Eur. Phys. J. B **56**, 1–5 (2007)
DOI: 10.1140/epjb/e2007-00003-1

THE EUROPEAN
PHYSICAL JOURNAL B

Ab initio study of the structural and elastic properties of spinels MgX_2O_4(X = Al, Ga, In) under pressure

A. Bouhemadou[1,a], R. Khenata[2], and F. Zerarga[1]

[1] Department of Physics, Faculty of Science, University of Setif, 19000 Setif, Algeria
[2] Laboratoire de Physique Quantique et de Modélisation Mathématique (LPQ3M), Département de Technologie, Université de Mascara, 29000 Mascara, Algeria

Received 23 September 2006 / Received in final form 9 November 2006

Abstract. We perform ab initio calculations using a pseudo-potential plane-wave method based on density functional theory, within the local density approximation and generalized gradient approximation, in order to determine and predict the pressure dependence of structural and elastic properties of spinel compounds: $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$. The results are in agreement with the available experimental data and other theoretical calculations.

PACS. 71.20.Nr Semiconductor compounds – 71.15.Mb Density functional theory, local density approximation, gradient and other corrections – 62.20.Dc Elasticity, elastic constants – 74.62.Fj Pressure effects

1 Introduction

Quantum mechanical calculations have reached a sufficient level of sophistication to reproduce satisfactorily experimental data, and predict interesting properties in the cases in which experimental measurements are fully absent. Among these properties, elastic constants represent a good test for estimating the quality of a theoretical approach. They require calculation, point by point, of the hypersurface of the total energy for appropriate lattice deformations, and numerical calculation of the second derivatives of the energy with respect to strain components.

Elastic properties of a solid are important because they are closely related to various fundamental solid-state phenomena such as interatomic bonding, equations of state, and phonon spectra. Elastic properties are also linked thermodynamically with specific heat, thermal expansion, Debye temperature, and the Grüneisen parameter. Most importantly, knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermoelastic stress, internal strain, sound velocities, and fracture toughness.

MgX_2O_4 (X = Al, Ga, In) are members of the class of inorganic materials called spinels. These compounds have been the subject of many experimental and theoretical studies, focusing on the structural [1], electronic [2–4], mechanical [5–9] and optical properties [10–14]. They are characterized by several desirable properties, e.g. a high melting point, high reflectivity, high strength, chemical resistivity at elevated temperatures and low electrical loss [15,16] which makes them candidate materials for numerous applications [17–20].

To the best of our knowledge no experimental or theoretical calculations on the first-order elastic constants of $MgGa_2O_4$ and $MgIn_2O_4$ compounds have been carried out. Moreover, there appear to be no earlier calculations of the strain effect on elastic properties of $MgGa_2O_4$ and $MgIn_2O_4$ compounds. Hence in order to help to understand and control the material and device properties under stress, we report in this paper a numerical investigation based on a theoretical study of the pressure dependence of structural and elastic properties of $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$ compounds. The study is performed using a pseudo-potential plane wave method (PP-PW), in the framework of density functional theory (DFT) within the local density approximation (LDA) and generalized gradient approximation (GGA).

The paper is organized as follows: Section 2 briefly describes the computational details regarding the methods used in our calculations of structural and elastic properties. In Section 3, the results are presented and compared with available experimental and theoretical data. Conclusions are given in Section 4.

2 Computational method

The first-principle calculations are performed using a pseudo-potential plane wave approach based on density functional theory [21] as implemented in the most

---

[a] e-mail: `a_bouhemadou@yahoo.fr`

Table 1. The parameters of the ground-state structures (a_0 (in Å) and u), bulk modulus B_0 (in GPa) and its pressure derivative (obtained from the EOS fitting) for $MgAl_2O_4$, $MgAl_2O_4$ and $MgIn_2O_4$ spinel compounds.

