys. Soc. Lond. 58 (2) (1946) 133.
[2] R. Ubic, I.M. Reaney, W.E. Lee, Int. Mater. Rev. 43 (5) (1998) 205.
[3] V.M. Goldschmidt, Die Naturwiss. 14 (21) (1926) 477.
[4] H.D. Megaw, Crystal Structures: A Working Approach, W.B. Saunders Co. Ltd., London, 1973.
[5] I.M. Reaney, E.L. Colla, N. Setter, Jpn. J. Appl. Phys. Part 1 33 (7A) (1994) 3984.
[6] C.J. Howard, B.J. Kennedy, B.C. Chakoumakos, J. Phys.: Condens. Matter 12 (2000) 349.
[7] G. Demazeau, C. Parent, M. Pouchard, P. Hagenmuller, Mater. Res. Bull. 7 (1972) 913.
[8] J.L. García-Muñoz, J. Rodriguez-Carvajal, P. Lacorre, J.B. Torrance, Phys. Rev. B: Condens. Matter 46 (1992) 4414.
[9] P.D. Battle, T.C. Gibb, P. Lightfoot, J. Solid State Chem. 84 (1990) 271.
[10] P.M. Woodward, Acta Crystallogr. B53 (1997) 44.
[11] R. Ubic, Y. Hu, I. Abrahams, Acta Crystallogr. B62 (2006) 521.
[12] R.S. Roth, J. Res. NBS 58 (1957) 75.
[13] R.E. Newnham, J. Mater. Ed. 5 (6) (1983) 947.
[14] D.M. Giaquinta, H.-C. zur Loye, Chem. Mater. 6 (1994) 365.
[15] A. Salinas-Sanchez, J.L. García-Muñoz, J. Rodriguez-Carvajal, R. Saez-Puche, J.L. Martinez, J. Solid State Chem. 100 (1992) 201.
[16] P.M. Woodward, J. Appl. Cryst. 30 (1997) 206.
[17] M.W. Lafaso, P.M. Woodward, Acta Crystallogr. B57 (2001) 725.
[18] L.Q. Jiang, J.K. Guo, H.B. Liu, M. Zhou, X. Zhou, P. Wu, C.H. Li, J. Chem. Phys. Solids 67 (2006) 1531.
[19] R. Ubic, J. Am. Ceram. Soc. 90 (10) (2007) 3326.
[20] A.S. Verma, A. Kuma, R.S. Bhardwaj, Phys. Stat. Sol. (b) 245 (8) (2008) 1520.
[21] A.M. Glazer, Acta Crystallogr. A31 (1975) 756.
[22] C.J. Howard, B.J. Kennedy, P.M. Woodward, Acta Crystallogr. B59 (2003) 463.
[23] M.I. Kotelyanski, I.M. Kotelyanski, V.B. Kravchenko, Technol. Phys. Lett. 26 (2) (2000) 163.
[24] K. Eisenbeiser, R. Emrickm, R. Droopad, Z. Yu, J. Finder, S. Rockwell, J. Holmes, C. Overgaard, W. Ooms, IEEE Electron Dev. Lett. 23 (6) (2002) 300.
[25] A. Kumar, A.S. Verma, J. Alloys Compd. 480 (2009) 650.
[26] R.D. Shannon, Acta Crystallogr. A32 (1976) 751.
[27] E.F. Bertaut, J. Mareschal, J. Phys. France 29 (1968) 67.
[28] M. Hervieu, F. Studer, B. Raveau, J. Solid State Chem. 22 (3) (1977) 273.