



Dynamic and thermodynamic properties of antiperovskite compound BiNCa_3

YASSINE CHAUCHE

Laboratoire de Physique Appliquée et Théorique, Larbi Tebessi University, 12002 Tebessa, Algeria
yassine.chaouche@univ-tebessa.dz; ch.yassine@gmail.com

MS received 11 October 2020; accepted 6 November 2020

Abstract. In this study, we detailed the density functional theory (DFT) simulations of the structure parameters, lattice dynamic properties and the temperature effect of the ideal cubic antiperovskite semiconductor compound BiNCa_3 by using the code ABINIT in the edge work of DFT. This code is supported by the pseudopotentials technique with the potential of exchange and correlation local density approximation. Initially we proposed the structural parameters as lattice constant and bulk modulus, and their derived values are compared very well with available results in the literature. We are interested in computing of the lattice dynamic and thermodynamic properties of BiNCa_3 compound. We applied the approach of linear response in the density function perturbation theory to compute the phonon dispersion curves and phonon density of states (DOS). We got 15 phonon modes; 3 acoustic vibrate by Bi atoms and 12 optical modes, of which 9 of them vibrate by Ca atoms and the rest vibrate by N atoms. The effective charges of Born and dielectric parameters, static and electronic are computed. Using the phonon DOS, we have investigated the thermal properties with the temperature effect such as internal energy, free energy and entropy, which gives the disorder and the heat capacity that converged to the limit of Dulong–Petit at highest temperature.

Keywords. Antiperovskite-type nitrides; *ab-initio* calculations; lattice dynamic and thermodynamic properties.

1. Introduction

In 1839, Gustav Rosein discovered the mineral ‘perovskite’ through an experience, which was established in the Ural Mountains. Later, he was called the Russian mineralogist, Count Lev Aleksevichvon Perovski [1]. The first material established was the oxide calcium titanium (CaTiO_3) [2]. Soon after, it used the general formula ABO_3 to describe the group of oxides possessing the same structures. Even non-oxides with similar structure are labelled as perovskite. The scientific researchers are interested in perovskite compounds, which play a very important role in technical applications like electronics, refractories and ceramics. They demonstrate a diversity of properties in physics like superconducting [3], catalytic and magnetic properties [4,5], ionic conducting [6] and optical property [7–9]. On the other hand, the general formula of the antiperovskite families is AXM_3 , which has the same structure of the perovskite oxides [10–12], defined as follows: A = the principal group element, X = the atoms of carbon or nitrogen (C or N) and M = transition metal. Nowadays, this group includes special characteristics, like higher magnetoresistance [13,14], an early coefficient of resistance, nearly zero temperature [15] and superconductivity [16], in the metallic antiperovskites.

The experience of addition and pressing powders of Ca_3N_2 and one of the elements P, As, Sb and Bi [12] creates

the family of antiperovskite-type nitrides or ternary calcium nitrides under the name XNCa_3 (X = P, As, Sb and Bi). This family of antiperovskite is crystallized in the ideal cubic antiperovskite structure with space group (#221) and it contains single type through the atom positions of Wyckoff as: X 1a (0, 0, 0), N 1b (1/2, 1/2, 1/2) and Ca 3c (0, 1/2, 1/2) [17,18]. These compounds are divided into two categories by the compute of the electrical conductivity; BiNCa_3 and SbNCa_3 are characterized by small bandgaps so they are semiconductors, whereas PNCa_3 and AsNCa_3 are insulators [19–21].

Many properties of these compounds are determined from two methods, theoretical and experimental. In this article, we are interested in the structure parameters, lattice dynamic properties and temperature effect on BiNCa_3 semiconductor; in our best knowledge, there is no experiment or theoretical studies of dynamic and thermal properties of antiperovskite material.