	$MgAl_2O_4$			$MgGa_2O_4$			$MgIn_2O_4$		
	Present	Expt.	Others	Present	Expt.	Others	Present	Expt.	Others
a_0	8.0747*	8.0832^a	7.886^b	8.460*	8.27^c	8.081^b	9.1022*	–	8.884^d
	8.0072**	8.06^e	8.072^d	8.3122**		8.341^d	8.9447**		
u	0.2649*	0.2624^f	0.2688^b	0.2616*	0.2614^c	0.2683^b	0.2561*	–	–
	0.2644**	0.2615^g		0.2616**			0.2558**		
B_0	208*	$196^{f,h}$	215.2^i	163*	–	211.2^i	132*	–	–
	198**		205.01^b	188**		206.91^b	146**		
		220^j							
		227^k							
		213^l							
B'	3.20*	4.7 ± 0.3^f	3.56^m	3.75*		3.77^b	3.9*		
	3.38**		3.4^l	3.67**			4.16**		

* Using the GGA; ** using the LDA, [a] Reference [27]; [b] reference [30]; [c] reference [31]; [d] reference [1]; [e] reference [32]; [f] reference [32]; [g] reference [34]; [h] reference [8]; [i] reference [6]; [j] reference [3]; [k] reference [35]; [l] reference [2]; [m] reference [10].

recent version of the CASTEP package [22]. The exchange-correlation potential is treated within both the LDA, developed by Ceperley and Alder and parameterized by Perdew and Zunger [23,24], and GGA based on Perdew et al. [25]. The major advantages of the PP-PW approach are: the ease of computing forces and stresses; good convergence control with respect to all computational parameters employed; favorable scaling with number of atoms in the system and the ability to make cheaper calculations by neglecting core electrons. The chemically inactive core electrons are effectively replaced with ultra-soft pseudo-potentials, which in this work were taken from the CASTEP database. Two parameters that affect the accuracy of calculations are the kinetic energy cut-off, which determines the number of plane waves in the expansion and the number of special k points used for the Brillouin zone (BZ) integrations. We have studied convergence with respect to BZ sampling and the size of the basis set. Converged results are achieved with a $5 \times 5 \times 5$ special k-points mesh [26]. The size of the basis set is given by cut-off energy equal to 380 eV. Careful convergence tests show that with these parameters relative energies are converged to better than 10^{-6} eV/atom, forces below 0.03 eV Å^{-1} and total stresses below 0.05 eV Å^{-3}.

3 Results and discussion

3.1 Structural properties

Spinels MgX_2O_4 (X = Al, Ga, In) have a closed-packed face-centered-cubic structure [27], with space group *Fd-3m* (Number 227 in the International Tables). Their unit cell contains eight MgX_2O_4 molecules. The oxide ions are positioned at the (u, u, u) positions, the eight X^{2+} ions at (1/8, 1/8, 1/8) and the 16 X^{3+} ions at (1/2, 1/2, 1/2). Then its crystal structure is characterized by two parameters: the lattice constant a_0 and the internal oxygen parameter u. The method used to optimize the geometry of the structure involves computation of the self-consistent total energy of the system by solution of the Kohn-Sham equations, the forces and stresses, using the Hellman-Feynman theorem, and the subsequent relaxation of the electrons, ions and unit cell. The crystal structure was determined using the condition that the total energy is minimized from all atomic configurations. The ions were relaxed until the Hellman-Feynman forces were below 0.03 eVÅ^{-1} and the cell parameters were relaxed until total stresses were below 0.05 eVÅ^{-3}. In Table 1 we summarize our calculated structural properties (lattice constant a_0 and the internal parameters u) of $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$ at zero pressure. When we analyze these results we find that there is an agreement between our results and the reported experimental and theoretical investigations. We note that the lattice parameter a_0 increases and the internal parameter u decreases going from $MgAl_2O_4$ to $MgGa_2O_4$ and then to $MgIn_2O_4$. The same behavior is also found for other spinel oxides [28,29] and is essentially due to the size differences between the trivalent cations In^{+3}, Ga^{+3} and Al^{+3}.

In order to show how the structural parameters under pressure in these compounds behave, the equilibrium geometries of MgX_2O_4 unit cells were computed at fixed values of applied hydrostatic pressure in the range from 0 to 50 GPa, where, at each pressure, a complete optimization of the structural parameters is performed. Pressure dependence of the unit cell volume (V) is shown in Figure 1. The solid curves $p(V)$ were obtained by fitting the calculated values to Murnaghan's equation of state (EOS) [36]. Bulk modulus B_0 and its pressure derivative B' extracted from EOS fitting are listed in Table 1. Pressure dependence of the internal parameter (u) is shown in Figure 2. We clearly observe a quadratic dependence in all curves of these compounds in the considered range of pressure. The solid curve is a quadratic least-squares fit. The values of linear and quadratic pressure coefficients for the internal parameter of these compounds are given in Table 3. These curves show that these compounds behave the same way under pressure. Moreover, these compounds exhibit negative u vs. p slopes, indicating that when under pressure

