Solid State Sciences 29 (2014) 12–23

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Structural, elastic, electronic and optical properties of the newly synthesized monoclinic Zintl phase $BaIn_2P_2$

N. Guechi [a], A. Bouhemadou [b,*], R. Khenata [c], S. Bin-Omran [d], M. Chegaar [e], Y. Al-Douri [f], A. Bourzami [a]

[a] Laboratoire d'Etudes des Surfaces et Interfaces des Matériaux Solides (L.E.S.I.M.S), Département de Physique, Faculté des Sciences, Université de Setif 1, 19000 Setif, Algeria
[b] Laboratory for Developing New Materials and their Characterization, Department of Physics, Faculty of Science, University of Setif 1, 19000 Setif, Algeria
[c] Laboratoire de Physique Quantique et de Modélisation Mathématique (LPQ3M), Département de Technologie, Université de Mascara, 29000 Mascara, Algeria
[d] Department of Physics and Astronomy, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia
[e] Department of Physics, Faculty of Science, University of Setif 1, 19000 Setif, Algeria
[f] Institute of Nano Electronic Engineering, Universiti Malaysia Perlis, 01000 Kangar, Perlis, Malaysia

ARTICLE INFO

Article history:
Received 3 October 2013
Received in revised form
2 January 2014
Accepted 3 January 2014
Available online 13 January 2014

Keywords:
Zintl phase $BaIn_2P_2$
Ab initio calculations
Elastic moduli
Electronic properties
Optical constants

ABSTRACT

The present study explores the structural, elastic, electronic and optical properties of the newly synthesized monoclinic Zintl phase $BaIn_2P_2$ using a pseudopotential plane-wave method in the framework of density functional theory within the generalized gradient approximation. The calculated lattice constants and internal coordinates are in very good agreement with the experimental findings. Independent single-crystal elastic constants as well as numerical estimations of the bulk modulus, the shear modulus, Young's modulus, Poisson's ratio, Pugh's indicator of brittle/ductile behaviour and the Debye temperature for the corresponding polycrystalline phase were obtained. The elastic anisotropy of $BaIn_2P_2$ was investigated using three different indexes. The calculated electronic band structure and the total and site-projected *l*-decomposed densities of states reveal that this compound is a direct narrow-band-gap semiconductor. Under the influence of hydrostatic pressure, the direct D–D band gap transforms into an indirect B-D band gap at 4.08 GPa, then into a B–Γ band gap at 10.56 GPa. Optical macroscopic constants, namely, the dielectric function, refractive index, extinction coefficient, reflectivity coefficient, absorption coefficient and energy-loss function, for polarized incident radiation along the [100], [010] and [001] directions were investigated.

1. Introduction

The classic Zintl phases constitute a class of intermetallic compounds that are composed of electro-positive elements (alkali and alkali-earth metals) in combination with the elements of the groups 13 and 15 [1]. In recent years, the field of Zintl-phases has been extended to include the rare-earth metals, which has led to the discovery of many complex new structures [2]. With the great expansion of Zintl phases since the first presentation of the Zintl concept by E. Zintl in 1939 [3], a large number of Zintl compounds have recently been synthesized, and these diverse structures offer abundant and interesting physical properties, such as semiconductivity, superconductivity, colossal magnetoresistance, magnetic order, mixed-valence character and thermoelectricity [4–10].

In a recent experimental study, Rauscher and colleagues [11] synthesized the novel Zintl phase $BaIn_2P_2$ (barium indium phosphide) and analyzed its crystalline structure. According to [11], $BaIn_2P_2$ crystallizes in a new monoclinic structure type in the space group $P2_1/m$ (No. 11). Each atom resides on a crystallographic mirror plane. To the best of the authors' knowledge, no theoretical or experimental studies of the elastic, electronic and optical properties of this newly synthesized material have yet been conducted. Therefore, such calculations are performed in the present work with the inclusion of pressure effects. The reported results in the present paper may be useful for assessing potential technological applications of $BaIn_2P_2$.