Theoretically, by using the augmented plane wave approach, Papaconstantopoulos and Pickett [22] determined the bond in the conduction bands of both antiperovskite compounds BiNCa_3 and PbNCa_3 . They have a narrow gap semiconductor and a metal, respectively. In the BiNCa_3 compound, the p-bands are filled and separated from the conduction bands with energy gap 0.1 eV, but the other compound PbNCa_3 has unfilled p band, which is

predicted correctly to be metallic [22]. By means of the norm-conserving Troullier–Martins pseudopotentials, Vansant *et al* [23] studied the phase transition and they confirm that, at zero pressure and zero temperature, the stable phases of AsNCa_3 and PNCa_3 are orthorhombic with space group Pbnm and simple cubic for BiNCa_3 . The bandgap energies are calculated with 0.87 eV for the orthorhombic structure, it is much higher than the one for the cubic symmetry 0.53 eV. At 59 GPa, a possible transition from the orthorhombic structure to an eightfold coordinated cubic phase SC15 [23] was observed. Then, the structural parameters of the A_3BN (B = As, Sb and Bi; A = Ca) compounds are computed by Beznosikov [24]. He predicted about 80 new cubic metallic perovskite nitrides from crystal-chemical analysis. The crystals of the formula A_3BN , in which A is the Ca atom and B the As, Sb and Bi atoms, may be phases other than addition phases, these crystals correspond to the general formula $\text{A}_3^{(+2)}\text{B}^{(-3)}\text{N}^{(-3)}$. The compounds A_3BN are ionic antiperovskite nitrides [24]. Using the pseudopotentials method implemented on the CASTEP code, Haddadi *et al* [17] evaluated the pressure effect on the independent elastic constants and energy band structures of ANCa_3 (A = P, As, Sb, and Bi) compounds. From the criteria of the elastic constants, the ANCa_3 antiperovskite cubic structure is mechanically stable in the studied pressure range. The shear modulus, Young's modulus and Poisson's ratio for ideal polycrystalline PNCa_3 , AsNCa_3 , SbNCa_3 and BiNCa_3 are calculated to study their hardness. These compounds are brittle from the value of the B/G ratio, which is minor than the critical value separating brittle and ductile behaviour. The calculated sound velocity and the Debye temperature for ANCa_3 compounds are determined [17]. In 2015, Bilal *et al* [25] presented a research on theoretical density functional theory (DFT) approach with local density approximation of BiNCa_3 and SbNCa_3 compounds on the profiles of energy bands, structural and optical properties. The compounds showed semiconducting behaviour using the modified Becke–Johnson (mBJ) potential, which determined the precise direct bandgap as about 1.1 and 1.09 eV for SbNCa_3 and BiNCa_3 , respectively [25].

The principal goal of this study is to add information about the physical properties of BiNCa_3 compound, as we are interested in the lattice dynamical and thermodynamic properties.

2. Procedures of calculations

In this study we have used the DFT functionals, which is the most used quantum mechanical method applied to most finite (atoms and molecules) and infinite (surfaces and solids) systems. It is a general-purpose computer technique to predict diverse properties as crystal

structures of solids and energy barriers to various processes with low computational cost and reasonable accuracy [26]. The approach of pseudopotentials and plane waves (PP–PW) was used to examine the structure parameters, dynamic and thermodynamic properties of cubic antiperovskite compound BiNCa_3 . This approach is in the edge of DFT [27] as applied in the ABINIT code [28–31]. The potential of exchange and correlation is treated by local density approximation [32] of the Hartwigsen–Goedecker–Hutter (HGH) scheme [33]. All the pseudopotentials of HGH type are offered on ABINIT network of Bi, N and Ca atoms. These pseudopotentials are selected to explain the relations of the valence of an electron and their nuclei and core [34–36]. The input variables of ABINIT are chosen after convergence test. The kinetic energy cutoff describes the plane wave basis as about 60 Hartree. The Brillouin zone was tested and converged in $4 \times 4 \times 4$ as k-points Monkhorst Pack mesh [37]. We applied the approach of linear-response [38,39], which was founded on the density functional perturbation theory (DFPT) to obtain the phonon modes and temperature effect on this compound. The thermodynamic properties containing the phonon contribution to the free energy ΔF of Helmholtz, the phonon contribution to the internal energy ΔE , the entropy S and the specific heat at constant volume C_v are evaluated within the harmonic approximation.