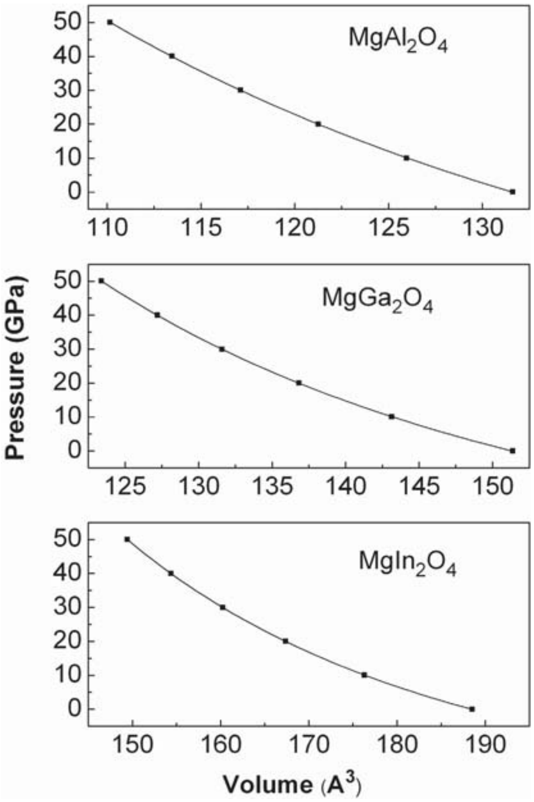

Fig. 1. Equations of state for $MgAl_2O_4$, $MgAl_2O_4$ and $MgIn_2O_4$ compounds.

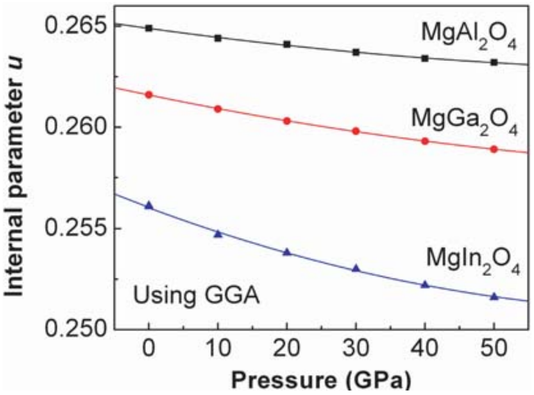

Fig. 2. The internal parameter-pressure relation (u–p); the solid line is a quadratic least-squares fit: $u(p) = u(0) + Qp + Rp^2$ for $MgAl_2O_4$, $MgAl_2O_4$ and $MgIn_2O_4$ compounds.

these spinels increasingly approach the ideal structure characterized by $u = 0.25$.

3.2 Elastic properties

It is well established that first principle studies based on DFT can be used to obtain reliable elastic properties of inorganic compounds. Several methods are available for computation of stiffness coefficients, but currently the 'stress-strain' method seems to be most commonly used and this is the method used in present work. In this approach, the ground state structure is strained according to symmetry-dependent strain patterns with varying amplitudes and subsequent computation of the stress tensor after re-optimization of the internal structure parameters, i.e. after a geometry optimization with fixed cell parameters. The elastic stiffness coefficients are then the proportionality coefficients relating the applied stress to the computed strain. One strain pattern, with non-zero first and fourth components, is sufficient to extract all three independent stiffness coefficients C_{11}, C_{12} and C_{44} of the MgX_2O_4 cubic structure via linear fitting of the stress-strain dependence [37–39]. We used four strain amplitudes, with a maximum applied strain of 0.3%. In Table 1, we list our calculated values of the elastic constants (C_{11}, C_{12} and C_{44}), bulk modulus B_0, Young's modulus E and Poisson's ratios ν for these materials together with the available experimental data and results of other calculations on $MgAl_2O_4$. The elastic constants of $MgGa_2O_4$ and $MgIn_2O_4$ compounds have not yet been calculated or measured. We therefore used the available experimental data on $MgAl_2O_4$ to judge the reliability and accuracy of our predicted results for $MgGa_2O_4$ and $MgIn_2O_4$ compounds. From Table 2, we can see that our LDA calculated values for the elastic constants and bulk modulus for $MgAl_2O_4$ are in good agreement with the available experimental results. From Tables 1 and 2, we can see that the calculated value of the bulk modulus B_0 from the elastic constants has nearly the same value as the one obtained from the EOS fitting. These might be an estimate of the

