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Parametrization of perovskite structures: an *ab initio* study

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An overview of the pressure, temperature and chemical composition dependence of the lattice distortion in orthorhombic ABO_3 perovskite structures is presented. Within the framework of the so-called global parametrization method (GPM) [Thomas (1998). *Acta Cryst.* B**54**, 585–599] an improved description for the position of the A cation in terms of the AO_{12} and BO_6 polyhedral volume ratio is proposed. The relationship is derived from an extensive *ab initio* study based on the density functional theory. The applicability of the improved GPM in combination with *ab initio* total energy calculations in the prediction of changes in the structural distortion under increasing hydrostatic pressure is investigated. Test calculations are performed for the geophysically important magnesium silicate perovskite and the results are compared with the available theoretical and experimental data.

1. Introduction

The ideal perovskite structure, ABO_3, has $Pm\bar{3}m$ symmetry with the A cation in the center of a cube defined by eight corner-sharing BO_6 octahedra. Comparatively few perovskites have this ideal structure, most of them being to some extent distorted. The degree of distortion away from the cubic symmetry can be described by a tilting of the BO_6 octahedra. The effect of increasing pressure or temperature on the tilting of the octahedra might lead to phase transformations between orthorhombic, rhombohedral, tetragonal and cubic symmetries.

During the last century several phenomenological or semi-empirical models of the perovskite distortion have been developed. The phenomenological model by Goldschmidt (1926) is based on the tolerance factor that defines the limits of the perovskite structure stability. A parametrization of the orthorhombic perovskites, in terms of the tilting of the BO_6 octahedra, was proposed by Glazer (1972, 1975) and applied by Woodward (1997) in connection with semiempirical total energy methods. A detailed group theoretical analysis of the interconnections between the various perovskite structures was presented by Howard & Stokes (1998).

Recently Thomas (1996, 1998) developed a *global parametrization method* (GPM) for the perovskite structures, in which approximate, semi-empirical relationships are established between the structural parameters and the *polyhedral volume ratio*, V_A/V_B, and *the unit-cell volume*, V. The polyhedral volume ratio is obtained by dividing the volume of the AO_{12} polyhedron (V_A) by the volume of the BO_6 polyhedron

Table 1
Experimental (Horiuchi *et al.*, 1987) structure parameters of zero pressure orthorhombic (*Pbnm*) $MgSiO_3$ perovskite.

The atomic coordinates are expressed in units of lattice parameters: $a = 4.7787$, $b = 4.9313$ and $c = 6.9083$ Å.

	Position	x	y	z
Mg	4(*c*)	0.5141	0.5560	1/4
Si	4(*b*)	1/2	0.0	1/2
O(I)	4(*c*)	0.1028	0.4660	1/4
O(II)	8(*d*)	0.1961	0.2014	0.5531

(V_B) (Thomas, 1996). The knowledge of V_A/V_B and V enables one to determine, within the accuracy of the GPM, the crystal structure of a hypothetical composition, or to predict changes in the structural distortion under increasing pressure or temperature. The GPM variables can be deduced empirically by interpolating between structures of similar composition (Thomas, 1998). An alternative possibility of deriving these parameters is based on electronic structure calculation methods, *viz.* V_A/V_B and V are determined from the minimum of the total energy of the system $E_{\rm tot}(V, V_A/V_B)$. In this optimization procedure the structural parameters are given by the GPM. The main purpose of the present work is to investigate the applicability of the GPM in conjunction with *ab initio* total energy calculations in the prediction of the high-pressure crystal structure of orthorhombic perovskites.

In the first part of §2.1 we briefly review the original GPM for the perovskite structures proposed by Thomas (1996, 1998). Since the orthorhombic structure with *Pbnm* symmetry is a widely adopted crystal structure by perovskites, we focus our attention on this system, although the GPM can be used to describe other crystal structures as well. In the second part of §2.1 we point out the shortcomings of the original parametrization of the A cation displacement. In §2.2, starting from an *ab initio* study based on the Density Functional Theory (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), we establish a correlation between V_A/V_B and the position of the A cation. Using this expression in connection with the original GPM for the perovskites we perform *ab initio* calculations for structural relaxation of the geophysically important $MgSiO_3$ perovskite for pressures up to 150 GPa. The results of this study are compared with the available theoretical (Wentzcovitch *et al.*, 1993) and experimental (Kudoh *et al.*, 1987) data in §3.

2. Generalized approach for structural changes in perovskites

2.1. The global parametrization method of *Pbnm* perovskite structures

In the *Pbnm* orthorhombic structure the A cations and four O atoms [O(I)] occupy the 4(*c*) positions. The B cations are in the 4(*b*) positions, and the remaining O atoms [O(II)] are situated in the general 8(*d*) positions. The three lattice constants and seven internal coordinates determine the crystal structure. In the case of $MgSiO_3$ perovskite these parameters are listed in Table 1. Within the GPM the ten independent structural parameters are expressed in terms of the length of the octahedral stalks (Thomas, 1996), denoted by s_1, s_2 and s_3; the A cation displacement from the center of the coordinates of O(I) ions, d_A; and six angles: θ_1, θ_3, Γ_1 and Γ_3 describing the tilt of the stalks relative to the pseudo-cubic axis (Thomas, 1996), the pseudo-cubic angle $\gamma_{\rm pc}$, and the orientation α_A of the A cation relative to the four nearest-neighbor O(I) atoms. The exact definitions of these parameters may be found in the recent works by Thomas (1996, 1998), and the transformation between the Thomas parameters and the three orthorhombic lattice constants and seven internal coordinates are given in *Appendix A*.

The variations of the octahedral stalk-length ratios, s_1/s_3 and s_2/s_3, and of α_A with the chemical composition are small (Thomas, 1998). Therefore, these parameters are assumed to have constant values within the GPM ($s_1/s_3 \simeq 1.010$, $s_2/s_3 \simeq 1.001$, $\alpha_A \simeq 81.5°$). The remaining seven parameters are expressed as functions of the polyhedral volume ratio, V_A/V_B, and the *Pbnm* unit-cell volume, $V = 4(V_A + V_B)$. The tilt angles θ_3, Γ_1, Γ_3 and $\gamma_{\rm pc}$ are determined from the empirical relations

$$\begin{aligned}\theta_3 &= 73.0 - 13.13(V_A/V_B),\ \Gamma_1 = 30.0 + 3.60(V_A/V_B),\\ \Gamma_3 &= 44.0 - 16.50(V_A/V_B),\ \gamma_{\rm pc} = 62.8 + 5.79(V_A/V_B),\end{aligned} \qquad (1)$$

(expressed in degrees) derived from a numerical fit to a database of structural parameters of 32 perovskites (Thomas, 1998). The second octahedral tilt angle θ_1 is obtained from the relations (Thomas, 1996)

$$V_A/V_B = 6\cos^2[(\theta_1 + \theta_2)/2]\cos\theta_3 - 1,\ \ s_1\sin\theta_1 = s_2\sin\theta_2, \qquad (2)$$

which are valid within the assumption that the three octahedral stalks intersect at right angles. The length of the stalk along the pseudo-cubic z axis is determined from the volume of the orthorhombic unit cell

$$V = s_3^3\big[(s_1/s_3)\cos\theta_1 + (s_2/s_3)\cos\theta_2\big]^2\cos\theta_3\sin\gamma_{\rm pc}. \qquad (3)$$

In the original work on GPM (Thomas, 1998) two alternative methods were proposed for the determination of the displacement of the A cation relative to the center of the four O atoms O(I). The first approach involves the ionic radii, r_A and r_O, and the volume V_A of the AO_{12} polyhedron. It is given by

$$V_A(1.26287r_A + r_O)^{-3} = md_A + n, \qquad (4)$$

where the parameters $m = 1.01$ Å^{-1} and $n = 2.16$ were obtained from a least-squares fit to a database of d_A, V_A and r_A parameters of 20 perovskite structure (Thomas, 1998). The root mean-square (r.m.s.) error of (4) for these structures is 0.064 Å. In the second approach, based on bond-valence parameters, the r.m.s. error is slightly higher, 0.088 Å. Therefore, this approach will not be discussed in the present work.

The structural parameters predicted from the GPM for the perovskites generally agree remarkably well with the experimental values. However, we have found that the experimentally or theoretically observed variation of the position of the A cation, in particular the variation of d_A, with pressure and

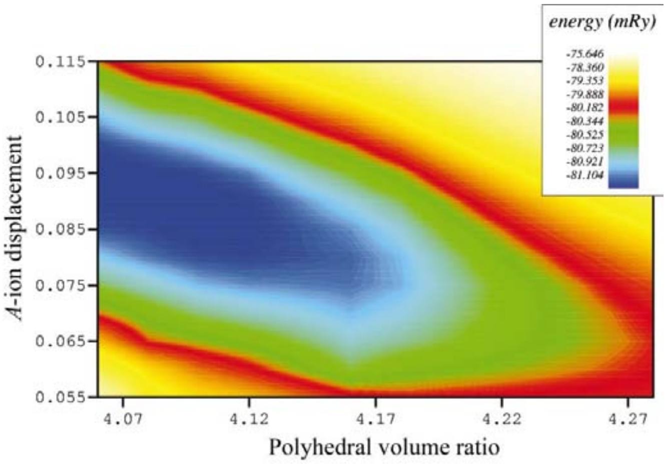

Figure 1
Total energy of $MgSiO_3$, evaluated using the FCD-EMTO method (Vitos, 2001; Vitos *et al.*, 2000; Kollár *et al.*, 2000), as a function of the A ion displacement (d_A, in units of lattice parameter a) and polyhedral volume ratio (V_A/V_B).

temperature is not correctly reproduced within this method. In the following we expand on the arguments that support this conclusion.

For the $Pm\bar{3}m$ cubic structure the displacement of the A cation vanishes, *i.e.* $d_A = 0$, and the relation $V_A(1.26287r_A + r_O)^{-3} \simeq 2.16$ should hold independently of pressure or temperature. This condition is not always fulfilled and, therefore, the original GPM is inadequate to describe the pressure-induced orthorhombic cubic phase transition observed, *e.g.* in $SrZrO_3$ perovskite (Andrault & Poirier, 1991).

With increasing pressure the volume of the AO_{12} polyhedron decreases, which, according to (4), leads to decreasing d_A. This trend is in contrast to the experimental and theoretical observations for $MgSiO_3$ (Kudoh *et al.*, 1987; Wentzcovitch *et al.*, 1993).

Finally, the increasing temperature in the case of $NaMgF_3$ perovskite results in an increasing volume V_A of the AO_{12} polyhedron (Thomas, 1998). In accordance with (4) this should increase the displacement of the A cation, which is in contradiction with the orthorhombic cubic phase transition reported (Zhao, 1998) at T = 1038 K.

2.2. Correlation between d_A and V_A/V_B

Within the framework of the GPM (Thomas, 1998) the ratio of the orthorhombic lattice constants, b/a and c/a, and the relative coordinates of the O atoms (expressed in units of lattice constants) are determined by the polyhedral volume ratio V_A/V_B. At the same time, the relative coordinates of the A cation, which, according to (4), are proportional to the volume of the AO_{12} polyhedron, depend on the volume of the unit cell. In this section, using an *ab initio* total energy calculation method, we investigate the existence of a direct correlation between d_A and V_A/V_B. We note that such a relationship was not detected for the database of 32 orthorhombic perovskite structures (Thomas, 1998).