Knowledge of the elastic constants of crystalline materials is essential to understanding many of their fundamental physical properties. In particular, these constants provide information

* Corresponding author. Tel./fax: +213 36620136.
E-mail addresses: a_bouhemadou@yahoo.fr, abdelmadjidbouhemadou@gmail.com (A. Bouhemadou).

1293-2558/$ – see front matter © 2014 Elsevier Masson SAS. All rights reserved.
http://dx.doi.org/10.1016/j.solidstatesciences.2014.01.001

regarding the stability and stiffness of the material against externally applied strains [12]. Knowledge of the pressure dependence of the elastic constants and lattice parameters is significant for many modern technologies [12,13]. For example, semiconductor layers are commonly subjected to large built-in strains because they are often grown on different substrates with considerable lattice mismatch [14,15]. An accurate experimental determination of the elastic constants and lattice parameters under the influence of pressure effects is often rather difficult, and here, theoretical simulations based on accurate *ab initio* theories can play an important role in establishing these lacking data. Thus, the first main objective of the present work is to study the evolution of the structural and elastic properties as a function of pressure.

The electronic structure and optical properties of a material are the first required data for any eventual applications of the material in optoelectronic technology. Thus, the prediction of the electronic and optical properties of this newly discovered Zintl phase $BaIn_2P_2$ constitutes the second main objective of the present work.

2. Computational methodology

All calculations were performed using an *ab initio* pseudopotential plane-wave (PP-PW) method based on the density functional theory (DFT) as it is implemented in the CASTEP (Cambridge Serial Total Energy Package) code [16]. The exchange-correlation effects were treated using the new generalized gradient approximation, the so-called GGA-PBEsol [17]. In all electronic total energy calculations, a Vanderbilt-type ultra-soft pseudo-potential [18] was used to treat the potential seen by the valence electrons because of the nucleus and the frozen-core electrons. The Ba $5s^25p^66s^2$, In $4d^{10}5s^25p^1$ and P $3s^23p^3$ electron orbitals were explicitly treated as valence electron states. Valence electronic wave functions were expanded in a plane-wave basis set truncated at a maximum plane-wave energy (the cut-off energy) of 350 eV. The Brillouin zone (BZ) was sampled on a $2 \times 5 \times 2$ Monkhorst-Pack special k mesh [19]. This set of parameters ensures the self-consistent convergence of the total energy of 5×10^{-6} eV/atom.

The optimized structural parameters were determined using the Broyden–Fletcher–Goldfarb– Shanno (BFGS) minimization technique [20], which provides a fast way to find the lowest-energy structure. The elastic constants were determined by applying a set of given homogeneous deformations with a finite value and calculating the resulting stresses with respect to optimizing the internal atomic freedoms [21]. Four strain patterns – one with nonzero ε_{11} and ε_{23} components, the second with nonzero ε_{33} and ε_{12}, the third with nonzero ε_{22} and the fourth with nonzero ε_{31} – caused stresses related to all thirteen independent elastic constants for the monoclinic unit cell: C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, C_{15}, C_{23}, C_{25}, C_{11} and C_{35}. Three positive and three negative amplitudes were used for each strain component with a maximum strain value of 0.5%, and the elastic constants were determined from a linear fit of the calculated stress as a function of strain. For the elastic-constant calculations, the atoms were allowed to relax to their equilibrium positions when the energy change of each atom between successive steps was less than 1×10^{-6} eV/atom, the force on each atom was less than 0.002 eV/Å^{-1}, the stress on each atom was less than 0.02 GPa, and the displacement was less than 1×10^{-6} Å.

