First-principles calculations of pressure and temperature dependence of thermodynamic properties of anti-perovskite BiNBa$_3$ compound

Kada Bidai[a], Mohammed Ameri[a], Slamani Amel[a], Ibrahim Ameri[b], Y. Al-Douri[c,d,*], Dinesh Varshney[e], C.H. Voon[f]

[a] *Laboratoire Physico-Chimie des Matériaux Avancés (LPCMA), Université Djilali Liabès de Sidi Bel-Abbès, Sidi Bel-Abbès, 22000-Algeria*
[b] *Djillali Liabes University, Faculty of Exact Sciences, Department of Physics, PO Box 089, Sidi Bel Abbes, 22000-Algeria*
[c] *Nanotechnology and Catalysis Research Center (NANOCAT), University of Malaya, 50603 Kuala Lumpur, Malaysia*
[d] *Physics Department, Faculty of Science, University of Sidi-Bel-Abbes, 22000-Algeria*
[e] *Materials Science Laboratory, School of Physics, Vigyan Bhavan, Devi Ahilya University, Khandwa Road Campus, Indore 452001, India*
[f] *Institute of Nano Electronic Engineering, University Malaysia Perlis, 01000 Kangar, Perlis, Malaysia*

ARTICLE INFO

ABSTRACT

The structural, elastic and thermodynamic properties of the antiperovskite BiNBa$_3$ compound are studied under the effects of pressure and temperature using the full-potential augmented plane wave plus the local orbitals method (FP-APW+lo). The exchange–correlation potential is treated using the generalized gradient approximation within the Perdew, Burke and Ernzerh scheme (GGA-PBE). The calculated lattice constants, the bulk moduli and their pressure derivatives are in reasonable agreement with the available data. The elastic constants C$_{ij}$ and interrelated quantities have also been calculated. The thermodynamic quantities under pressure and temperature are also calculated and elaborated upon.

1. Introduction

The perovskite structure with the formula ABX$_3$ is adopted by many oxide compounds, where A and B are cations and X is oxygen. This structure, which emphasizes the twelve fold coordination of the A atom, can be described by a cubic unit cell which contains an A atom at the center of the cube, B atoms at the corners and X atoms at the center of the cell edges. Another way to describe the structure is to shift the origin, so that the B atom is at the center of the cube, the A atoms at the corners and the X atoms are on the face centers. The latter emphasizes the octahedral coordination of the B atom by six X atoms. Anti-perovskite structures, in which X and B interchange their roles, are also known [1]; i.e. the X anion is at the cation B site and becomes the center of an octahedron formed by six metal atoms.

Ternary nitrides and carbides with the cubic anti-perovskite structure of the general formula AXM$_3$, where A is an element of the (III–V) groups, X is carbon or nitrogen, and M is a transition metal [2], are isostructural with the perovskite oxides [3–5]. However, this group and others have reported superconductivity [6], giant magnetoresistance [7,8] and a nearly zero temperature coefficient of resistance [9] in the metallic antiperovskites. The cubic antiperovskite structure for the

---

* Corresponding author.
  E-mail address: yaldouri@yahoo.com (Y. Al-Douri).

BiNBa$_3$ compound has one formula per unit cell with the Wyckoff positions of atoms at Bi: 1a (0, 0, 0), N: 1b (1/2, 1/2, 1/2) and Ba: 3c (0, 1/2, 1/2) [10,11]. Gäbler and Collaborators [12,13] have synthesized a class of antiperovskite XNBa$_3$ (X=As, Sb, Bi and Pb) based on nitrogen. The antiperovskite ternary nitrides have also been synthesized by DiSalvo and co-workers [14, 15], with the element X taken from either group V (X = Bi, As, Sb, P) or group VI (X = Pb, Sn, Ge). The field of ternary nitrides has had considerable interest over the last years [16–18]. Rached et al. [19] have applied the first-principles full-potential linear muffin-tin orbitals (FP-LMTO) method within the local density approximation (LDA) to study the structure, elastic, electronic and optical properties of the antiperovskite BiNBa$_3$. While Haddadi et al. [20] have investigated the structural, elastic and electronic properties of the hexagonal anti-perovskites BiNBa$_3$ by using the pseudopotential plane-wave method based on the DFT.