The present investigation was performed for the orthorhombic $MgSiO_3$ perovskite. For this study d_A and V_A/V_B were considered as independent variables, while the rest of the positions were fixed to the values calculated within the GPM. The total energy was calculated using the full charge density exact muffin-tin orbitals method (FCD-EMTO). The FCD-EMTO method (Vitos, 2001; Vitos *et al.*, 2000; Kollár *et al.*, 2000) is an *ab initio* electronic structure calculation method based on the density functional (Hohenberg & Kohn, 1964; Kohn & Sham, 1965) and exact muffin-tin orbitals theories (Andersen *et al.*, 1994, 1998). Details of numerical calculations are given in *Appendix B*.

All the calculations were carried out at the theoretical volume of V = 162.60 Å^3 obtained from the FCD-EMTO calculation (Vitos, 2001). We restricted our study to $4.06 \leq V_A/V_B \leq 4.28$, where the lower bound represents the empirical limit of stability for perovskites (Thomas, 1998) and the upper bound is the zero pressure experimental polyhedral volume ratio for $MgSiO_3$. The length d_A was expressed in units of the lattice constant a and the calculations were performed for values between $0.055a$ and $0.115a$.

The contour plot of the total energy per atom, as a function of V_A/V_B and d_A, is shown in Fig. 1. The plot shows a strong dependence of the A cation displacement on V_A/V_B and it clearly demonstrates the proportionality between these two parameters; d_A corresponding to the total energy minima, calculated for fixed V_A/V_B, decreases nearly linearly with the polyhedral volume ratio. We have found that the correlation between the displacement of the A cation and V_A/V_B can be well described by the relation

$$d_A = 0.147a[R - (V_A/V_B)], \tag{5}$$

where R is a parameter. The global energy minimum from Fig. 1 corresponds to $R \simeq 4.7$ and it is realised for $V_A/V_B \simeq 4.08$ and $d_A \simeq 0.09a$. These values should be compared to the zero pressure experimental (Thomas, 1998) and *ab initio* molecular dynamics (Wentzcovitch *et al.*, 1993) values of 4.9, 4.28 and $0.09a$, and 4.9, 4.17 and $0.11a$, respectively. Having in mind that eight of the ten parameters were fixed in our simulation, and the fact that the GPM is a semi-empirical method, this agreement may be considered as satisfactory. We note that the cubic perovskite structure limit, where $V_A/V_B = 5$ and $d_A = 0$, is correctly reproduced by (5) for $R = 5$.

The relationship between V_A/V_B and d_A from (5) is in perfect accordance with both *ab initio* molecular dynamics simulation (Wentzcovitch *et al.*, 1993) and experimental measurements (Kudoh *et al.*, 1987) on $MgSiO_3$; d_A increases and V_A/V_B decreases with applied pressure. The accuracy of (5) on the database of 20 perovskites (Thomas, 1998) is demonstrated in Fig. 2. The r.m.s. error for $R = 5$ is 0.0016 Å, which is remarkably much smaller than that obtained from (4). In the inset of Fig. 2 we compare the experimentally observed temperature dependence of d_A for $NaMgF_3$ perovskite with that estimated from (5) using the temperature-dependent V_A/V_B values (Thomas, 1998). It is remarkable how well the temperature-induced orthorhombic cubic phase transition

(Zhao, 1998) at T = 1038 K is reproduced by the present parametrization of d_A.

3. Application: the magnesium silicate perovskite under pressure

The understanding of the pressure-induced structural changes in $MgSiO_3$ is an issue of great concern and it presents important geophysical implications for the Earth's lower mantle (Stixrude & Cohen, 1993). Here, using the GPM for the perovskite structures in combination with (5) and the FCD-EMTO method (Vitos, 2001; Vitos *et al.*, 2000; Kollár *et al.*, 2000), we investigate the crystal structure of $MgSiO_3$ perovskite in the pressure range 0–150 GPa, which covers the entire pressure regime of the Earth's lower mantle (24–136 GPa).

Within the present technique the problem of lattice relaxation at each unit cell volume reduces to a one-dimensional optimization procedure. The polyhedral volume ratio, calculated from the total energy $E_{\rm tot}(V, V_A/V_B)$, is used in (1)–(3) and (5) to determine the volume dependence of the lattice constants and internal atomic positions. The hydrostatic pressure is derived from the equation of state as $P = -dE_{\rm tot}(V)/dV$, where $E_{\rm tot}(V) \equiv \min_{V_A/V_B} E_{\rm tot}(V, V_A/V_B)$ denotes the minimum of the total energy. For the present structural relaxation of $MgSiO_3$ we used $R = 5$ in (5).

The calculated V_A/V_B ratio decreases continuously with pressure from 4.17 at 0 GPa to 3.99 at 150 GPa. This trend, which was observed experimentally as well (Kudoh *et al.*, 1987), is a strong indication that the $MgSiO_3$ perovskite diverges from the cubic symmetry with applied hydrostatic pressure.

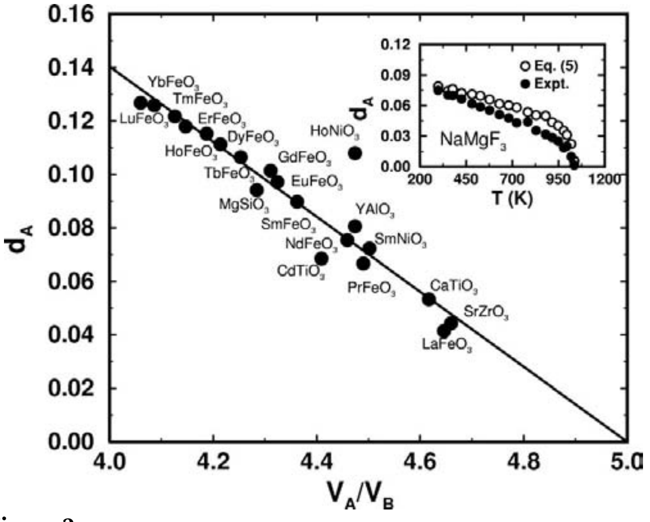

Figure 2
The V_A/V_B dependence of the A cation displacement (in units of lattice constant a) for different chemical compositions shown in the figure. The circles are the experimental values (Thomas, 1998) and the solid line is (5) with $R = 5$. In the inset the temperature dependence of d_A for the $NaMgF_3$ perovskite is compared with the d_A values estimated from (5) using the temperature-dependent V_A/V_B values (Thomas, 1998).

In Fig. 3 the present results for the lattice constants of $MgSiO_3$ are compared with available *ab initio* molecular dynamics (Wentzcovitch *et al.*, 1993) and experimental (Kudoh *et al.*, 1987) data. The agreement between the different sets of results is very satisfactory. The anisotropies of the axial compressibility at 60 GPa obtained in molecular dynamics simulation are $(b/b_0) : (a/a_0) \simeq 1.02$ and $(c/c_0) : (a/a_0) \simeq 1.01$, and these ratios become more enhanced with pressure. These anisotropies calculated from the present results are 1.015 and 1.009, respectively, and show no significant changes with increasing hydrostatic pressure.

The seven internal parameters of *Pbnm* $MgSiO_3$ structure are plotted in Fig. 4. The similarity between the present values and the molecular dynamics data (Wentzcovitch *et al.*, 1993) again supports the validity of the improved GPM in high-pressure studies of *Pbnm* perovskite structures. The distortions relative to the cubic $Pm\bar{3}m$ structure, as concluded from Fig. 4, increase slightly with pressure. Therefore, the $MgSiO_3$ perovskite is unlikely to undergo a phase transition to the high-symmetry cubic structure, at least not in the range of pressures up to 150 GPa. This observation is consistent with the results obtained from calculations based on the linearized augmented plane wave method (Stixrude & Cohen, 1993) and on *ab initio* molecular dynamics simulations (Wentzcovitch *et al.*, 1993). We note that the present result is strictly valid only at T = 0 K. In the Earth's lower mantle the temperature increases with the depth (~2000–3000 K), which might offset the effects of increasing pressure to some extent.

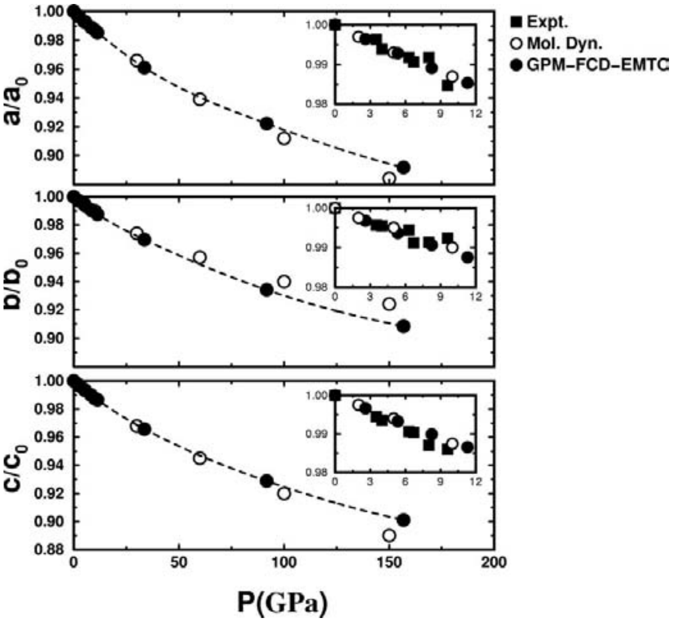

Figure 3
Comparison between the theoretical and experimental (Kudoh *et al.*, 1987) relative compressibilities of the lattice parameters of $MgSiO_3$. The present results (GPM-FCD-EMTO) are calculated using the GPM (Thomas, 1998) in conjunction with the FCD-EMTO method (Vitos, 2001; Vitos *et al.*, 2000; Kollár *et al.*, 2000) and the *ab initio* molecular dynamics data (Mol.Dyn.) were determined by Wentzcovitch *et al.* (1993).

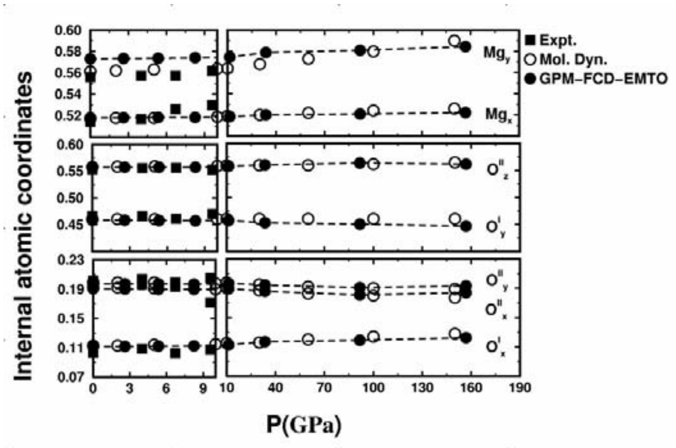

Figure 4
Comparison between the theoretical and experimental internal structural parameters (in units of lattice constants) of $MgSiO_3$. See caption of Fig. 3.

4. Conclusions

We have presented a revised version of the global parametrization method of perovskite structures proposed by Thomas. Based on an *ab initio* study we have suggested a linear correlation between the A cation displacement and polyhedral volume ratio. Our approach describes correctly the pressure, temperature and chemical composition dependences and it does reproduce the high-symmetry cubic perovskite structure.

The improved global parametrization method has been applied in conjunction with *ab initio* determinations of the polyhedral volume ratio. We have shown that this combined technique can reproduce with high accuracy the theoretically and experimentally observed structural distortion with pressure in the geophysically important $MgSiO_3$ mineral. We consider that the global parametrization method, together with the revisions proposed in this work, will become a complete technique for predicting structural changes in the orthorhombic perovskites."