The optical properties of a material are usually described by the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, which characterizes the linear response of a material to electromagnetic radiation and therefore governs the propagation behaviour of radiation in a medium [22]. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ represents the absorption in the crystal, which can be calculated from the momentum matrix elements between the occupied and unoccupied wave functions [23,24]. The real part of the dielectric function $\varepsilon_1(\omega)$, which determines how electromagnetic energy is dispersed when it penetrates a medium, is then evaluated from the imaginary part $\varepsilon_2(\omega)$ via the Kramers-Kronig transformation. The knowledge of both the real and imaginary parts of the dielectric function allows one to calculate the other important linear optical properties, such as the refractive index $n(\omega)$, the extinction coefficient $k(\omega)$, the optical reflectivity $R(\omega)$, the absorption coefficient $\alpha(\omega)$ and the energy-loss spectrum. For the computation of the optical properties, the numerical integration of the Brillouin zone was performed using a $5 \times 12 \times 4$ Monkhorst-Pack k-point sampling procedure [19].

3. Results and discussion

3.1. Structural properties

The newly synthesized Zintl phase $BaIn_2P_2$ possesses a new monoclinic structure type of the space group $P2_1/m$ (No. 11), with four formula units in one unit cell ($Z = 4$) [11]. The unit-cell crystalline structure of $BaIn_2P_2$ is depicted in Fig. 1 (views along the [100] and [010] directions are also shown). In this structure, there are two inequivalent atomic positions for the barium atoms, Ba1 and Ba2; four inequivalent atomic positions for the indium atoms, In1, In2, In3 and In4; and four inequivalent atomic positions for the phosphorous atoms, P1, P2, P3 and P4, which occupy the Wyckoff 2 $e(x, 0.25, z)$ site. Thus, the unit cell is characterized by 24 structural parameters that are not fixed by the symmetry: three lattice constants (a, b and c), one angle β and twenty internal coordinates (x and z). To facilitate descriptions of the chemical bonding, all atoms in the unit cell have been numbered (Fig. 1). As the first step in the present work, the equilibrium structural parameters, including the lattice constants (a_0, b_0, c_0), the angle β_0, the unit-cell volume V_0, and the 20 internal coordinates (x_0, z_0) were calculated. The obtained results are summarized in Tables 1and 2 alongside the available measurements for comparison [11]. As seen from Tables 1and 2, the theoretical and experimental lattice constants and internal coordinates of all ions in a unit cell are in good agreement. The relative difference between the calculated value and measured one for all lattice parameters, $d(\%) = (|\text{Calculated value} - \text{Measured value}| \times 100)/(\text{Measured value})$, is very small. This serves as proof of the reliability of these theoretically obtained results and lends confidence in the results of the following calculations of the elastic, electronic and optical properties of $BaIn_2P_2$ presented in the next sections.

The chemical and structural stability of the monoclinic Zintl phase $BaIn_2P_2$ were estimated by means of the cohesive energy E_{coh} and the formation enthalpy ΔH. The cohesive energy E_{coh} is the energy that is required for the crystal to decompose into free atoms. The cohesive energy E_{coh} of $BaIn_2P_2$ was calculated using the following expression [25]:

$$E_{coh} = \frac{1}{N_{Ba} + N_{In} + N_P}\left[E_{Tot}^{MIn_2P_2} - \left(N_{Ba}E_{Tot}^{Ba(atom)} + N_{In}E_{Tot}^{In(atom)} + N_PE_{Tot}^{P(atom)}\right)\right]$$

Here $E_{Tot}^{MIn_2P_2}$, $E_{Tot}^{M(atom)}$, $E_{Tot}^{In(atom)}$ and $E_{Tot}^{P(atom)}$ represent the total energy of the primitive cell of $BaIn_2P_2$ and the total energies of the isolated Ba, In and P atoms, respectively. N_{Ba}, N_{In} and N_P are the number of Ba, In and P atoms in the primitive cell, respectively. The energy of the free atom was calculated using a cubic box with a large lattice constant that contained the considered atom. The formation enthalpy ΔH of $BaIn_2P_2$ was calculated using the following expression [25]: