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The Relation Between Ionic Radii and Cell Volumes in the Perovskite Compounds

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More than 200 cell volumes of perovskite oxides were calculated with good accuracy using a relation between cubic root of cell volume and tolerance factor of the form $V^{1/3} = 2(\mathrm{m}r(B) + nr(X)) - d(s-1)$, where $V^{1/3}$ is cubic root of cell volume; m, n, and d are adjustable parameters; $r(B)$ and $r(X)$ are B-cation and anion radius, respectively; and s are reciprocal tolerance factors. The parameters m, n, and d were determined empirically from the plots $V^{1/3}$ versus s in the selected $A^{2+}B^{4+}O_3$-type perovskites.

In ABO_3 type perovskites, the parameters m, n, and d are given to be 1.185, 0.882, and 2.00, respectively. Linear relations between $V^{1/3}$ and s are found to hold in ABF_3 and $ABCl_3$ type perovskites, also. General radii–volume relation in ABX_3 (X = Cl, F, and O) perovskites was thus given by

$$V = a^3 r(\mathrm{B})^3 + 3a^2 br(\mathrm{B})^2 + 3ab^2 r(\mathrm{B}) + b^3,$$

where $a = 2\mathrm{m} - \sqrt{2}(d/R_{\mathrm{A-X}})$ and $b = 2nr(\mathrm{X}) - \sqrt{2}(dr(\mathrm{X})/R_{\mathrm{A-X}})$, and $R_{\mathrm{A-X}} = r(\mathrm{A}) + r(\mathrm{X})$.

The above relation was applied for the estimation of ionic radii with twelve and six fold coordination and for the calculation of cell volume of hypothetical high pressure stable perovskite of the form Fe_2O_3. This relation should be useful for predicting the molar volume of perovskite by a given combination of elements.

Introduction

The largest group of ABX_3 compounds crystallizes in the perovskite structure. The estimation of cell volume of ABX_3 perovskite as a function of ionic radii provides important information on various crystal chemical aspects of perovskites. In the ideal perovskite structure, the atoms are in the following positions: A; 000, B; 1/2 1/2 1/2 X; 1/2 1/2 0, 1/2 0 1/2, 0 1/2 1/2. The coordination number (CN) of B-cation and anion are 6 and of A-cation 12. Goldschmidt (*1*) defines the tolerable limits on the radius $r(\mathrm{A})$ of A-cation relative to $r(\mathrm{X})$ and $r(\mathrm{B})$ of anion and B-cation as a tolerance factor t;

$$t = R_{\mathrm{A-X}}/\sqrt{2}R_{\mathrm{B-X}} \tag{1}$$

where $R_{\mathrm{A-X}} = r(\mathrm{A}) + r(\mathrm{X})$ and $R_{\mathrm{B-X}} = r(\mathrm{B}) + r(\mathrm{X})$. The perovskite structure occurs only within the range $0.75 < t < t_c \simeq 1$ (*2*).

On the assumption that B and X ions are ideally spherical and rigid and that they contact each other along each direction as they build up cubic perovskite structure having a value $t < 1$, the lattice constant is given by $2R_{\mathrm{B-X}}$.

The recent set of ionic radii by Shannon and Prewitt (*3*, *4*) gives a fairly good calculation of interatomic distance in low symmetry compounds using the above mentioned simple additivity rule of cation and anion radius. However, the sum of the ionic radius in the perovskites does not give a proper interatomic distance. In this paper we attempt to clarify this situation somewhat by introducing the effect of A–X bond against B–X bond length of perovskites. Based on this idea, we develop a new empirical formula for the interatomic distance which produces an error of less than 1%.

The content of this paper follows. In Sect. 1, we develop our empirical formula for the calculation of averaged interatomic distance or cubic root of cell volume in the perovskite. In Sect. 2, we calculate $V^{1/3}$ in more than 200 perovskite oxides, and discuss the origin of an anomalous error of $V_{\mathrm{calc}}^{1/3}$ which is found for some special cases. In Sect. 3, we propose some new values of ionic radius which are obtained from cell volume calculation of perovskite oxides. In Sect. 4 we discuss the general trend of radii–volume relation, taking an example in $BaBO_3$ series of perovskites. In Sect. 5, we calculate the cell volume of hypothetical perovskite, Fe_2O_3 which is predicted to be obtained at very high pressure, and show that the caculated cell volume is closely consistent with the observed molar volume obtained by shock-wave experiments.

Sources of Calculations

Observed cell-volume data were taken from a new collection of perovskite compounds by Goodenough and Longo (*5*). If a compound has more than two allotropes, the calculated cell volume was taken for the structure of highest symmetry. Effective ionic radii tables by Shannon and Prewitt (*3*, *4*) were used. We define two reciprocal tolerance factors, s and s' as

$$s = \sqrt{2}[r(\mathrm{B}) + r(\mathrm{X})]/[r({}^{\mathrm{XII}}\mathrm{A}) + r(\mathrm{X})]^* \quad (2)$$

$$s' = \sqrt{2}[r(\mathrm{B}) + r(\mathrm{X})]/[r({}^{\mathrm{VIII}}\mathrm{A}) + r(\mathrm{X})] \quad (3)$$

The use of s' instead of s allows one to calculate a cell volume for a wide variety of ABX_3 perovskites because of more citation of eight-fold cation radius than twelve-fold one in the table of ionic radii.

Results and Discussions

(1) *Radii–Volume Relation*

According to the simple additivity rule of ionic radius, the cubic root of cell volume $V^{1/3}$ in a perovskite is related to the ionic radii by the formula,

$$V^{1/3} = 2R_{\mathrm{B-X}}. \quad (4)$$

Unfortunately, Eq. (4) produces a large calculating error as pointed out by Shannon and Prewitt (*3*).

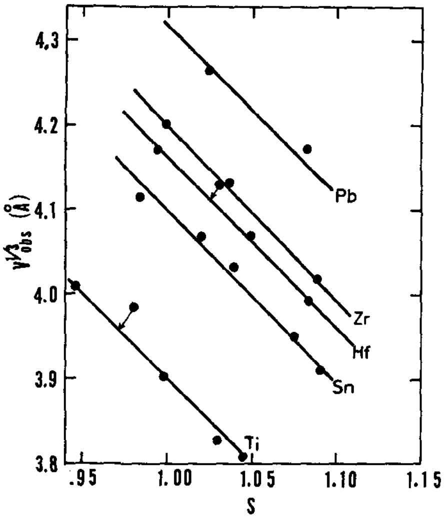

FIG. 1. Observed cubic root of cell volume versus s curves for compounds $A^{2+}B^{4+}O_3$ with the perovskite structure. The elements cited in the figure denote B-cations in ABO_3.

Our present model is based on an empirical linear relation between $V^{1/3}_{\mathrm{obs}}$ and the reciprocal tolerance factor, s, which is found to be valid for a wide region. Figure 1 shows this relation in $A^{2+}B^{4+}O_3$ type perovskites, where A = Ba, Pb, Sr, Ca and Cd, B = Zr, Hf, Sn, and Ti. It was found that a wide variety of ABO_3 perovskites shows a unique slope, d, for a set of straight lines of $V^{1/3}$ versus s plots. Therefore, we present an unified relation for all ABO_3 perovskites to be

$$V^{1/3} = V_o^{1/3} - d(s-1), \quad (5)$$

where $V_o^{1/3}$ is the extrapolated value of $V^{1/3}$ at $s = 1$. Figure 2 shows the straight-line plots

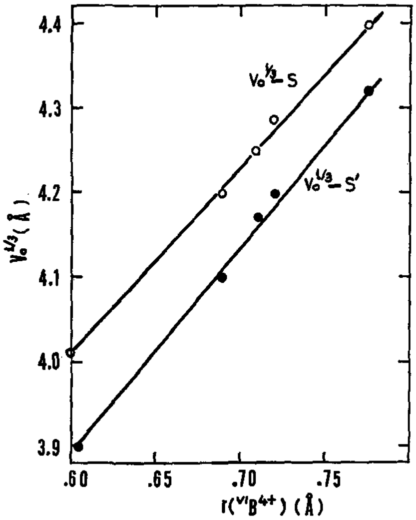

FIG. 2. Observed cubic root of cell volume at s = 1, ($V_o^{1/3}$) versus B-cation radius for the series of ABO_3 perovskites. Each point corresponds to a group of ABO_3, where B = Ti, Sn, Hf, Zr and Pb.

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* A Roman numeral at upper left of the element is used to designate coordination number (CN) in a crystal lattice.

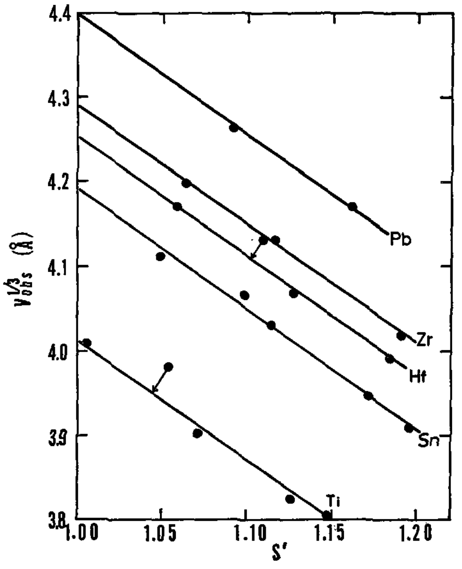

FIG. 3. Observed cubic root of cell volume versus s′ curves for the same compounds as in Fig. 1.

between $V_0^{1/3}$ and $r(B)$ for the selected $A^{2+}B^{4+}O_3$ perovskites which appeared in Fig. 1. Combining the results of Figs. 1 and 2, we present an empirical formula

$$V^{1/3} = 2[mr(B) + nr(X)] - d(s-1) \quad (6)$$

to apply to a wide variety of ABX_3 perovskites. We assume that the parameters m, n, and d are determined by the kind of anion alone.

To obtain a direct radii–volume relation, we rewrite Eq. (6) as

$$V^{1/3} = ar(B) + b \quad (7)$$

where $a = 2m - \sqrt{2}(d/R_{A-X})$, $b = 2nr(X) - \sqrt{2}(dr(X)/R_{A-X})$ and $R_{A-X} = r(A) + r(X)$. Cell volume V is thus given by

$$V = a^3 r(B)^3 + 3a^2 br(B)^2 + 3ab^2 r(B) + b^3. \quad (8)$$

It must be noted here that Eq. (7) supports the linear relation between $V^{1/3}$ and $r(B)$ in a fixed A-cation series of ABX_3 perovskites, but it does

TABLE I

CELL VOLUME CALCULATIONS IN $A^{2+}B^{4+}O_3$ TYPE PEROVSKITES. CALCULATIONS WERE CARRIED OUT USING THREE DIFFERENT MODELS, RIGID-SPHERE, KUGIMIYA–STEINFINK TYPE AND OUR PRESENT MODEL[a, b]

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
$BaPbO_3$	4.265	4.35	−0.085	4.296	−0.031	4.257	0.008	4.259	0.006
$SrPbO_3$*	4.174	4.35	−0.176	4.183	−0.009	4.141	0.033	4.161	0.013
$BaZrO_3$	4.20	4.24	−0.040	4.241	−0.041	4.178	0.022	4.180	0.020
$PbZrO_3$	4.135	4.24	−0.105	4.164	−0.029	4.102	0.033	4.107	0.028
$CaZrO_3$	4.008	4.24	−0.232	4.065	−0.057	3.996	0.012	4.002	0.006
$BaHfO_3$	4.172	4.22	−0.048	4.231	−0.059	4.163	0.009	4.165	0.007
$PbHfO_3$	4.134	4.22	−0.086	4.154	−0.020	4.087	0.047	4.094	0.040
$SrHfO_3$*	4.069	4.22	−0.151	4.118	−0.049	4.051	0.018	4.070	−0.001
$CaHfO_3$	3.994	4.22	−0.226	4.055	−0.064	3.983	0.008	3.989	0.005
$BaSnO_3$	4.117	4.18	−0.063	4.211	−0.094	4.135	−0.018	4.136	−0.019
$PbSnO_3$	4.07	4.18	−0.110	4.134	−0.064	4.059	0.011	4.065	0.005
$SrSnO_3$*	4.035	4.18	−0.145	4.098	−0.063	4.023	0.012	4.043	−0.008
$CaSnO_3$	3.951	4.18	−0.229	4.035	−0.084	3.955	−0.004	3.961	−0.010
$CdSnO_3$	3.912	4.18	−0.268	4.006	−0.094	3.923	−0.011	3.928	−0.016
$BaTiO_3$	4.012	4.01	0.002	4.126	−0.114	4.014	−0.002	4.014	−0.002
$PbTiO_3$	3.985	4.01	−0.115	4.049	−0.063	3.942	0.043	3.945	0.040
$SrTiO_3$*	3.905	4.01	−0.095	4.013	−0.108	3.908	−0.003	3.923	−0.018
$CaTiO_3$	3.825	4.01	−0.185	3.950	−0.125	3.842	−0.017	3.846	−0.021
$CdTiO_3$	3.805	4.01	−0.205	3.921	−0.116	3.811	−0.006	3.814	−0.009

[a] *Columns* (1) Compounds (2) and (3) Observed and calculated $V^{1/3}$ by Eq. (4), respectively. (4) observed minus calculated (=R). (5) Calculation by Eq. (11) (6) R (7) Calculation by Eq. (9) (8) R. (9) Calculation by Eq. (10) (10) R.

[b] *Remarks*: All numerals are angstrom unit. * Sr^{2+} = 1.44 a.u. was used.

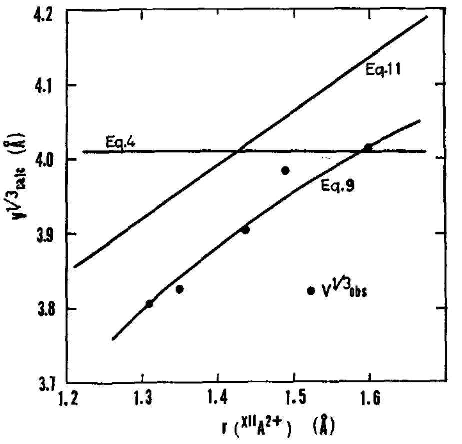

FIG. 4. Comparison between observed and calculated $V^{1/3}$ for $A^{2+}Ti^{4+}O_3$ type perovskites. Calculations were carried out by the use of three models, rigid-sphere [Eq. (4)], Kugimiya–Steinfink type [Eq. (11)] and present [Eq. (9)].

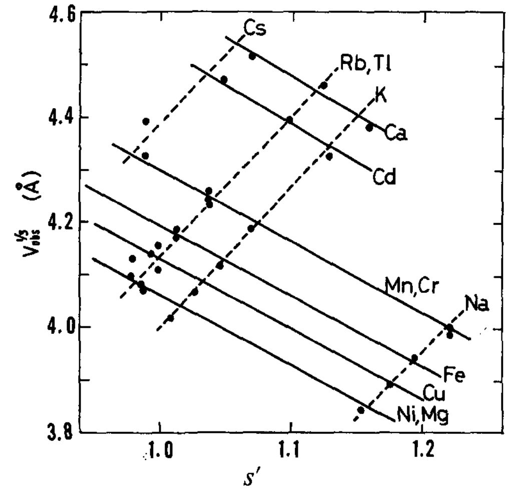

FIG. 5. Observed cubic root of cell volume versus s' curves for ABF_3 type perovskites. The elements Cs, Rb, Tl, K, and Na are A-site cations and the others are B-site cations.

not support the trends of unique slope for different A-cation sets in a plot of $V^{1/3}$ versus $r(B)$.

Figure 3 shows a relation between $V^{1/3}_{obs}$ and s', where s' is the reciprocal tolerance factor defined by Eq. (3). The results in Fig. 3 show that the linear relation between $V^{1/3}$ and s' is valid for perovskites. The numerical formulas applicable to all ABO_3 perovskites were determined using the results in Figs. 1–3 to be

$$V^{1/3} = 2.37r(B) + 2.47 - 2.00(s - 1) \quad (9)$$

or

$$V^{1/3} = 2.15r(B) + 2.72 - 1.40(s' - 1) \quad (10)$$

where we put the oxygen radius as $r(^{VI}O^{2-}) = 1.40$ a.u.

In comparison with our model, we have applied the radii–volume relation which was derived by Kugimiya and Steinfink (*6*). Their model was based on the average of an ionic radii summation in the $1/\sqrt{2}[110]$ and [100] directions of oxides and sulfides of spinel structure. If a similar treatment is applicable to the perovskite structure, the relation is given by

$$V^{1/3} = r(B) + r(X) + (1/\sqrt{2})R_{A-X}. \quad (11)$$

Table I shows the results of calculations based on Eqs. (4) and (9–11). The agreement between calculated and observed $V^{1/3}$ by the present relation is outstandingly good. It is remarkable that no systematic difference is found between the two calculations, Eq. (9) and Eq. (10): this suggests practical availability of cell volume calculation by using the eightfold coordination radius. Figure 4 shows a graphical comparison among the above-mentioned three different

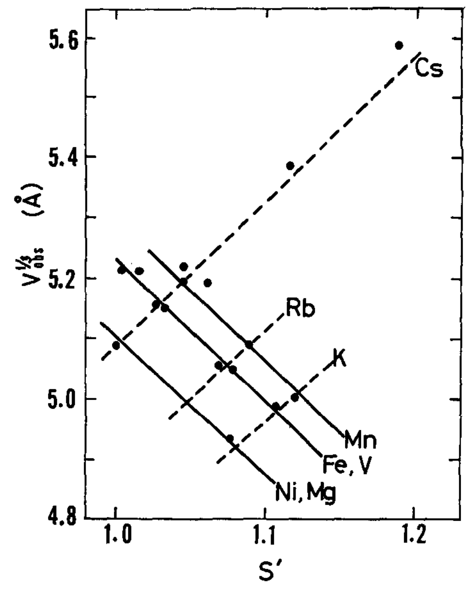

FIG. 6. Observed cubic root of cell volume versus s' curves for $ABCl_3$ type perovskites. The elements Cs, Rb, and K correspond to A-site cations and the others are B-site cations.

relations for the series of $A^{2+}Ti^{4+}O_3$ type perovskites, where A = Ba, Sr, Pb, Ca, and Cd.

Figures 5 and 6 show the linear relation between $V^{1/3}$ and s' in ABF_3 and $ABCl_3$ type perovskites, respectively. Although some of the data were scattered, the general trends toward the linear relation between $V^{1/3}$ and s' are seen.

Our relation [Eq. (6)] shows that even an ideal perovskite structure ($s = 1$), A and B-cation and anion overlap each other to a considerable extent. We can rewrite Eq. (9) as $V^{1/3} = 2[1.185r(B) + 0.882r(O)]$ at $s = 1$. This can be explained from the phenomenologic standpoint that B-cation penetrates into oxygen somewhat. In the case of ABO_3 perovskite, the overlap was estimated to be about 2–3% of the ionic radius sum.

The main contribution to the overlap between B-cation and anion can be explained if one considers the effects of the A–X bond in a perovskite. Unlike low symmetry and simple compounds, perovskites have high symmetry and close-packed structure. In addition, we must consider that a perovskite has two principal bonds, A–X and B–X, in its structure. The present empirical relation suggests that the B–X distance of perovskite is affected by A–X bond separation and by the bond nature of the anion. Geometrical separation between A-cation and anion, which is evaluated by the tolerance factor, tends to decrease by producing overlap of the B–X bond. The order of this A–X bond attraction seems affected by the deviation from ideal perovskite ($s - 1$) and by the nature of anion, d. The second term of the right hand of Eq. (6), $-d(s-1)$, is explained by the attractive power of the A–X bond against the B–X bond in perovskite.

It is interesting that the parameter d depends only on the species of anion. From the results in Figs. 3, 5, and 6, one can estimate that $d(Cl) = 2.30$, $d(O) = 1.40$ and $d(F) = 1.47$ as slopes of the plots $V^{1/3}$ vs s'. The fact that parameter d becomes smaller on going from Cl to F suggests that the power of A–X bond attraction varies with anion radius.

(2) *Cell Volume Calculations for Perovskite Oxides*

The cubic root of cell volume for ABO_3 and $A_2BB'O_6$ type perovskites has been calculated according to Eq. (10). The results are shown in Figs. 7 and 8. In general, calculated $V^{1/3}$ for ABO_3 perovskites falls within the limit ± 0.025 a.u., except for a few cases. The large deviation between calculated and observed $V^{1/3}$ in Pb^{2+} and Bi^{3+} containing perovskites

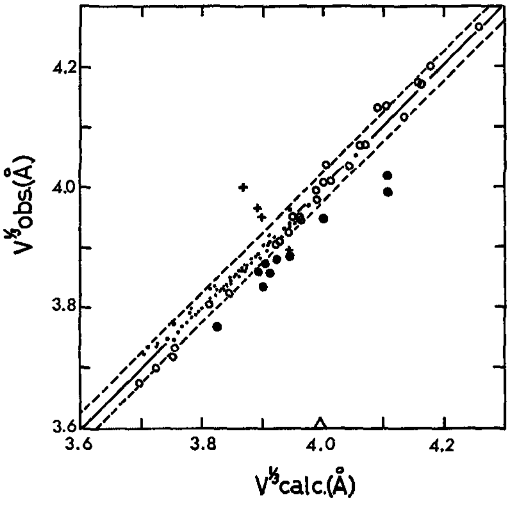

FIG. 7. The relation between calculated and observed cubic root of cell volume in ABO_3 perovskites. Small solid circles represent $A^{3+}B^{3+}O_3$, open circles are $A^{2+}B^{4+}O_3$. Plus marks are Pb^{2+} or Bi^{3+} containing perovskites and solid circles are each K^+, V^{4+}, or Ti^{3+} containing ABO_3. Triangle is $AgNbO_3$. Dashed lines indicate ±0.025 a.u. error limits.

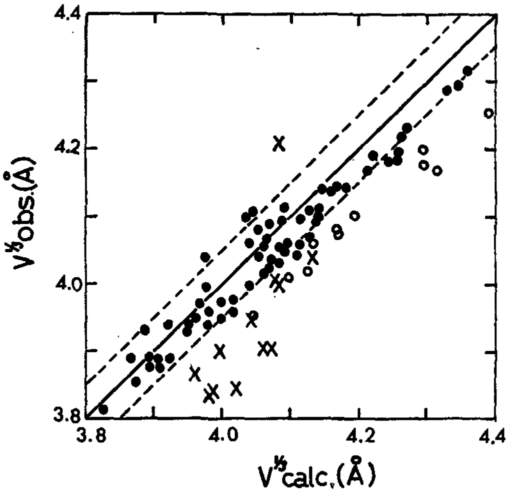

FIG. 8. The relation between calculated and observed cubic root of cell volume in $A_2BB'O_6$ type perovskites. Cross marks are A_2BWO_6 or A_2BMoO_6 type perovskites and open circles represent $A_2BB'O_6$ with large size gap between B and B′-cation. Solid circles fall within ±0.05 a.u. error limit.

such as $PbCrO_3$, $BiFeO_3$ and $BiMnO_3$ is considered to be the effect of the nonspherical electron orbital of the $6s^2$ electron in Pb^{2+} and Bi^{3+}.

The deviation in the series containing K^+, V^{4+}, Ag^+ and Ti^{3+} perovskites such as $KNbO_3$, $CaVO_3$, $AgTaO_3$ and $ReTiO_3$ (Re = rare-earth elements), is considered due to the error of ionic radius values used in the calculations. The unusual deviation of $AgNbO_3$ may be attributed to error of the measurements of lattice parameters or to the problem of sample preparations.

In calculations of $V^{1/3}$ for $A_2BB'O_6$-type perovskites, we have put an averaged value of $r(B)$ and $r(B')$ into Eq. (10). In most materials, the calculated $V^{1/3}$ falls within the limit ± 0.05 a.u.; a large deviation (about 3%), however, is observed in two typical cases. (1) The calculating error in $A_2CaB'O_6$, $A_2SrB'O_6$ and some of $A_2ReB'O_6$ may be the effect of a large size gap between B and B'-cation. (2) The deviation in A_2BMoO_6 and A_2BWO_6 is difficult to explain. The case, A_2FeMoO_6, A_2FeWO_6, Ca_2CrMoO_6 and Ca_2CrWO_6, may be due to uncertainty of charge valences of Fe or Cr and Mo or W. We have calculated $V^{1/3}$ for these perovskites by assuming the combination of B^{2+}–B'^{6+} for B-site cations. On the other hand, the error in Ba_2ZnMoO_6 ($V_{\text{calc}}^{1/3} = 4.021$ a.u. and $V_{\text{obs}}^{1/3} = 3.847$ a.u.) can not be explained by the variation of charge valence in B-site cations because Zn has strong tendency to possess a divalent state. The satisfactory explanation for the origin of the error of calculation for such a case requires further study.

The deviation between calculated and observed $V^{1/3}$ for $A_2BB'O_6$ is to obtain a larger calculated value than that observed. This suggest that the use of a simple arithmetic average of the radius of B and B'-cation needs some modifications.

In conclusion, the present relation is valid for the calculation of cell volume of a perovskite from known combination of ionic radius. It is interesting that the present relation is valid for distorted perovskites such as $GdFeO_3$ type orthorhombic perovskites. As discussed by Marezio, Remeika and Dernier (*7*), in $GdFeO_3$ the A-cation has eight nearest oxygens and four second nearest oxygens. This distortion from an ideal perovskite structure must affect the parameters *m*, *n*, and *d* in Eq. (6). However, within the calculated accuracy there is no evidence on which to change the parameters of Eq. (6) in $GdFeO_3$-type compounds. In addition, there is no difference in the calculated $V^{1/3}$ between $ReBO_3$ when B = Al, Ga, Fe, Cr, or V and $ReScO_3$, whereas a difference of coordination number is assumed between them (*7*).

(3) *Ionic Radii Calculations for Some B-site and A-site Ions in Perovskite*

The results in Fig. 7 suggest that ionic radii such as V^{4+}, Ti^{3+}, and K^+ need refinement. Although the plots V versus $r(B)^3$ or $V^{1/3}$ versus $r(B)$ in perovskites may be useful to estimate an unknown ionic radius, it must be noted that this method needs comparison with the same A or B-cation series of perovskites. Our present relation, however, allows estimation of an ionic radius from individual observed cell volume data.

The high pressure form of $CaSiO_3$ is the only predicted perovskite containing Si^{4+}. Ringwood (*8*) estimated the lattice parameter a_0 of pure $CaSiO_3$ perovskite from high pressure experiments of $Ca(Ge, Si)O_3$ solid solution to be $a_0 = 3.61 \pm 0.01$ a.u. The estimation of an ionic radius of Si^{4+} by the plots V versus $r(B)^3$ or $V^{1/3}$ versus $r(B)$ cannot be applicable for this case. Using Eq. (10), we estimate $r({}^{VI}Si^{4+})$ to be 0.44 a.u., which is larger than the Shannon–Prewitt value of 0.400 a.u. Our new radii–volume plot in rutile structure (*9*) supports the value 0.44 a.u.

Shannon and Prewitt (*3*) give $r({}^{VI}B^{4+})$ where B = Ce, Pr and Pu from these lattice parameters

TABLE II

PREDICTED IONIC RADIUS BY THE USE OF RADII–VOLUME RELATION OF PEROVSKITE

		Ionic radius (a.u.)	
Ion	CN	Shannon and Prewitt	Present
Ce^{4+}	VI	0.80	0.87
Fe^{4+}	VI		0.55
K^+	VI	1.51	1.31
Np^{4+}	VI		0.86
Pr^{4+}	VI	0.78	0.84
Pu^{4+}	VI	0.80	0.85
Si^{4+}	VI	0.400	0.44
Th^{4+}	VI	1.00	0.97
Ti^{3+}	VI	0.67	0.65
U^{4+}	VI		0.86
V^{4+}	VI	0.59	0.55

of $BaBO_3$ perovskites by the use of the simple relation of Eq. (4). As we have seen, the relation by Eq. (6) is more reliable than the simple additivity rule of Eq. (4) in the radii–volume relation of perovskite.

By the above reasoning we have calculated the ionic radius of some elements based on the present radii-volume relation of a perovskite structure. The results are shown in Table II. Present results were found to fall on the ionic radius versus CN trends by Shannon and Prewitt (*3*).

(4) *Radii–Volume Relation in $BaBO_3$-type Perovskite*

The present model was based on a linear relation between $V^{1/3}$ and s. Then the cell volume of perovskite is given by Eq. (8). The numerical expression of Eq. (8) in the series of $BaBO_3$, where B = Th, Pu, Pb, Zr, Hf, Sn, Tc and Ti is

$$V = 2.906r(\mathrm{B})^3 + 19.24r(\mathrm{B})^2 + 42.48r(\mathrm{B}) + 31.26(\mathrm{a.u.})^3 \quad (12)$$

Shannon, however, has proposed a linear relation between V and $r(\mathrm{B})^3$ in $A^{3+}B^{3+}O_3$ (*10*). Moreover, he found many examples that follow this relation (*11*) and used one for a stand point for the calculation of an unknown ionic radius (*3*).

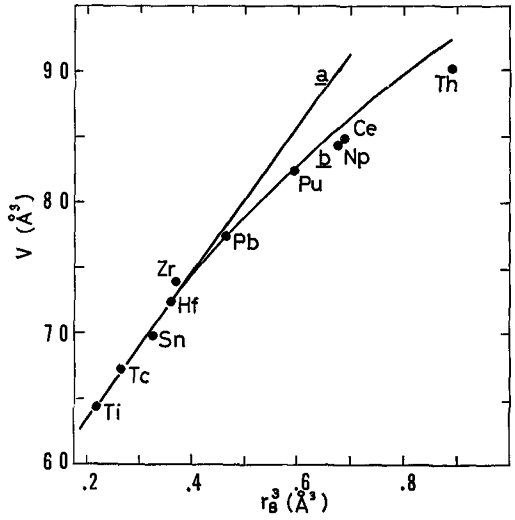

FIG. 9. The relation between cell volume of $BaBO_3$ type perovskites and $r(\mathrm{B})^3$. Curve a represents a linear relation between V and $r(\mathrm{B})^3$ and curve b shows the relation of Eq. (12).

In Fig. 9, we plot V_{obs} versus $r(\mathrm{B})^3$ for $BaBO_3$ type perovskites and show that a linear relation between V and $r(\mathrm{B})^3$ holds over a relatively narrow region of $r(\mathrm{B})$ variation. To clarify this situation somewhat, we checked the relation between cation–anion bond length or cation–anion radius sum and cell parameters and found a linear relation for wide structure variations such as rutile, fluorite, A, B, C-rare earth oxides, ilmenite, corundum, etc. (*9*). This relation is equivalent to Eq. (8).

(5) *Cell Volume Calculation of High Pressure Modification of Fe_2O_3*

It has been shown by shock-wave experiments that Fe_2O_3 changes its molar volume discontinuously at about 600 kb. The estimation of cell volume for the high-pressure form of Fe_2O_3 retained to zero pressure was given to be 44.5 $(\mathrm{a.u.})^3$ by Reid and Ringwood (*12*). From this result, they proposed a possibility of pressure-induced phase transition from corundum to perovskite structure based on their octahedral bond length versus cell volume relation.

Another prediction of this problem was made by Syono, Akimoto and Endoh (*13*). They discussed a possibility of high spin–low spin electronic transition in Fe^{3+} ion without change of crystal structure.

The present radii–volume relation allows one to estimate the cell volume of Fe_2O_3 perovskites. We have calculated cell volumes of two hypothetical perovskites, $Fe^{3+}(\mathrm{HS})Fe^{3+}(\mathrm{LS})O_3$ and $Fe^{2+}Fe^{4+}O_3$. Unfortunately, since we lack more than sixfold coordination of $r(Fe^{2+})$ and $r(Fe^{3+})$ in the ionic radii table, we need to estimate $r(^{\mathrm{VIII}}Fe^{2+})$ and $r(^{\mathrm{VIII}}Fe^{3+})$ from the linear relation between ionic radius and coordination number using a diagram by Shannon and Prewitt (*3*). The ionic radii estimated here were $r(^{\mathrm{VIII}}Fe^{3+})\mathrm{HS} = 0.80$ a.u., $r(^{\mathrm{VI}}Fe^{3+})\mathrm{LS} = 0.55$ a.u. and $r(^{\mathrm{VIII}}Fe^{2+})\mathrm{HS} = 0.91$ a.u. The calculated cell volumes for $Fe^{3+}(\mathrm{HS})Fe^{3+}(\mathrm{LS})O_3$ and $Fe^{2+}Fe^{4+}O_3$ perovskite were 44.7 and 47.8 $\mathrm{a.u.}^3$, respectively. The results suggest that the possible high-pressure form of Fe_2O_3 is a $Fe^{3+}Fe^{3+}O_3$ type perovskite.

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