For the given, it is clear that there are only a few reported theoretical studies for the BiNBa$_3$ compound. A number of basic properties of this compound are still unknown: for example, there are no experimental and theoretical calculations exploring the thermodynamic properties of this compound. In order to fully take advantage of the properties of BiNBa$_3$ for eventual technological applications, a theoretical investigation of the structural, elastic and thermodynamic properties is necessary. For this purpose we used first-principles calculations for the structural, elastic and thermodynamic properties under various pressures and temperatures of BiNBa$_3$ in the anti-peroveskite-type nitrides, using the full potential (linear) augmented plane wave plus local orbital (FP-APW + lo) method within the density functional theory (DFT) based on the Perdew-Burke-Ernzerhof (PBE) functional. This work is organized as follows. A brief description of the calculations is given in Section 2. The results and discussion are presented in Section 3, followed by a brief conclusion in Section 4.

2. Computational method

The zero temperature energy calculations are performed using the FP-LAPW method implemented in the Wien2k computer package [21], which is based on the density functional theory. The space in this method is divided into the interstitial region (IR) and non-overlapping muffin–tin (MT) spheres centered at the atomic sites. The exchange and correlation functional are given by the generalized-gradient approximation of Perdew et al. (GGA96) from [22]. The valence wave functions inside the muffin–tin spheres are expanded up to $l_{max} = 10$. The wave functions in the interstitial regions are expanded in terms of plane waves (PWs). The wave functions and derivatives are made continuous at the boundaries of the spheres, and there are no shape approximations imposed on either the crystalline charge density or potential. The PW cut-off was used with the highly recommended condition $R_{MT}K_{max} = 8$, where R_{MT} is the average of the muffin-tin spheres and K_{max} is the PW cut-off. The sphere radii used in the calculations are 2.9, 2.0 and 2.4 a.u. for Bi, N and Ba, respectively. The k-integration over the Brillouin zone was performed using a mesh of 56 k-points in the irreducible wedge of the Brillouin zone. To ensure proper convergence of the self-consistency calculation, the calculated total energy of the crystal was required to be converged to less than 0.1 mRy.

In our work, the investigation of thermal effects was done within the quasi-harmonic Debye theory of crystals. From an energy–volume (E–V) relationship in the static approximation, obtained via first-principles calculations, the quasi-harmonic Debye model [23–27] as implemented in the Gibbs program [23] allows us to calculate all the thermodynamic parameters that depend on temperature and pressure which are used to derive the other macroscopic properties. In this model, the non-equilibrium Gibbs function $G^*(V; P, T)$ has the following form:

$$G^*(V, P, T) = E(V) + PV + A_{Vib}(\Theta(V), T), \tag{1}$$

where $E(V)$ is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and A_{vib} is the vibrational term, which can be written using the Debye model of the phonon density of states as [24,25]

$$A_{Vib}(\Theta, T) = nk_B T \left[\frac{9\Theta}{8T} + 3\ln\left(1 - e^{-\Theta/T}\right) - D(\Theta/T) \right], \tag{2}$$

where n is the number of atoms per formula unit, k_B the Boltzmann constant and $D(\Theta/T)$ represents the Debye integral. For an isotropic solid, Θ is expressed as [24]:

$$\Theta = \frac{\hbar}{K} \left[6\pi^2 V^{1/2} n \right]^{1/3} f(\sigma) \sqrt{\frac{B_s}{M}}, \tag{3}$$

where M is the molecular mass per unit cell; B_s is the adiabatic bulk modulus, which is approximated by the static compressibility [23]:

$$B_s \cong B(V) = V\left(\frac{d^2 E(V)}{dV^2}\right), \tag{4}$$

and $f(\sigma)$ is given by

$$f(\sigma) = \left\{ 3 \left[2\left(\frac{2(1+\sigma)}{3(1-2\sigma)}\right)^{3/2} + \left(\frac{1+\sigma}{3(1-\sigma)}\right)^{3/2} \right]^{-1} \right\}^{1/3}, \tag{5}$$