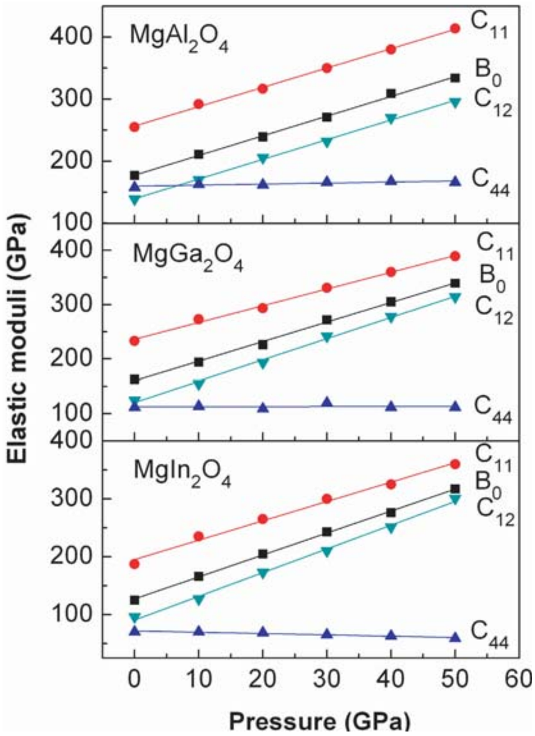

Fig. 3. Calculated pressure dependence of the elastic constants (C_{11}, C_{12}, and C_{44}) and bulk modulus (B_0) for $MgAl_2O_4$, $MgAl_2O_4$ and $MgIn_2O_4$ compounds.

Table 2. The bulk modulus B_0, calculated using the relation $B_0 = (C_{11} + 2C_{12})/3$ (in GPa), elastic constants (C_{11}, C_{12}, and C_{44} (in GPA)), Young's modulus E (in GPa) and Poisson's ratios ν for $MgAl_2O_4$, $MgAl_2O_4$ and $MgIn_2O_4$ spinel compounds.

	$MgAl_2O_4$			$MgGa_2O_4$			$MgIn_2O_4$		
	Present	Expt.	Others	Present	Expt.	Others	Present	Expt.	Others
B_0	180^{*} 196^{**}	$196^{a,b}$	215.2^{c} 205.01^{d} 220^{e} 227^{f} 213^{g}	163^{*} 186^{**}	–	211.2^{c} 206.91^{d}	125^{*} 147^{**}	–	–
C_{11}	262^{*} 276^{**}	282^{k}	293.32^{l} 378^{e} 332^{f}	233^{*} 262^{**}	–	–	182^{*} 213^{**}	–	–
C_{12}	140^{*} 154^{**}	154^{k}	157.09^{l} 140^{e} 174^{f}	129^{*} 145^{**}	–	–	96^{*} 114^{**}	–	–
C_{44}	154^{*} 153^{**}	154^{k}	150.26^{l} 124^{e}	112^{*} 118^{**}	–	–	68^{*} 71^{**}	–	–
E	153^{*} 161^{**}		183.74^{l}	140^{*} 158^{**}	–	–	115^{*} 134^{**}	–	–
ν	0.3558^{*} 0.3625^{**}		0.3488^{l}	0.3566^{*} 0.3571^{**}	–	–	0.3471^{*} 0.3484^{**}	–	–

* Using the GGA; ** using the LDA, ^{a} Reference [32]; ^{b} reference [8]; ^{c} reference [6]; ^{d} reference [30]; ^{e} reference [3]; ^{f} reference [35]; ^{g} reference [2]; ^{k} reference [40]; ^{l} reference [41].

Table 3. Calculated linear and quadratic pressure coefficients of the internal parameter: $u(p) = u(0) + Qp + Rp^2$. Calculated pressure derivatives for the elastic modulus for spinel $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$ compounds.

	$MgAl_2O_4$		$MgGa_2O_4$		$MgIn_2O_4$	
	LDA	GGA	LDA	GGA	LDA	GGA
$Q(10^{-5}\ \mathrm{GPa}^{-1})$	–4.7192	–4.7393	–7.1797	–7.0679	–12.216	–1.2729
$R(10^{-7}\ \mathrm{GPa}^{-2})$	0.0221	0.02678	0.03369	0.0339	0.0695	0.0786
$\frac{\partial B_0}{\partial p}$	3.37	3.16	3.7	3.597	3.82	3.794
$\frac{\partial C_{11}}{\partial p}$	2.59	3.107	2.45	3.083	2.39	3.266
$\frac{\partial C_{12}}{\partial p}$	3.79	3.19	4.31	3.894	4.56	4.097
$\frac{\partial C_{44}}{\partial p}$	0.29	0.162	0.005	0.014	–0.305	–0.228

reliability and accuracy of our calculated elastic constants for MgX_2O_4 compounds. We note a decrease of the corresponding elastic constants C_{11}, C_{12} and C_{44} in going from $MgAl_2O_4$ to $MgIn_2O_4$. The value of calculated bulk modulus decreases from $MgAl_2O_4$ to $MgIn_2O_4$, suggesting that $MgIn_2O_4$ is more compressible than the other oxides. From the elastic constants we obtain the anisotropy parameter $A = 2C_{44}/(C_{11} - C_{12}) = 2.76$, 2.15 and 1.58 for $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$, respectively. This indicates that elastic properties of the Mg spinels are highly anisotropic.

We next study the pressure dependence of the elastic properties. In Figure 2, we present the variation of the elastic constants (C_{11}, C_{12} and C_{44}) and the bulk modulus B_0 of $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$ with respect to the variation of pressure. We clearly observe a linear dependence in all curves of these compounds in the range of pressure considered. In Table 2, we list our results for the pressure derivatives $\partial C_{11}/\partial p$,$\partial C_{12}/\partial p$,$\partial C_{44}/\partial p$ and $\partial B_0/\partial p$ of all the compounds considered. It is easy to observe that the elastic constants C_{11}, C_{12} and bulk modulus B_0 increase with pressure for all the compounds. Moreover the shear mode modulus C_{44} decreases linearly with increasing pressure for $MgIn_2O_4$. The negative value of $\partial C_{44}/\partial p$ for $MgIn_2O_4$ obtained in this study may highlight the relatively low kinetic barrier for structural phase transformation in this compound. A linear extrapolation of C_{44} to higher pressures puts the high-pressure phase transformation at over 66 GPa. The same behavior is also observed in other spinels [42]. To our knowledge no experimental or theoretical data for the pressure derivatives of elastic constants for $MgGa_2O_4$ and $MgIn_2O_4$ compounds are given in the literature. Our results may be considered as reliable predictions of the pressure dependence of the elastic properties of $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$ compounds.

4 Conclusions

Employing the pseudo-potential plane-wave approach based on density functional theory, within the local density approximation and generalized gradient approximation, we have studied the structural and elastic properties of $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$ spinel compounds under pressure. A summary of our results follows.

(i) The calculated equilibrium structural parameters are in agreement with the available experimental and theoretical data.

(ii) The variation of the internal parameters of these compounds with pressure is examined. A quadratic dependence is found. The results predict that the spinel oxides try to reach the ideal spinel structure characterized by $u = 0.25$, in agreement with pervious theoretical studies.

(iii) A numerical ab initio method was used to calculate the elastic constants C_{11}, C_{12} and C_{44} for these compounds. The reliability of the predicted elastic constants of $MgGa_2O_4$ and $MgIn_2O_4$ is checked by comparing the calculated elastic constants of $MgAl_2O_4$ to the experimental data. Calculated elastic constants of $MgAl_2O_4$ are in agreement with the available experimental data.

(iv) We have found a linear dependence of bulk modulus and elastic constants with applied pressure. Our results may be considered as reliable predictions of the pressure dependence of the elastic constants of $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$ compounds.

The first author would like to express his sincere gratitude to Dr. Claude Demangeat and Dr. Cyril Bourgogne from the Institut de Physique et Chimie des Matériaux de Strasbourg-France, for their hospitality and computing facilities.