3. Results and discussion

3.1 Structural properties

The model cubic is the crystal lattice of antiperovskite compound XNCa_3 (#221), it contains one form through the atom positions of Wyckoff, i.e., X 1a (0, 0, 0), N 1b (1/2, 1/2, 1/2) and Ca 3c (0, 1/2, 1/2). This model of cubic antiperovskite structure is illustrated in figure 1.

In the *ab-initio* calculations, the first step is determined by the equilibrium parameters of the structural properties. The lattice parameter of BiNCa_3 compound was obtained by computing of full energy for the unit cell vs. to the volume. The values of total energies were fitted to the Murnaghan's equation of state [40]. Figure 2 depicts the variation of the full energy to respect to the volume of the studied compound. The calculations of the structural parameters such as lattice constant, bulk modulus and its pressure derivative are presented in table 1.

Our results are compared very well with the previous experimental and theoretical works with an error, which is in the frame of the suitable error bars. This underestimates with the experimental data probably due to the fact of the temperature; because our calculations are in the absolute zero temperature but the experience is done in the room temperature, which augments the equilibrium volume and reduces the bulk modulus [41].

3.2 Dynamic properties

The lattice dynamic theory or the dispersion relation [42] is defined as the vibration frequency W with respect to the wave vector q . The expression of the phonon modes is if a crystal lattice contains n atoms in the element cell, we have $3n$ modes or branches, i.e., three are acoustic and the remaining are optical.

The phonon spectra as well as total and partial phonon density of states (DOS) of the studied antiperovskite

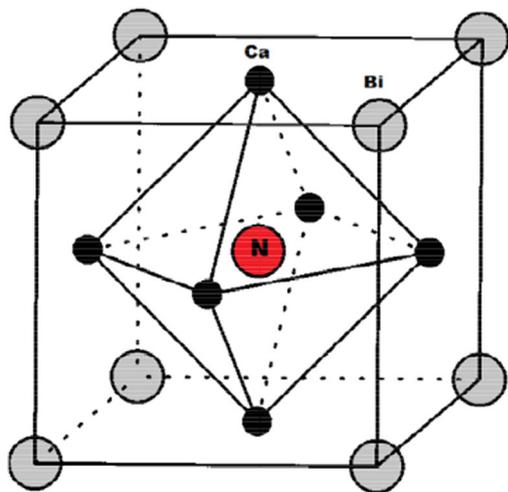


Figure 1. The cubic antiperovskite structure of BiNCA₃.

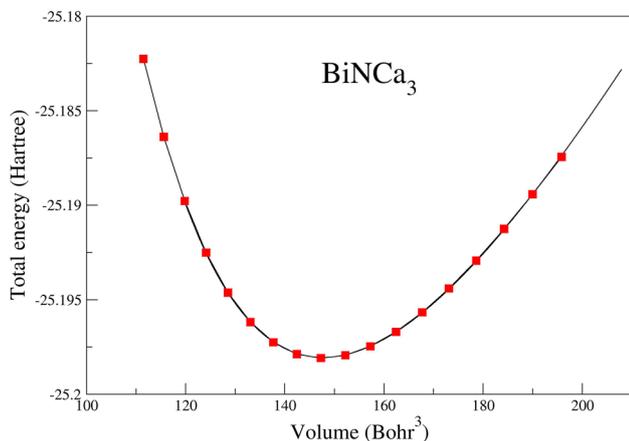


Figure 2. The total energy as function of the volume of BiNCA₃.

compound BiNCA₃ along the high symmetry lines in the Brillouin zone are shown in figure 3. We confirm the theory of lattice dynamic with five atoms, as shown in figure 3, and 15 branch modes. The first 3 phonon modes are acoustic with lower frequencies and the rest 12 are optic, transversal and longitudinal modes. In general, they are two transversal modes and one longitudinal mode. All the frequencies mode are positives, which signify that the cubic antiperovskite structure is stable dynamically.

At the zone centre Γ , we observed gaps separated by the optical phonon modes. These gaps are between longitudinal optical (LO) and transverse optical (TO) phonon mode and it produced the different mass between both atoms Ca and N. This gap is labelled as splitting (LO–TO). This splitting is created by the dipole–dipole interaction, which corresponds to the macroscopic electric field due to the ionic displacements. On the basis of different mass between the atoms constituted the compound BiNCA₃, we can cite that acoustic region (transverse and longitudinal acoustical) vibrate by Bi atoms because it has superior mass than other atoms (N and Ca). On the other hand, for the optical modes, nine of them are due to vibrations of Ca atoms and the last three phonon modes are due to the vibrations of N atoms. Our study of lattice dynamic has predicted that, in our best knowledge, there is no study of this property from both methods theoretical and experimental, so we have added this information to the literature. Some values of frequencies at the line of high symmetry lines Γ , X, M and R are presented in table 2.

Figure 3 depicts the phonon DOS, total and partial by atoms. Within the range of 400 to 480 cm^{-1} , there are two peaks due the optical modes with high frequencies, which are probably vibrated by the Ca and N atoms. Two peaks at 180 and 270 cm^{-1} are because of the vibration of Bi and Ca atoms. Due to the vibration of the Bi atoms with low frequency and superior mass, we observed a clear peak at 180 cm^{-1} .

We have applied the DFPT to obtain the phonon modes. In addition, we can determine other vibrational quantities as the Born effective charges Z^* and dielectric function, electronic one $\epsilon(\infty)$ and static $\epsilon(0)$. The definition of the Born charge effective is the dynamic response produced by the two physical facts of system; the displacement and the electric field perturbation [43]. To know the influence of the macroscopic electric field on vibrational properties [44,45], it is necessary to calculate both tensors of dielectric function and Born effective charge. There is a relation between the

Table 1. Computed lattice parameter a_0 (Å), bulk modulus B (GPa) and its pressure derivative B' of BiNCA₃ compound.

BiNCA ₃ compound	This work	Others	Expt.
a_0	4.782	4.862 [23], 4.85 [24], 4.783 [40], 4.77 [17]	4.888 [12]
B	62.882	65.89 [46], 65.21 [17]	—
B'	4.286	3.96 [46], 4.05 [17]	—

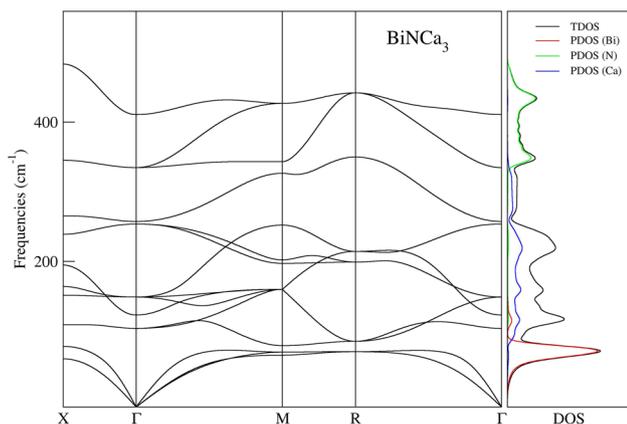


Figure 3. The phonon dispersion curves and one-phonon density of states of BiNCA₃.

polarizability matrix and the dielectric permittivity, as we know that the application of potential to a solid, we have the density response that explains the polarizability [47]. In the same way, by means of a displacement, it induced the polarization in computing of born effective charge [34]. We determined the values of Z^* of BiNCA₃ compound as follows: -2.9075 , -4.0918 and 2.3331 for Bi, N and Ca, respectively. The sum of the Z^* values satisfy the acoustic sum rule [48,49]. The computed values of both static dielectric $\epsilon(0)$ and electronic dielectric $\epsilon(\infty)$ are: 25.883 and 12.327, respectively. We recollect that vibrational properties are calculated for the first time, as there is no other data in the literature.

3.3 The temperature effect

The understanding of the full phonon spectra using the DFPT assures the possibility to calculate numerous essential thermodynamical quantities with the effect of temperature T [50]. Within the quasiharmonic approximation, several quantities of the thermodynamic properties such as free energy ΔF of Helmholtz, internal energy ΔE , entropy S and

heat capacity at constant volume C_v are estimated using the following relations [51]:

$$\Delta F = 3nNk_B T \int \ln[2 \sinh(\hbar\omega/2k_B T)] g(\omega) d\omega \quad (1)$$

$$\Delta E = 3nN \frac{\hbar}{2} \int_0^{\omega_1} \omega \coth(\hbar\omega/2k_B T) g(\omega) d\omega \quad (2)$$

$$S = 3nNk_B \int_0^{\omega_1} [(\hbar\omega/2k_B T) \coth(\hbar\omega/2k_B T) - \ln\{2 \sinh(\hbar\omega/2k_B T)\}] g(\omega) d\omega \quad (3)$$

$$C_v = 3nNk_B \int_0^{\omega_1} (\hbar\omega/2k_B T)^2 \csc^2(\hbar\omega/2k_B T) g(\omega) d\omega \quad (4)$$

where n is the amount of atoms for every element cell, N is the amount of unit cells, ω_1 the biggest mode frequency, k_B and \hbar are the constant of Boltzman and Plank divided by 2π , respectively.

Figure 4 illustrates the calculated effect of temperature on the thermodynamic quantities in the scope of 0 to 1200 K of the compound BiNCA₃.

We can observe that while the temperature augments the internal energies augment too. This augmentation is approximately linear with temperature. In the opposite, the free energy diminishes with the temperature. We can add information at zero temperature about both the quantities; internal energy and free energy, which are equal: $\Delta F_0 = \Delta E_0 = 14.30$ KJ (mol-c)⁻¹, and can be computed by the asymptotic expressions:

$$\Delta F_0 = \Delta E_0 = 3nN \int_0^{\omega_1} \left(\frac{\hbar\omega}{2}\right) g(\omega) d\omega$$

For the entropy S , at phase of molecular, it is frequently described as the variation of entropy like the change to a more disorder status [51]. In harmonic approximation, the main point contributed and important to the thermal partition function is the phonon DOS ($g(\omega)$). The calculation of

Table 2. The obtained values of phonon frequencies (in units of cm⁻¹) of BiNCA₃ compound.

Γ point	Frequencies	X point	Frequencies	M point	Frequencies	R point	Frequencies
TA(Γ)	00.00	TA(X)	70.490	TA(M)	75.118	TA(R)	80.513
LA(Γ)	00.00	LA(X)	86.167	LA(M)	79.891	LA(R)	80.513
TO1(Γ)	115.315	TO1(X)	125.056	TO1(M)	84.300	TO1(R)	86.939
LO1(Γ)	130.187	LO1(X)	166.374	LO1(M)	175.305	LO1(R)	86.940
TO2(Γ)	166.650	TO2(X)	179.588	TO2(M)	175.837	TO2(R)	231.941
LO2(Γ)	166.650	LO2(X)	214.517	LO2(M)	251.097	LO2(R)	231.941
TO3(Γ)	272.306	TO3(X)	258.942	TO3(M)	267.707	TO3(R)	258.305
LO3(Γ)	286.292	LO3(X)	312.028	LO3(M)	366.253	LO3(R)	386.571
TO4(Γ)	431.240	TO4(X)	437.217	TO4(M)	437.363	TO4(R)	479.397
LO4(Γ)	498.821	LO4(X)	514.389	LO4(M)	467.386	LO4(R)	479.397

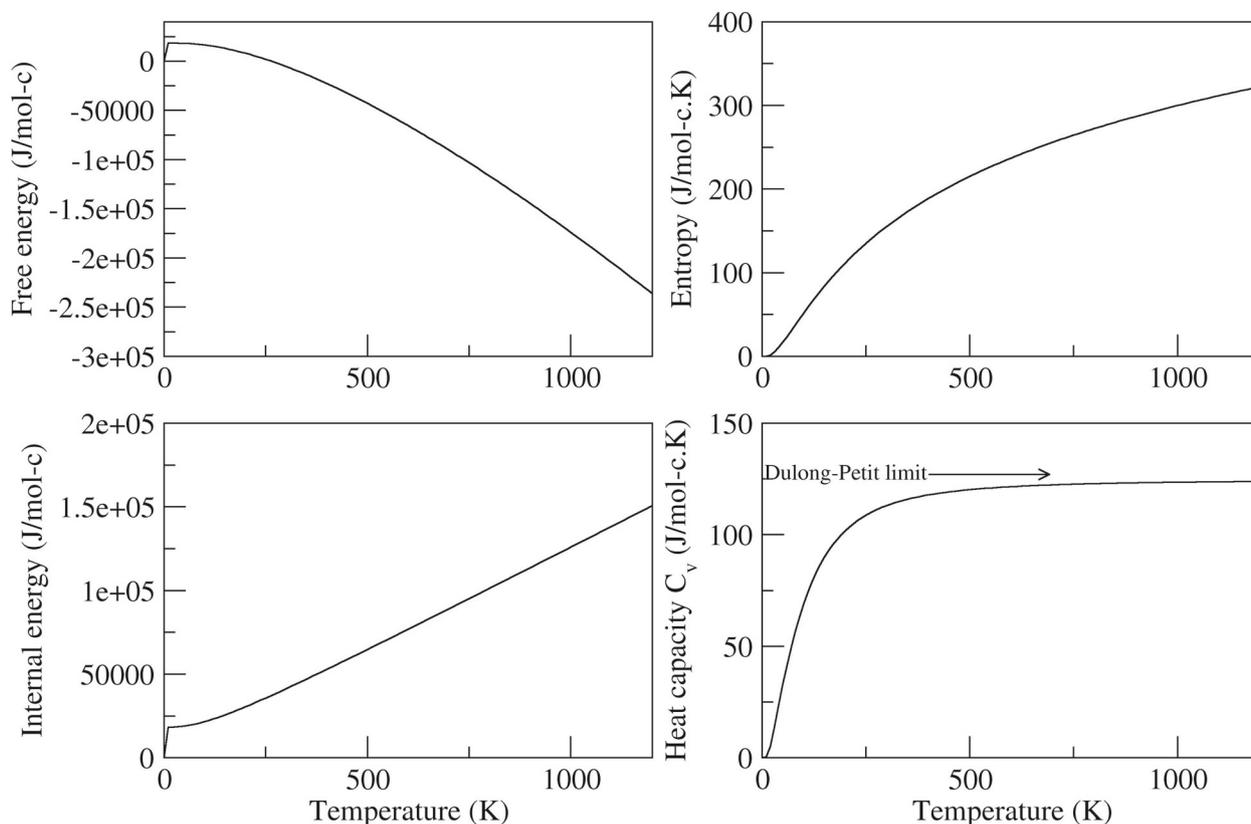
BiNCa₃

Figure 4. The calculated thermodynamical quantities of BiNCa₃; internal energy, free energy, entropy and heat capacity C_v .

the phonon DOS is essential to understand the entropy contribution of material [52]. Stern [53] gives details of several studies observation important to lattice dynamics in 1916. Importantly, he illustrates that the draw of the dynamical matrix is identical to the product of the square of the normal mode frequencies. The entropy values of the compound BiNCa₃ shows that the disorder augments while the temperature increases.

As it is mentioned the thermodynamic properties are evaluated at 0 to 1200 K. For the contribution of total heat capacity to the lattice vibrations of antiperovskite compounds, BiNCa₃ are divided into three phases, when T inferior to 250 K, C_v raises very fast with temperature; when T superior to 250 K, C_v augments gradually as function of the temperature. The last phase of the C_v is at the higher temperature, the C_v augments approximately come close to a stable value named the Dulong–Petit limit.

4. Conclusion

In this study, we have presented both properties dynamical and thermodynamical of the cubic antiperovskite compound BiNCa₃, using the ABINIT code based on the

pseudopotential approach in framework of DFT. We established firstly that the structural parameters such as lattice constant, bulk modulus and its first derivatives are close to other data, theoretical and experimental with tiny errors that are acceptable in the frame of error bars. We applied the DFPT to get the relation of the dispersion of the studied compound, in which we have obtained 15 phonon modes, with three acoustic and the rest are optic. At the centre of the Brillouin zone, there are gaps and splitting between the longitudinal and transversal optical modes. In addition, we have determined both the vibrational quantities; Born effective charge and dielectric function (static and electronic). The Born effective charges satisfy the sum acoustic rule. Using the phonon DOS, we calculated the thermodynamic properties. The internal energy augments when the free energy decreases with the function of temperature. The entropy rises with temperature so the disorder rises. The heat capacity increases with three phases, the last phase after 450 K shows C_v close to approximately to the limit of Dulong–Petit.

Acknowledgements

We extend our honest thanks to the Algerian Ministry of Higher Education and Scientific Research and the DGRSDT

(Direction Générale de la Recherche Scientifique et du Développement Technologique) for their financial support.

References

- [1] Hichour M, Rached D, Rabah M, Benalia S, Khenata R and Semari F 2009 *Physica B* **404** 4034
- [2] Navrotsky A and Weidner D J 1989 *Geophys. Monogr. Ser.* **45** 67
- [3] Ihringer J, Maichle J, Prandl W, Hewat A and Wroblewski T 1991 *Z. Phys. B: Condens. Matter* **82** 171
- [4] Spinicci R, Tofanari A, Delmastro A, Mazza D and Ronchetti S 2002 *Mater. Chem. Phys.* **76** 20
- [5] Gilleo M 1956 *J. Chem. Phys.* **24** 1239
- [6] Huang K, Feng M, Goodenough J and Milliken C 1997 *J. Electrochem. Soc.* **144** 3620
- [7] Jona F, Shirane G and Pepinsky R 1955 *Phys. Rev.* **97** 1584
- [8] Moret M, Devillers M, Worhoff K and Larsen P 2002 *J. Appl. Phys.* **92** 468
- [9] Rao K and Yoon K 2003 *J. Mater. Sci.* **38** 391
- [10] Fruchart D and Bertaut E F 1978 *J. Phys. Soc. Jpn.* **44** 781
- [11] Cherrad D, Maouche D, Louail L and Maamache M 2010 *Solid State Commun.* **150** 782
- [12] Chern M Y, Vennos D A and Disalvo F J 1992 *J. Solid State Chem.* **96** 415
- [13] Kamishima K, Goto T, Nakagawa H, Miura N, Ohashi M, Mori N *et al* 2000 *Phys. Rev. B* **63** 024
- [14] Kim W S, Chi E O, Kim J C, Choi H S and Hur N H 2001 *Solid State Commun.* **119** 507
- [15] Chi E O, Kim W S and Hur N H 2001 *Solid State Commun.* **120** 307
- [16] Zhao J T, Dong Z C, Vaughey J T, Ostenson J E and Corbett J D 1995 *J. Alloys Compd.* **230** 1
- [17] Haddadi K, Bouhemadou A, Louail L, Maabed S and Maouche D 2009 *Phys. Lett. A* **373** 1777
- [18] Ýyigör Ahmet and Selgin A L 2019 *Sakarya University J. Sci.* **23** 700
- [19] Bouhemadou A and Khenata R 2007 *Comput. Mater. Sci.* **39** 803
- [20] Okoye C 2006 *Mater. Sci. Eng. B* **130** 101
- [21] Shein I and Ivanovskii A 2004 *J. Solid State Chem.* **177** 61
- [22] Papaconstantopoulos D A and Pickett W E 1992 *Phys. Rev. B* **45** 4008
- [23] Vansant P R, Van Camp P E and Van Doren V E 1998 *Phys. Rev. B* **57** 7615
- [24] Beznosikov BV 2003 *J. Struct. Chem.* **44** 885
- [25] Bilal M, Jalali-Asadabadi S, Ahmad R and Ahmad I 2015 *J. Chem.* **2015** 11
- [26] Tran F, Laskowski R, Blaha P and Schwarz K 2007 *Phys. Rev. B* **75** 115
- [27] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [28] Gonze X, Beuken J M, Caracas R, Detraux F, Fuchs M, Rignanese G M *et al* 2002 *Comput. Mater. Sci.* **25** 478
- [29] The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors, <http://www.abinit.org>
- [30] Gonze X, Amadond B, Anglade P M, Beuken J M, Bottin F, Boulanger P *et al* 2009 *Comput. Phys. Commun.* **180** 2582
- [31] Gonze X, Rignanese G M, Verstraete M, Beuken J M, Pouillon Y, Caracas R *et al* 2005 *Z. Kristallogr.* **220** 558
- [32] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864
- [33] Hartwigsen C, Goedecker S and Hutter J 1998 *Phys. Rev. B* **58** 3641
- [34] Troullier N and Martins J L 1991 *Phys. Rev. B* **43** 1993
- [35] Troullier N and Martins J L 1990 *Solid State Commun.* **74** 613
- [36] Fuchs M and Scheffler M 1999 *Comput. Phys. Commun.* **119** 67
- [37] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [38] Gonze X and Lee C 1997 *Phys. Rev. B* **55** 10355
- [39] Baroni S, de Gironcoli S, dal Corso A and Giannozzi P 2001 *Rev. Mod. Phys.* **73** 515
- [40] Murnaghan F D 1944 *Proc. Natl. Acad. Sci. USA* **30** 244
- [41] Zhang H F, Yu Y, Zhao Y N, Xue W H and Gao T 2010 *J. Phys. Chem. Solids* **71** 976
- [42] Omar M A 1975 *Elementary solid state physics: principles and applications* (Reading, Massachusetts: Addison-Wesley Publishing Company)
- [43] Yassine C and Mourad S 2019 *Pramana J. Phys.* **93** 65
- [44] Choudhury N, Wu Z G, Walter E J and Cohen R E 2005 *Phys. Rev. B* **71** 125
- [45] Zhao Y, Tian X, Xue W and Gao T 2009 *Solid State Commun.* **149** 2130
- [46] Moakafi M, Khenata R, Bouhemadou A, Semari F, Reshak A H and Rabah M 2009 *Comput. Mater. Sci.* **46** 1051
- [47] Nunes R W and Vanderbilt D 1994 *Phys. Rev. Lett.* **73** 712
- [48] Pike N A, Dewandre A, Van Troeye B, Gonze X and Verstraete M J 2018 *Phys. Rev. Mater.* **2** 063608
- [49] Bellaiche L 2000 *Phys. Rev. B* **61** 12
- [50] Yu Y, Han H L, Wan M J, Cai T and Gao T 2009 *Solid State Sci.* **11** 1343
- [51] Lee C and Gonze X 1995 *Phys. Rev. B* **51** 8610
- [52] Fultz B 2010 *Prog. Mater. Sci.* **55** 247
- [53] Stern O 1916 *Ann. Phys. (4e Folge)* **51** 237