

New view of the high-pressure behaviour of GdFeO₃-type perovskites

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Recent determinations of the structures of several GdFeO₃-type orthorhombic perovskites (*ABO*₃) show that the octahedra in some become more tilted with increasing pressure. In others the octahedra become less tilted and the structure evolves towards a higher-symmetry configuration. This variety of behaviour can be explained in terms of the relative compressibilities of the octahedral and dodecahedral cation sites in the perovskite structure. If the *BO*₆ octahedra are less compressible than the *AO*₁₂ sites then the perovskite will become more distorted with pressure, but the perovskite will become less distorted if the *BO*₆ site is more compressible than the *AO*₁₂ site. In this contribution we use the bond-valence concept to develop a model that predicts the relative compressibilities of the cation sites in oxide perovskites. We introduce the site parameter *M*_{*i*} defined in terms of the coordination number *N*_{*i*}, average bond length at room pressure *R*_{*i*}, and the bond-valence parameters *R*₀ and *B*,

$$M_i = (R_i N_i / B) \exp[(R_0 - R_i) / B].$$

*M*_{*i*} represents the variation in the bond-valence sum at the central cation in a polyhedral site because of the change of the average bond distance. Experimental data suggest that the pressure-induced changes in the bond-valence sums at the two cation sites within any given perovskite are equal. With this condition we show that the ratio of cation-site compressibilities is given by $\beta_B / \beta_A = M_A / M_B$. This model, based only upon room-pressure bond lengths and bond-valence parameters, correctly predicts the structural behaviour and some physical properties of the oxide perovskites that have been measured at high pressure.

1. Introduction

Oxide perovskites are relatively simple structures. Ideally they are comprised of corner-linked *BO*₆ cation-centered octahedra with larger 'A' cations occupying the voids within the three-dimensional framework of the octahedra. The GdFeO₃-type perovskites exhibit orthorhombic *Pbnm* symmetry, because tilting and distortion of the *BO*₆ octahedra reduce the symmetry from the *Pm3m* symmetry exhibited by the ideal cubic structure (Glazer, 1972; Woodward, 1997), as shown in Fig. 1. As a result of the tilting of the octahedra, the coordination of the 'A' cation site is reduced from the regular dodecahedron found in the cubic structure. The distortions from cubic symmetry give rise to changes in the physical and thermodynamic properties that are important not only for the

use of perovskites in materials science, but also for understanding the behaviour of the Earth's lower mantle which is comprised of more than 60% (Mg, Fe)SiO₃ perovskite (e.g. Navrotsky & Weidner, 1989). The purpose of this paper is to explore whether the evolution with pressure of the structural distortions of *Pbnm* perovskites can be predicted by a conceptually simple model.

However, as pointed out by O'Keeffe *et al.* (1979), the changes in distortion of a perovskite under even 10 GPa of pressure change are expected to be small – they estimated to be *ca* 1° of tilt – and this was beyond the achievable precision of even single-crystal diffraction methods at high pressures for a long time. Recently several improvements have been made to attempt to reduce the experimental uncertainties and systematic errors in high-pressure determination to the level approaching those obtained from crystals in air. These improvements have enabled the evolution of distortion and tilting of polyhedra in relatively stiff materials, including YAlO₃, CaSnO₃ and GdFeO₃ perovskites (e.g. Ross *et al.*, 2004a; Zhao *et al.*, 2004a; Ross *et al.*, 2004c), to be determined up to pressures of *ca* 8 GPa. These studies have shown that several perovskites that exhibit similar distortions from the cubic aristotype at room pressure evolve very differently when subjected to even quite modest pressures.

Consideration of Fig. 1 suggests that this variety of compressional behaviour can be parameterized in terms of the relative compressibilities of the AO₁₂ and BO₆ polyhedra, or

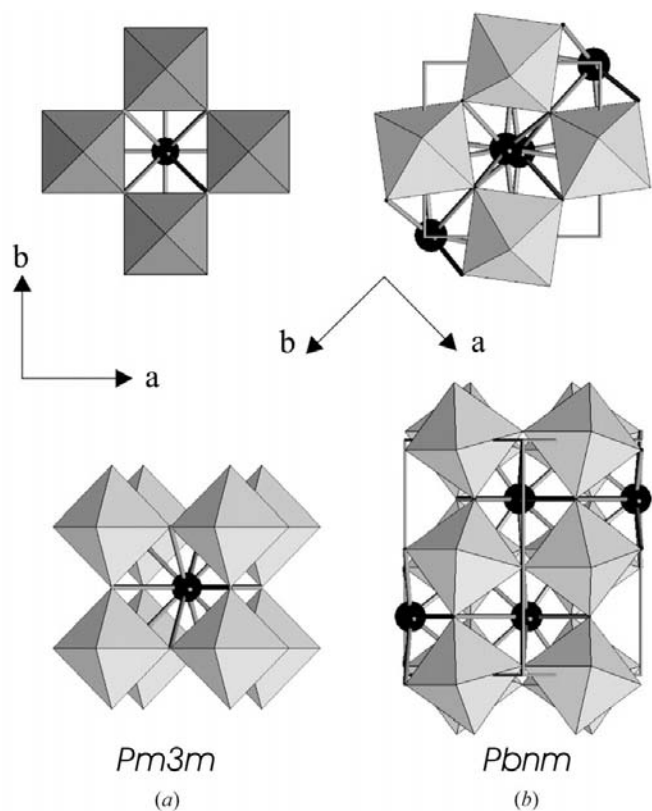


Figure 1
Polyhedral representations of (a) cubic perovskite with *Pm3m* symmetry and (b) orthorhombic perovskite with *Pbnm* symmetry. The A cation is shown as a sphere.

of the compressibilities of the A–O and B–O bonds. Clearly, if the A–O bonds are much more compressible than the B–O bonds, then volume reduction will be accommodated by increasing the tilts of the BO₆ octahedra. An extreme case would be one in which the BO₆ octahedra were completely rigid (the *rigid unit model*), which would always result in an increased distortion of the perovskite structure away from cubic symmetry with increasing pressure. On the other hand, if the BO₆ octahedra were to be more compressible than the AO₁₂ site, then one might expect the structure to evolve back towards the cubic aristotype with increasing pressure. Thus, it is clear that the relative compressibilities of the AO₁₂ and BO₆ sites must play a role in determining whether the perovskite structure becomes more or less distorted with increasing pressure (e.g. Andraut & Poirier, 1991; Yagi *et al.*, 1978; O'Keeffe *et al.*, 1979; Ross, 1996, 1998, 2000).

The question therefore arises as to how to estimate the compressibilities or other forces involved in determining the compression behaviour of perovskites. Andraut & Poirier (1991) proposed a relationship between the ratio of bulk moduli of the AO₁₂ and BO₆ sites and the ratio of their volumes. They concluded that the 'excess' volume of the AO₁₂ dodecahedron deviated from that of the 'ideal' AO₁₂ dodecahedron and that this deviation determines the relative compressibilities of the AO₁₂ and BO₆ sites. However, it is not clear that a generally applicable method exists to estimate the 'ideal' volume. Recently, another model, based on the global parameterization method (Thomas, 1998) combined with *ab initio* total energy calculations, suggested that a balance between the interaction of the semicore states of the A and B atoms and the oxygen ions determines which perovskite structure is adopted by a particular composition. According to this model high pressure always stabilizes the cubic phase, while small or negative pressures favor octahedral tilting (Magyari-Köpe *et al.*, 2002).

The bond-valence model, a semi-empirical model based on Pauling's concept of a chemical bond, has been widely used to predict and interpret atomic arrangements and especially bond distances between cations and anions in inorganic crystal structures (Pauling, 1960; Brown & Altermatt, 1985; Brese & O'Keeffe, 1991; Brown, 1992, 1997; Brown *et al.*, 2003). The bond-valence model relates the valence S_{ij} of an individual bond to the length of the bond R_{ij} through the expression

$$S_{ij} = \exp[(R_0 - R_{ij})/B], \quad (1)$$

in which R_0 is a constant for a particular atom pair and B is a universal constant, which is equal to 0.37 Å. Since the parameters R_0 and B are derived from room-pressure structures, the empirical bond valence defined in (1) is only relevant at room pressure, especially if the requirement is imposed that, in a stable structure, the bond-valence sum at an atom should be equal to its formal valence. In the latter case, Brown *et al.* (2003) showed that the compressibility of a bond should be

$$\beta = gR_e^3/[k_0q^2(1/B - 2/R_e)]. \quad (2)$$

This expression contains one observable parameter, R_e , the equilibrium bond length at room pressure, and the constants B

and $k_o = 1/4\pi\epsilon_o = 23 \text{ nN}\text{\AA}^2 \text{ e}^{-2}$. Brown *et al.* (2003) showed that with reasonable estimates for q , the effective (and partially shielded) charge associated with the bond, and g , a geometric factor that represents the effective area supported by the bond, this expression does represent the compressibility of dense simple structures. However, the use of this expression to predict the compressibilities of individual bonds in more complex structures such as perovskites requires not only proper evaluation of the parameters q and g , but also the assumption that stress (*i.e.* pressure) is distributed equally across all of the bonds in the structure (Brown *et al.*, 2003).

Therefore, in this paper we propose a new model for the compression behaviour of perovskites that has been proven to be useful in explaining our experimental results. It is also based upon the bond-valence model of Brown & Altermatt (1985), but makes use of the concept that structures in which the bond-valence sum rule is not met are considered to be 'strained' (Brown, 1992). The logical extension of this concept is to assume that the additional bond strain (reflected in a valence-sum mismatch) induced by an increase in pressure has to be distributed equally across the cation sites within the structure. Our approach differs from the assumption of an equal distribution of stress implicit in the use of (2). As Brown (2004) has pointed out, our approach is equivalent to the structure responding to pressure so as to minimize the deviation of the total bond-valence sum from the ideal values given by the formal charges on the cations. In the next section we show how the relative compressibilities for AO_{12} and BO_6 sites in the perovskite structure can be directly deduced from just the basic bond-valence parameters taken from Brown & Altermatt (1985), together with the bond lengths measured at room pressure. Consequently, the pressure-induced structural changes in $GdFeO_3$ -type perovskites can be predicted. These predictions are then compared in §3 to recent crystallographic measurements of bond compression in perovskites and a number of predictions for the behaviour of rare-earth perovskites with the $GdFeO_3$ structure type are made.

2. The model

According to the bond-valence model (Brown & Altermatt, 1985; Brown, 1997), each bond valence between cation and anion is calculated from (1). The valence-sum rule (Brown, 1997) states that the sum of the valences of the individual bonds to a cation should equal the formal charge V_0 on the cation

$$V_i = \sum S_{ij} = V_0. \quad (3)$$

As there are uncertainties in the R_{ij} values determined by experimental measurements, (3) is usually not satisfied exactly. However, in the absence of residual strain the bond-valence difference $|\Delta V_i|$ ($\Delta V_i = V_i - V_0 = \sum S_{ij} - V_0 \neq 0$) is usually no more than 0.1 v.u. (Brown, 1992; Rao *et al.*, 1998). Therefore, a bond-valence difference, $|\Delta V_i|$, that is more than 0.1 v.u. is considered to reflect a strain state among the bonds between the cation and surrounding anions (Brown, 1997). The application of pressure results in a reduction of bond distances, so

the summation $\sum S_{ij}(P)$ at each cation will increase with increasing pressure and consequently the corresponding bond-valence differences, $\Delta V_i = V_i(P) - V_i(0) = \sum S_{ij}(P) - \sum S_{ij}(0)$, will grow with increasing pressure. The rate of change of the bond-valence difference, ΔV_i , of a single site with pressure can be obtained from (1) and (3) as

$$d\Delta V_i/dP = \sum_j (\beta_{ij} R_{ij}/B) \exp[(R_0 - R_{ij})/B], \quad (4)$$

where $\beta_{ij} = -(1/R_{ij})(dR_{ij}/dP)$ are the individual linear compressibilities of the bonds between the central cation i and its bonded anions j . Equation (4) does not allow the prediction of $d\Delta V_i/dP$ without prior knowledge of both the bond lengths and their compressibilities. However, if the distortion of the site is small and all of the bond lengths R_{ij} are approximately equal, then the individual bond lengths and their compressibilities can be substituted by their average values, R_i and β_i . This allows the useful simplification of (4) to

$$(d\Delta V_i/dP) \simeq (\beta_i R_i N_i/B) \exp[(R_0 - R_i)/B] = \beta_i M_i, \quad (5)$$

in which N_i is the coordination number. For simplicity of notation we introduce the parameter M_i

$$(R_i N_i/B) \exp[(R_0 - R_i)/B] = M_i. \quad (6)$$

Since the expression $N_i \exp[(R_0 - R_i)/B] = \langle V_i \rangle$ is the total bond-valence sum at the central cation i calculated on the basis of the average bond length, it is clear that $M_i = -R_i(d\langle V_i \rangle/dR_i)$ represents the total estimated variation of bond valence in a polyhedral site due to the change of average bond distance.

Most orthorhombic perovskites have relatively undistorted octahedra so that (5) is a good approximation for the BO_6 site. However, the bond distances between atom A and its 12 coordinated anions vary considerably and therefore exhibit significant anisotropy in compressibility. The assumptions in our derivation of (5) are therefore not valid and the use of the average linear compressibility overestimates the contribution of the longer bonds to $d\Delta V/dP$ to the extent that it does not represent the true behaviour of the site under pressure. However, we can assume that there is an effective equivalent linear compressibility, β_A , and consequently (4) can be expressed as

$$d\Delta V_A/dP = \beta_A \left\{ \sum_{j=1}^{12} (R_{ij}/B) \exp[(R_0 - R_{ij})/B] \right\} \quad (7)$$

$$\begin{aligned} d\Delta V_A/dP &= \beta_A \left\{ \sum_{j=1}^8 R_{ij}/B \exp[(R_0 - R_{ij})/B] \right. \\ &\quad \left. + \sum_{j=9}^{12} R_{ij}/B \exp[(R_0 - R_{ij})/B] \right\} \\ &= \beta_A M_A. \end{aligned} \quad (8)$$

The summation in (7) has been split into two parts in (8), so that M_A is calculated from R_{AO8} , the mean bond length of eight shorter $A-O$ bonds within the polyhedral AO_{12} site, and

R_{AO4} , the mean length of the remaining four longer distances at room pressure

$$M_A \approx \left(\frac{8R_{AO8}}{B}\right) \exp\left(\frac{R_0 - R_{AO8}}{B}\right) + \left(\frac{4R_{AO4}}{B}\right) \exp\left(\frac{R_0 - R_{AO4}}{B}\right) \\ = -8R_{AO8} \left(\frac{d\langle V_i \rangle}{dR_i}\right)_{R_{AO8}} - 4R_{AO4} \left(\frac{d\langle V_i \rangle}{dR_i}\right)_{R_{AO4}} \quad (9)$$

M_A therefore describes the total estimated variation of bond valence in a polyhedral AO_{12} site with separate contributions

from the changes of the average of the eight shorter $A-O$ distances and the longer four $A-O$ distances. Usually the contribution from the second summation to the bond-valence variation is strongly related to the amount of distortion of the AO_{12} site, but is in general no more than 15% of the first summation.

We can now calculate M_A and M_B for orthorhombic perovskites at room pressure by using the bond-valence parameters R_0 from Brown & Altermatt (1985) and the observed individual bond lengths to calculate R_i . To determine

the evolution of the perovskite structure with pressure from these parameters, we apply our assumption that the additional valence-sum mismatch induced by pressure at the A and B sites is the same. The assumption can be expressed by

$$\Delta V_A(P) = \Delta V_B(P). \quad (10)$$

This can also be formulated as

$$(d\Delta V_A/dP) = (d\Delta V_B/dP). \quad (11)$$

It therefore follows from (5), (8) and (10) that

$$\beta_B/\beta_A = M_A/M_B. \quad (12)$$

Thus, if the matching relation expressed in (10) holds, the ratio of M_A over M_B determines the relative compressibilities of the AO_{12} and BO_6 sites. We can then infer that there are three possibilities of pressure-induced structural change for $GdFeO_3$ -type perovskites. Firstly, if M_A is greater than M_B then the octahedral BO_6 site should be more compressible than the AO_{12} site and the structure will become less distorted with increasing pressure. Conversely, if M_B is greater than M_A , then the octahedral AO_{12} site should be more compressible than the BO_6 site and the structure will become more distorted with increasing pressure. If the ratio M_A/M_B is close to unity, then we would predict that the degree of distortion does not change with pressure. Thus, it should be possible to predict the high-pressure behaviour of $GdFeO_3$ -type perovskites on the basis of only the bond-valence parameter R_0 and atomic parameters of crystals at room pressure through the calculation of the ratio between M_A and M_B .

The likely range of values of the ratio M_A/M_B can be estimated by

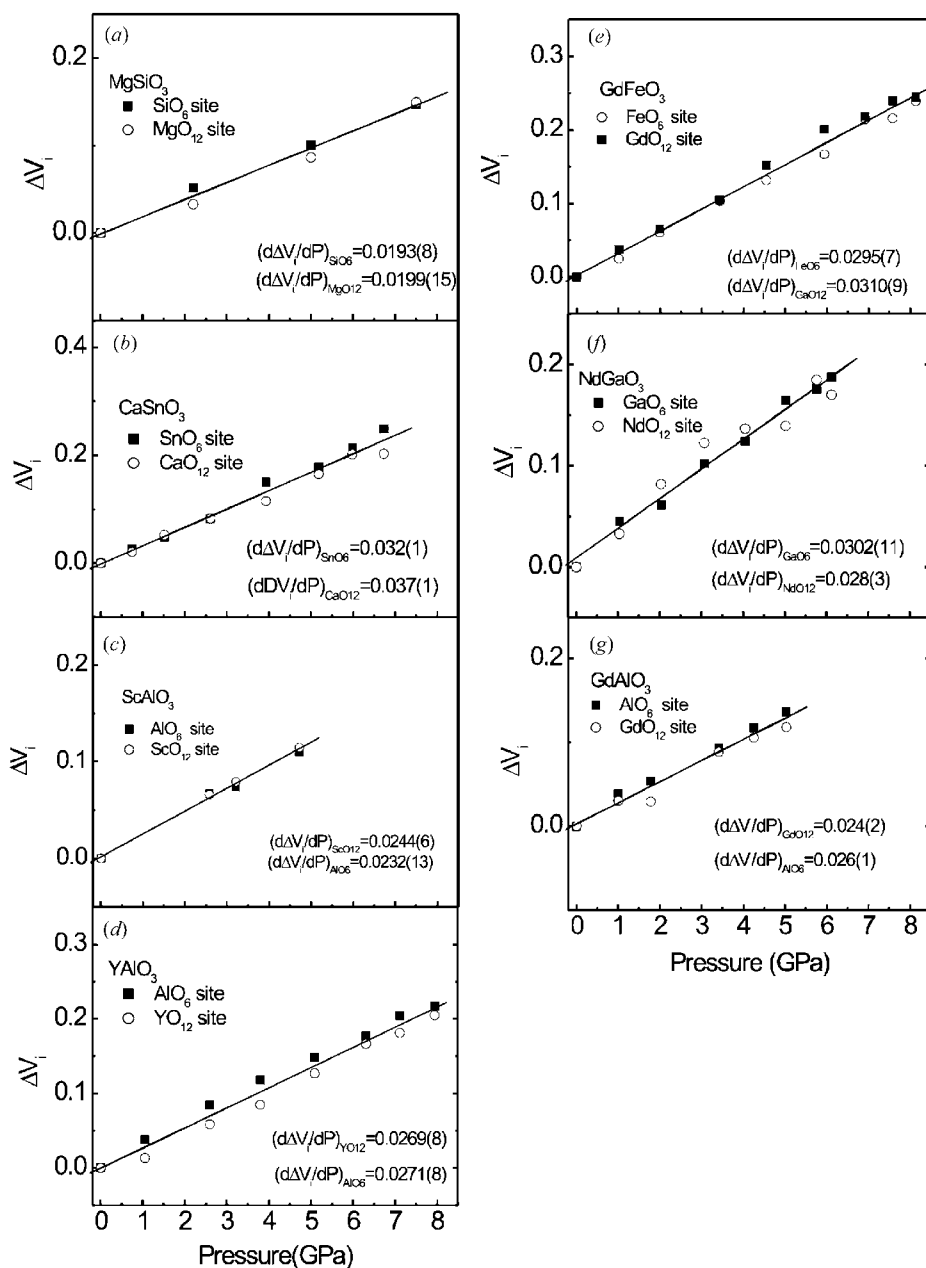


Figure 2 Variation of the bond-valence difference ΔV_i of the A and B sites in several $GdFeO_3$ -type perovskites with increasing pressure. Data from (a) Ross & Hazen (1990); (b) Zhao *et al.* (2004a); (c) Ross (1998); (d) Ross *et al.* (2004a); (e) Ross *et al.* (2004c); (f) Zhao *et al.* (2004b); (g) Ross *et al.* (2004c). The solid lines are the trends of the average of the bond-valence differences of the two sites in each structure.

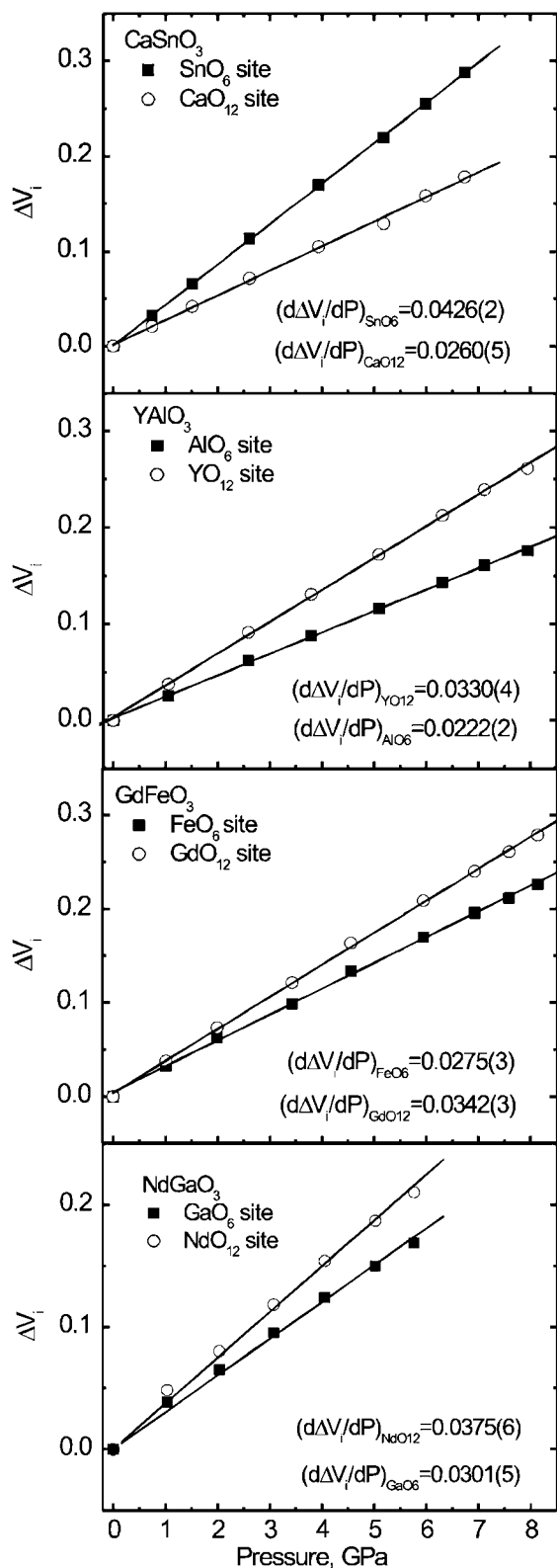


Figure 3
 Simulated variation of the bond-valence differences ΔV_i of the A and B sites in the 'fixed-coordinate' model structures with increasing pressure. The significant difference in the slopes for the A and B cations in each structure indicates that the structural variation of this fixed-coordinate model differs significantly from the experimental observations shown in Fig. 2 and that implied by the matching principle.

assuming that the bond-valence sum rule (3) is obeyed exactly in perovskites at room pressure, in which case $M_i = R_i V_0 / B$. One could also approximate the value of the R_A/R_B ratio by the value from cubic perovskites of $2^{1/2}$. This leads to the estimate (Brown, 2004) $\beta_B/\beta_A = M_A/M_B \approx 2^{1/2}(V_A/V_B)$ that immediately divides perovskites on the basis of the formal charges of the two cations on the A and B sites. For perovskites with a +2 cation on the A site and a +4 cation on the octahedral B site, $M_A/M_B \approx 0.7$. They are therefore predicted to become more distorted with pressure. Perovskites with two cations of formal charge +3 would have $M_A/M_B \approx 1.41$ and are thus predicted to become less distorted with pressure.

3. Tests and predictions

3.1. Tests

Fig. 2 shows the bond-valence difference ΔV_i calculated from measured individual bond lengths as a function of pressure on the basis of high-pressure single-crystal X-ray diffraction studies on a number of GdFeO₃-type perovskites. This figure clearly demonstrates that the changes with pressure of the bond valences $\Delta V_i(P)$ of the BO_6 and AO_{12} sites in each structure are equal within the uncertainties. This equality appears to confirm the assumption that led to the matching principle expressed by (10), at least within the resolution of the experimental data. However, the question may be posed as to whether $d\Delta V_A/dP$ and $d\Delta V_B/dP$ are really sensitive to the variation of structure when a unit cell is compressed. In other words, does the matching relation expressed by (10) really reflect the requirement of strain balance between the two sites, or is it merely some artifact?

To attempt to answer these questions we introduce an artificial structure model and make a simulation of its structural change with pressure. For our model we assume that the unit-cell parameters a , b and c of the GeFeO₃-type perovskites follow the actual measured variations with increasing pressure, but that the atom coordinates (x, y, z) in the asymmetric unit do not change with pressure. Here we present such simulations for YAlO₃, GdFeO₃, CaSnO₃ and NdGaO₃ as examples. The atomic parameters at room pressure and unit-cell parameters at different pressures used to calculate the bond valence were obtained from experimental measurements (Ross *et al.*, 2004*a,b*; Zhao *et al.*, 2004*a,b*). In this 'fixed coordinate' model the changes in the tilt angles of the octahedra with pressure are much smaller than in the observed structures. The variation with pressure of the bond-valence differences ΔV_i (Fig. 3) in the fixed coordinate model are very different from those observed with the experimentally determined structures at high pressures (*cf.* Fig. 2), indicating that the values of $d\Delta V_A/dP$ and $d\Delta V_B/dP$ are indeed sensitive to the structural parameters.

Furthermore, although this 'fixed coordinate' model does not obey the matching relation as expressed in (10) we see, for example in CaSnO₃, that $d\Delta V_A/dP$ of the model is less positive than the observed value in the real structure, while

Table 1

Bond-valence parameters, average bond lengths and M_A/M_B for 2:4 perovskites and 3:3 perovskites.

M_i : calculated from average bond lengths at room pressure using (5) and (8); t_{obs} : the observed tolerance factor (Sasaki *et al.*, 1983).

	Bond-valence parameter R_0	$\langle R_i(0) \rangle$	M_i	M_A/M_B	t_{obs}
2:4 Perovskites					
CaZrO ₃ ^a	BO ₆ site	1.928	2.096	21.58	0.53
	AO ₁₂ site		2.885	11.43	
	AO ₈ site	1.967	2.572	10.84	0.973
	AO ₄		3.510	0.59	
CaSnO ₃ ^b	BO ₆ site	1.905	2.0557	22.18	0.56
	AO ₁₂ site		2.835	12.45	
	AO ₈ site	1.967	2.537	11.75	0.975
	AO ₄		3.435	0.70	
CaTiO ₃ ^c	BO ₆ site	1.815	1.9547	21.73	0.63
	AO ₁₂ site		2.726	13.69	
	AO ₈ site	1.967	2.5188	12.26	0.986
	AO ₄		3.139	1.43	
CaGeO ₃ ^d	BO ₆ site	1.748	1.892	20.79	0.75
	AO ₁₂ site		2.647	15.46	
	AO ₈ site	1.967	2.481	13.37	0.989
	AO ₄		2.979	2.09	
MgSiO ₃ ^e	BO ₆ site	1.624	1.793	18.41	0.75
	AO ₁₂ site		2.472	13.85	
	AO ₈ site	1.693	2.203	12.00	0.975
	AO ₄		3.010	1.85	
SrZrO ₃ ^f	BO ₆ site	1.928	2.091	21.83	0.60
	AO ₁₂ site		2.917	12.98	
	AO ₈ site	2.118	2.719	11.58	0.986
	AO ₄		3.317	1.40	
3:3 Perovskites					
LaGaO ₃ ^g	BO ₆ site	1.730	1.980	16.34	1.22
	AO ₁₂ site		2.763	19.97	
	AO ₈ site	2.172	2.619	16.92	0.987
	AO ₄		3.053	3.05	
YAlO ₃ ^h	BO ₆ site	1.651	1.910	15.38	1.32
	AO ₁₂ site		2.654	20.32	
	AO ₈ site	2.019	2.399	18.57	0.983
	AO ₄		3.158	1.57	
GdAlO ₃ ⁱ	BO ₆ site	1.651	1.905	15.55	1.33
	AO ₁₂ site		2.658	20.67	
	AO ₈ site	2.065	2.457	18.42	0.987
	AO ₄		3.059	2.25	
ScAlO ₃ ^j	BO ₆ site	1.651	1.903	15.62	1.06
	AO ₁₂ site		2.608	16.37	
	AO ₈ site	1.849	2.273	15.62	0.969
	AO ₄		3.277	0.75	
GdFeO ₃ ⁱ	BO ₆ site	1.759	2.014	16.39	1.15
	AO ₁₂ site		2.782	18.89	
	AO ₈ site	2.065	2.469	17.91	0.977
	AO ₄		3.408	0.98	
NdNiO ₃ ^k	BO ₆ site	1.654	1.942	14.46	1.55
	AO ₁₂ site		2.711	22.40	
	AO ₈ site	2.105	2.519	17.79	0.987
	AO ₄		3.095	4.61	
PrNiO ₃ ^k	BO ₆ site	1.654	1.942	14.46	1.19
	AO ₁₂ site		2.714	17.20	
	AO ₈ site	2.138	2.541	18.49	0.988
	AO ₄		3.060	2.74	
NdGaO ₃ ^l	BO ₆ site	1.730	1.9808	16.31	1.18
	AO ₁₂ site		2.7559	19.23	
	AO ₈ site	2.105	2.5258	17.51	0.984
	AO ₄ site		3.217	1.72	

References: (a) Koopmans *et al.* (1983); (b) Zhao *et al.* (2004a); (c) Sasaki *et al.* (1987); (d) Sasaki *et al.* (1983); (e) Ross & Hazen (1990); (f) Ahtee *et al.* (1976); (g) Vasylychko *et al.* (1999); (h) Ross *et al.* (2004a); (i) Ross *et al.* (2004b); (j) Ross (1998); (k) García-Muñoz *et al.* (1992); (l) Vasylychko *et al.* (2000).

$d\Delta V_B/dP$ is more positive, making the mean of these model values approximately equal to that which is observed in the real structures upon compression. This means that the real pressure-induced structural change follows a path such that the variation of bond-valence sums about the two sites is matched (Fig. 2*b*). In the case of CaSnO₃, this matching requires that the CaO₁₂ site is more compressible than the SnO₆ site because $M_A/M_B < 1$. The simulations also suggest that the high-pressure behaviour of YAlO₃, GdFeO₃ and NdGaO₃ are similar to one another, but different from CaSnO₃. For these 3:3 perovskites the matching relation leads the pressure-induced structure change along a path that ensures that each AO₁₂ site is less compressible than the corresponding BO₆ site, because $M_A/M_B > 1$.

Now that we have shown that the matching relation is satisfied by the structures that have been measured at high pressures, we can now explore whether it can be used to successfully predict the change in distortion of GdFeO₃ perovskites at high pressures.

3.2. 2:4 perovskites

In perovskites with a cation of formal charge +4 occupying the octahedral sites the M_A/M_B ratio is significantly less than unity. Therefore, octahedral tilting will increase with increasing pressure in these 2:4 perovskites. This relationship also suggests that pressure-induced phase transitions from *Pbnm* orthorhombic symmetry to cubic symmetry are unlikely for these compounds. For example, in CaSnO₃ M_A is significantly smaller than M_B , irrespective of whether the Ca site is considered to be eight- or 12-coordinated (Table 1). The CaO₁₂ site should therefore be more compressible than the SnO₆ site (Table 1), which is in agreement with experimental results (Zhao *et al.*, 2004a). The experimental results have also shown that the compressibility of the SnO₆ site within CaSnO₃ is anisotropic and consequently that the distortion of SnO₆ increases with pressure. The distortion of SnO₆ is coupled to

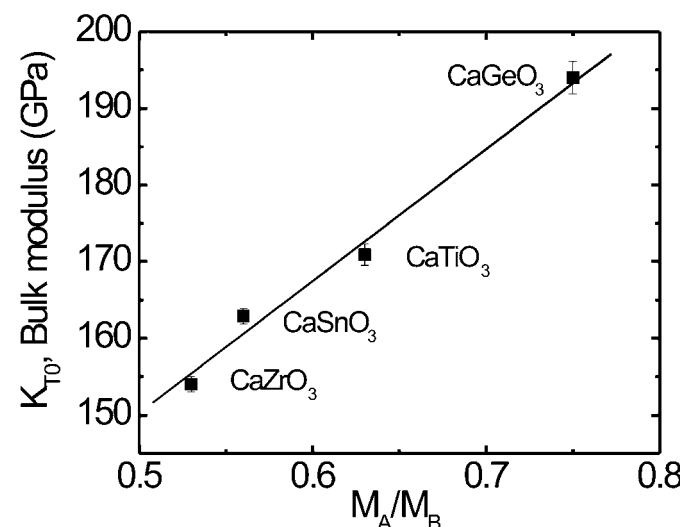


Figure 4
The correlation of the measured bulk moduli, K_{T0} , of Ca perovskites (Ross & Chaplin, 2003) with their M_A/M_B ratios.

an increase in distortion of the 12-fold coordination around the Ca site. However, the change in distortion is not sufficient to invalidate the prediction of the matching relation.

We also calculated the M_A/M_B ratio (Table 1) of the other calcium oxide perovskites for which room-pressure structural parameters are available in the literature (Sasaki *et al.*, 1983, 1987). For Zr, Sn, Ti and Ge in the B site, the ratio M_A/M_B ranges from 0.53 to 0.75. Most of this variation arises from the different values of M_A for the Ca site in the four structures. The correlation between the measured bulk moduli of these Ca perovskites and the M_A/M_B ratio (Fig. 4) suggests that not only is the CaO_{12} site more compressible than the octahedral

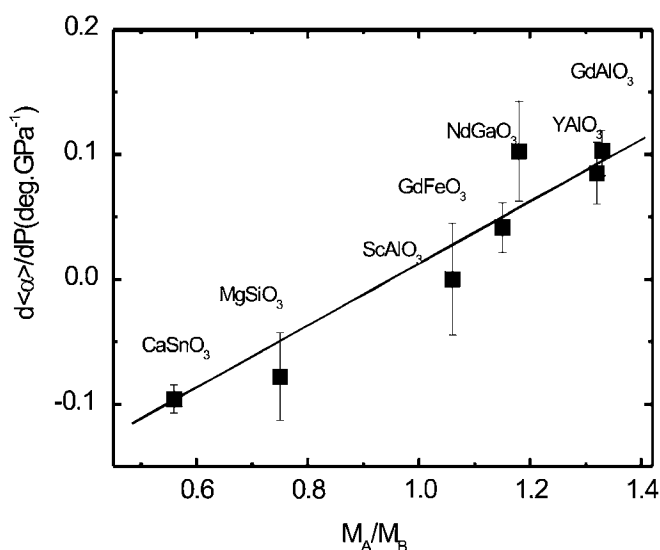


Figure 5
The rate of variation with pressure of the average bond angle, $\langle\alpha\rangle = (\angle B-O1-B + \angle B-O2-B)/2$, in several perovskites plotted against the ratio M_A/M_B determined from their room-pressure structures. Data from the sources are listed for Fig. 2.

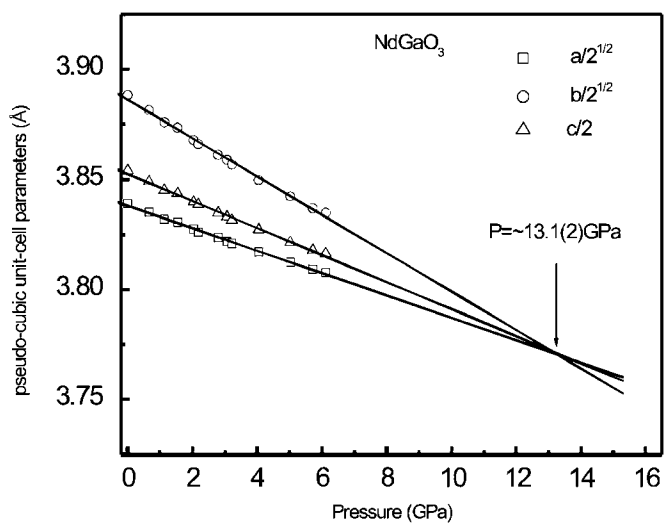


Figure 6
Pseudocubic sub-cell parameters of NdGaO_3 ($a = a_{\text{cell}}/2^{1/2}$, $b = b_{\text{cell}}/2^{1/2}$, $c = c_{\text{cell}}/2$, where a_{cell} , b_{cell} and c_{cell} are the lattice parameters of the orthorhombic cell) as a function of pressure (Zhao *et al.*, 2004b).

sites but, as the softest structural component, its compressibility is controlling the bulk moduli of these structures.

Understanding the pressure-induced structure change in MgSiO_3 orthorhombic perovskite is important because of the geophysical implications for the Earth's lower mantle (*e.g.* Navrotsky & Weidner, 1989). It is also a controversial one in crystal chemistry. Yagi *et al.* (1982) predicted that the orthorhombic $Pbnm$ distortion in MgSiO_3 should decrease with pressure, whereas O'Keeffe *et al.* (1979) suggested that the distortion should increase. The ratio M_A/M_B for MgSiO_3 is 0.75 (Table 1), so it is clear that the matching relation predicts that MgSiO_3 should behave in a structurally similar manner to CaGeO_3 and become more distorted with increasing pressure. This is consistent with high-pressure single-crystal X-ray diffraction measurements (Ross & Hazen, 1990).

In Table 1 we further list one $Pbnm$ perovskite, SrZrO_3 , with an M_A/M_B ratio much less than unity, suggesting that it should become more distorted with increasing pressure. A high-pressure EXAFS study (Andraut & Poirier, 1991) shows that this is the case, at least to 8 GPa, but that the distortion appears to decrease at higher pressure until it vanishes at about 25 GPa. Whether this result indicates that the pressure-induced distortion reaches some limiting state, some breakdown in our model, or that the sample was subject to non-hydrostatic conditions to which our model does not apply requires further experimental investigation.

3.3. 3:3 perovskites

In orthorhombic perovskites with both cations having a formal charge of +3, the ratio M_A/M_B is found to be significantly greater than unity (Table 1). Therefore, the AO_{12} sites are predicted to be significantly less compressible than the octahedral sites and the octahedral tilts should decrease with

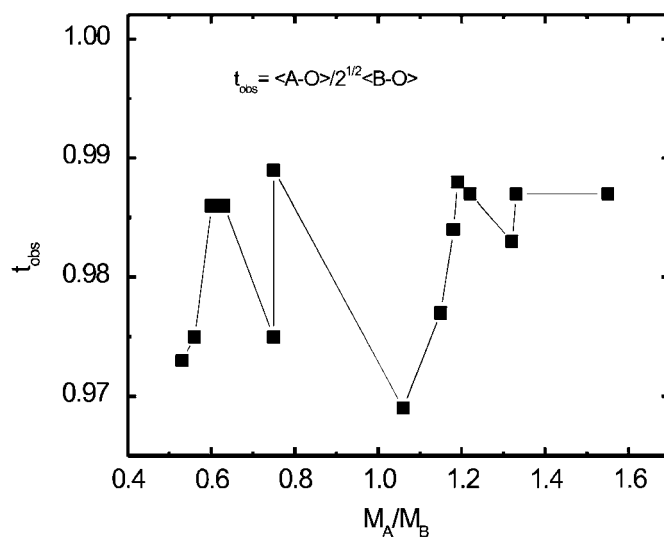


Figure 7
The observed tolerance factor for orthorhombic perovskites, as defined by Sasaki *et al.* (1983, 1987), plotted as a function of the ratio M_A/M_B . The lack of apparent correlation between these parameters suggests that the tolerance factor is not a good predictor of the structural evolution of perovskites at high pressures.

increasing pressure. This is certainly the case for those perovskites in this group for which we have experimental data at high pressures. Furthermore, the magnitude of the ratio M_A/M_B seems to show some correlation with the rate of change in octahedral tilts with pressure. For example, the Al—O1—Al and the Al—O2—Al tilt angles in YAlO_3 and GdAlO_3 with $M_A/M_B \simeq 1.33$ (Table 1) change by $ca\ 1^\circ$ from 0 to ~ 8 Pa (Ross *et al.*, 2004*a,c*), whereas the Fe—O2—Fe tilt angle in GdFeO_3 with $M_A/M_B = 1.15$ changes by about half this amount (Ross *et al.*, 2004*c*), as does the Ga—O2—Ga tilt angle in NdGaO_3 with $M_A/M_B = 1.18$ (Zhao *et al.*, 2004*b*). This general trend relating the average rate of tilting to the M_A/M_B ratio appears to include the 2:4 perovskites as well (Fig. 5).

The predicted decrease in octahedral tilt angles with increasing pressure suggests that pressure is also likely to induce phase transitions from orthorhombic symmetry to higher symmetry in all of these perovskites for which $M_A/M_B > 1$. The changes in pseudocubic sub-cell parameters of NdGaO_3 with increasing pressure up to 7 GPa (Zhao *et al.*, 2004*b*) clearly show a trend towards a higher symmetry (Fig. 6). Linear extrapolation of these trends to higher pressures suggests that a phase transition will occur at ~ 13 GPa. NdNiO_3 , for example, with $M_A/M_B = 1.55$, undergoes a phase transition to rhombohedral symmetry at 6 GPa (Medarde *et al.*, 1997). LaGaO_3 is orthorhombic under room conditions (*Pbnm*; Vasylechko *et al.*, 1999) and, from the calculated $M_A/M_B = 1.22$, our model predicts that the tilts of the GaO_6 octahedra will decrease with increasing pressure. A powder synchrotron X-ray diffraction study shows LaGaO_3 undergoes a phase transition to a rhombohedral structure near 2.5 GPa (Kennedy *et al.*, 2001).

3.4. Discussion

It has been shown that not only does the value of M_A/M_B calculated from (5) and (8) predict the trend of pressure-

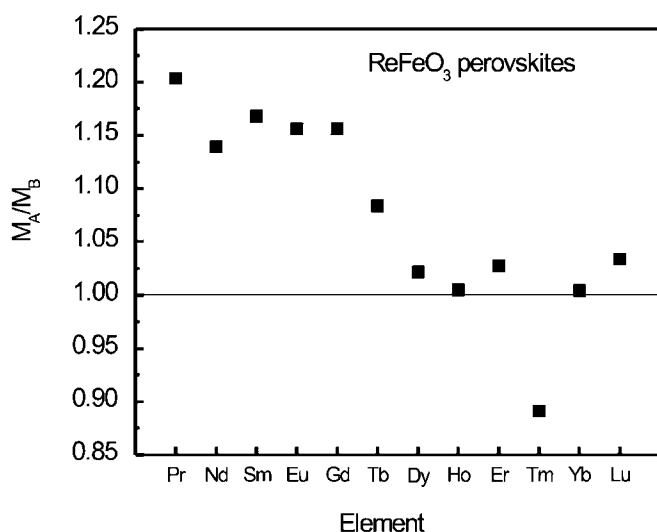


Figure 8

The ratio M_A/M_B for rare-earth ferrite perovskites calculated from the room-pressure structural data reported in Marezio *et al.* (1970).

induced structural changes of the GdFeO_3 -type perovskites, but that there is also a close relation between the value of M_A/M_B and the degree of pressure-induced distortion and tilting in the GdFeO_3 -type perovskites (Fig. 5). In addition, at least for the Ca-perovskites, there is a correlation between M_A/M_B and their bulk moduli (Fig. 4). This is not the case if one of the simpler approximations to the expressions for M_A and M_B is used. As noted above, the crudest approximation based upon ideal bond-valence sums and pseudo-cubic bond lengths yields $M_A/M_B \simeq 0.7$ for all 2:4 perovskites. If it is assumed that the bond-valence sums at the cations are ideal so that the observed bond lengths only are used to calculate the average bond length, then M_A/M_B ranges from 0.69 to 0.70 for the Ca-perovskites. By contrast, if the actual bond lengths are used to calculate both the bond-valence sum and the average bond length then M_A/M_B ranges from 0.53 for CaZrO_3 to 0.75 for CaGeO_3 (Table 1), and these are the values that show correlations with physical and structural properties.

Another widely used successful predictor of perovskite structures at room pressure has been the tolerance factor, defined as $t_{\text{obs}} = \langle A - O \rangle / (2^{1/2} \langle B - O \rangle)$ (Sasaki *et al.*, 1983, 1987). Fig. 7 shows that the variation of t_{obs} with the ratio M_A/M_B is very irregular. This suggests to us that the tolerance factor will not be as successful as the ratio M_A/M_B in predicting the high-pressure behaviour of perovskite structures.

4. Conclusions

The matching relation that we have proposed supplies a simple general method by which to predict the trends of structural changes with pressure in orthorhombic oxide perovskites. We should, however, point out that this model may not be applicable to perovskites in which the electronic structure plays a significant role in determining distortions of the cation sites. Examples would include cations such as Ti^{4+} in the octahedral sites of some perovskites in which the magnitude of the off-center displacement of the Ti^{4+} cation is a large contributor to the values of the Ti—O—Ti bond angles. Similarly, the stereochemical influence of the lone-pair electrons in cations such as Pb^{2+} on the compressional behaviour of perovskites deserves further investigation, as does the behaviour of perovskites containing Jahn–Teller distorted octahedra. The other limitation of the model is that it is explicitly static in its treatment of perovskite structures. Therefore, for those perovskites that show dynamic distortions of the structure even at room temperature the ‘average’ bond lengths are merely an artifact of time-averaging and not a true measure of the instantaneous local structure (*e.g.* Abramov *et al.*, 1995). In this case, the resulting ratio M_A/M_B cannot be expected to be a reliable predictor of the compressional behaviour. This may be the case for the one orthorhombic perovskite, SrZrO_3 , that appears inconsistent with the model as suggested by its increasing orthorhombic distortion with pressure which is reminiscent of its behaviour at high temperature (Howard *et al.*, 2000).

Aside from these limitations, the model appears general in its application. Therefore, as a last example, Fig. 8 shows the M_A/M_B ratio calculated from the room-pressure structures of all the rare-earth orthoferrites (Marezio *et al.*, 1970). The ratio M_A/M_B is greater than unity for the lighter rare-earth cations, as expected for 3:3 perovskites, and suggests that these will become less distorted and possibly transform to cubic phases on increasing pressure. The perovskites with the heavier rare-earth cations, however, have M_A/M_B close to unity and are predicted to show less of a decrease in distortion with pressure. TmFeO_3 is clearly an intriguing exception to these trends and a high-pressure neutron diffraction study (Mesot *et al.*, 1997) has shown that it becomes more distorted at high pressure in agreement with having $M_A/M_B < 1$.

Although our model was initially developed for orthorhombic perovskites, one might reasonably speculate as to its applicability to perovskites with higher symmetry. As one example, LaAlO_3 is rhombohedral under room conditions ($R\bar{3}c$) and the calculated $M_A/M_B = 1.42$ from the published data (Lehnert *et al.*, 2000) suggests that the AlO_6 octahedra should show a decrease of tilting with increasing pressure, which has been proven by our single-crystal X-ray study up to 7 GPa (Zhao *et al.*, 2004c). The recent Raman spectroscopy and synchrotron radiation study on a powder sample (Bouvier & Kreisel, 2002) further shows that LaAlO_3 undergoes a rhombohedral-to-cubic phase transition at about 14 GPa, so a general extension of the model to higher symmetries appears to be worth exploration.

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