References

1. S.H. Wei, S.B. Zhang, Phys. Rev. B **63**, 045112 (2001)
2. Shang-D. Mo, W.Y. Ching, Phys. Rev. B **54**, 16555 (1996)
3. R. Khenata, M. Sahnoun, H. Baltache, M. Rérat, A.H. Reshak, Y. Al-Douri, B. Bouhafs, Phys. Lett. A **344**, 271 (2005)
4. Yong-Nian Xu, W.Y. Ching, Phys. Rev. B **43**, 4461 (1991)
5. A. Wanner, Materials Science and Engineering A **248**, 35 (1998)
6. A. Martin Pandàs, Aurora Costales, M.A. Blanco, J.M. Recio, V. Luaña, Phys. Rev. B **62**, 13970 (2000)
7. C. Aksel, B. Rand, F.L. Riley, P.D. Warren, J. Eur. Ceram. Soc. **22**, 745 (2002)
8. A. Yoneda, J. Phys. Earth **38**, 19 (1990)
9. A. Chopelas, Phys. Chem. Minerals **23**, 25 (1996)
10. P. Thibaudeau, F. Gervais, J. Phys.: Condens. Matter **14**, 3543 (2002)
11. A. Ibarra, R. Vila, F.A. Garner, J. Nuclear Materials **233**, 1336 (1996)
12. I.V.A. Charkin, D.W. Cooke, V.T. Gritsyna, M. Ishimaru, K.E. Sickafus, Vacuum **58**, 2 (2000)
13. T. Suzuki, G.S. Murugan, Y. Ohishi, J. Luminescence **113**, 265 (2005)
14. R. Khenata, H. Baltache, M. Sahnoun, A. Bouhemadou, B. Bouhafs, M. Rérat, Algerian J. Adv. Materials **3**, 171 (2006)
15. J.M. Leger, J. Haines, M. Schmidt, J.P. Petitet, A.S. Pereira, J.A.H. daJordana, Nature **383**, 401 (1996)
16. W. Jones, L.J. Miles, Proc. Br. Ceram. Soc. **19**, 161 (1971)
17. A. Govindaraj, E. Flahaut, C. Laurent, A. Peigney, A. Rousset, C.N.R. Rao, J. Mater. Res. **14**, 2567 (1999)
18. G. Gusmano, G. Montesperelli, E. Traversa, G. Mattogno, J. Am. Ceram. Soc. **76**, 743 (1993)
19. N.J. van der Laag, *Environnemental effects on the fracture of oxide ceramics*, Doctorat thesis, Technical University-Eindhoven (2002)
20. T. Irifune, K. Fujino, E. Ohtani, Nature **349**, 409 (1991)
21. W. Kohn, L.J. Sham, Phys. Rev. A **140**, 1133 (1965)
22. M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, J. Phys.: Condens. Matter **14**, 2717 (2002)
23. D.M. Ceperly, B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980)
24. J.P. Perdew, A. Zunger, Phys. Rev. B **23**, 5048 (1981)
25. J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)
26. H.J. Monkhorst, J.D. Pack, Phys. Rev. B **13**, 5188 (1976)
27. R.J. Hill, J.R. Graig, G.V. Gibbs, Phys. Chem. Miner. **4**, 317 (1979)
28. L.W. Finger, R.M. Hazen, A.M. Hofmeister, Phys. Chem. Miner. **13**, 215 (1986)
29. R. Pandey, J.D. Gale, S.K. Sampath, J.M. Recio, J. Am. Ceram. Soc. **82**, 3337 (1999)
30. J.M. Recio, R. Franco, A.M. Pandàs, M.A. Blanco, L. Pueyo, Phys. Rev. B **63**, 184101 (2001)
31. P. D'arco, B. Silvi, C. Roetti, R. Orlando, J. Geophys. Res. **96**, 6107 (1991)
32. P. Fischer, Z. Kristallogr. **124**, 275 (1967)
33. M.B. Kruger, J.H. Nguyen, W. Caldwell, R. Jeanloz, Phys. Rev. B **56**, 1 (1997)
34. D. Semione, C. Dodane-Thiriet, D. Gosset, P. Daniel, M. Beauvy, J. Nuclear Materials **300**, 151 (2002)
35. M. Catti, G. Valerio, R. Dovise, M. Causà, Phys. Rev. B **49**, 14179 (1994)
36. F.D. Murnaghan, Proc. Natl. Acad. Sci. **30**, 244 (1944)
37. V. Milman, M.C. Warren, J. Phys.: Condens. Matter **13**, 214 (2001)
38. V. Milman, M.C. Warren, J. Phys.: Condens. Matter **13**, 5585 (2001)
39. V. Milman, B. Winkler, M.I.J. Probert, J. Phys.: Condens. Matter **17**, 2233 (2005)
40. G.V. Lewis, R.A.C. Catlow, J. Phys. C: Solid State Phys. **18**, 1149 (1985)
41. U.D. Wdowik, K. Parliñski, A. Siegel, J. Phys. Chem. Solids **67**, 1477 (2006)
42. H.J. Reichman, S.D. Jacobsen, American Mineralogist **89**, 1061 (2004)