APPENDIX *A*
Orthorhombic lattice parameters and GPM parameters

Within the GPM of the orthorhombic ABO_3 perovskites the crystal lattice is described (Thomas, 1998) by six angles, $\theta_1, \theta_3, \gamma_{pc}, \Gamma_1, \Gamma_3, \alpha_A$, and four distances, s_1, s_2, s_3, d_A. In the following we give the transformation from these parameters to the orthorhombic lattice constants and *Pbnm* internal atomic coordinates.

The relations between the tilt angles, octahedral stalks lengths and orthorhombic lattice parameters are

$$\begin{aligned} a &= (s_1 \cos\theta_1 + s_2 \cos\theta_2)\sin(\gamma_{\rm pc}/2),\\ b &= (s_1 \cos\theta_1 + s_2 \cos\theta_2)\cos(\gamma_{\rm pc}/2),\\ c &= 2s_3 \cos\theta_3. \end{aligned} \tag{6}$$

For a given value of the unit-cell volume, V, and polyhedral volume ratio, V_A/V_B, the lattice constants are calculated from (1)–(3) and (6).

The internal structural parameters (in units of lattice constants) of the O(I) and O(II) type of atoms are given by the relations

$$\begin{aligned} x_{\rm O(I)} &= (s_3/2a)\sin\theta_3 \sin[\Gamma_3 + (\gamma_{\rm pc}/2)],\\ y_{\rm O(I)} &= \tfrac{1}{2} - (s_3/2b)\sin\theta_3 \cos[\Gamma_3 + (\gamma_{\rm pc}/2)],\\ z_{\rm O(I)} &= (s_3/2c)\cos\theta_3, \end{aligned}$$

and

$$\begin{aligned} x_{\rm O(II)} &= (x^{\rm pc}_{\rm O(II)} + y^{\rm pc}_{\rm O(II)})/(a^2+b^2)^{1/2},\\ y_{\rm O(II)} &= \tfrac{1}{2} + (-x^{\rm pc}_{\rm O(II)} + y^{\rm pc}_{\rm O(II)})/(a^2+b^2)^{1/2},\\ z_{\rm O(II)} &= \tfrac{1}{2} - (z^{\rm pc}_{\rm O(II)})/c. \end{aligned}$$

where

$$\begin{aligned} x^{\rm pc}_{\rm O(II)} &= (s_1/2)\cos\theta_1 + y^{\rm pc}_{\rm O(II)}\cos\gamma_{\rm pc},\\ y^{\rm pc}_{\rm O(II)} &= -[s_1/2(f)^{1/2}]\sin\theta_1,\\ z^{\rm pc}_{\rm O(II)} &= y^{\rm pc}_{\rm O(II)}\tan\Gamma_1, \end{aligned}$$

are the pseudo-cubic coordinates of O(II) atoms and $f \equiv \sin^2\gamma_{\rm pc} + \tan^2\Gamma_1$. The coordinates of the A cation are determined as

$$\begin{aligned} x_A &= \tfrac{1}{2} + (d_A/a)\cos\alpha_A,\\ y_A &= y_{\rm O(I)} + (d_A/b)\sin\alpha_A,\\ z_A &= z_{\rm O(I)}, \end{aligned} \tag{7}$$

where d_A is given by (5). Finally, the B atom is situated in a high symmetry position (1/2, 0, 1/2)."

APPENDIX *B*
Details of the numerical calculations

The one-electron equations were solved within the scalar-relativistic and soft-core approximations. In the EMTO basis set we included s, p and d orbitals. The Mg 3s, Si 3s and 3p and O 2s and 2p states were treated self-consistently. For the exchange-correlation term we used the local density approximation with the Perdew–Wang parametrization (Perdew & Wang, 1992) of the results of Ceperley & Alder (1980). The Green's function was calculated for 32 complex energy points distributed exponentially on a semi-circular contour. The k-space integral was performed on 50 uniformly distributed k points in the irreducible part of the orthorhombic Brillouin zones.

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