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Materials Science and Engineering B 130 (2006) 101–107

MATERIALS SCIENCE & ENGINEERING B

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# First-principles optical calculations of $AsNMg_3$ and $SbNMg_3$

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Received 20 September 2005; received in revised form 12 January 2006; accepted 19 February 2006

**Abstract**

The structural, electronic and optical properties of antiperovskite semiconductors $AsNMg_3$ and $SbNMg_3$ have been studied using the full-potential augmented plane wave plus local-orbital (APW + lo) method. The exchange correlation has been treated using the generalized gradient approximation (GGA). The equilibrium lattice constant and other structural properties have been determined. The $AsNMg_3$ is found to be a direct band gap semiconductor while $SbNMg_3$ is indirect. The results for electronic band structures, density of states, charge densities as well as optical properties are presented and discussed.
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*Keywords:* Optical properties; Band structure calculations; Antiperovskite APW + lo; Structural properties; $AsNMg_3$; $SbNMg_3$

## 1. Introduction

The ternary nitrides or carbides with the cubic antiperovskite structure belong to a class of materials with the general formula $AXM_3$, where A is a main group (III–V) element, X is carbon or nitrogen, and M is a transition (s–d) metal [1]. It has been found that these antiperovskites display a variety of interesting properties such as giant magnetoresistance [2], nearly zero temperature coefficient of resistivity [3] and depending on their chemical composition, can also display a wide variety of physical properties ranging from semiconducting to magnetic and superconducting properties [4]. In particular, the recent discovery of superconductivity in the cubic antiperovskite $MgCNI_3$ [5] and in $MgB_2$ [6] compounds have generated interest in these intermetallic materials.

Recently, Chi et al. [7] reported the synthesis of $AsNMg_3$ and $SbNMg_3$, and used a semiempirical band structure calculation model to show that $AsNMg_3$ has a very wide ($\sim 9.0$ eV) energy gap, and as such, concluded that it is an insulator. Shortly after, Shein and Ivanovskii [8] applied the ab initio local density full-potential LMTO-GGA method to account for the electronic structure in the newly synthesized antiperovskites and found them to be semiconductors.

Our aim in this paper is to study the optical properties of these compounds using full-potential method as embodied in the wien2k package [9]. The optical properties of these compounds have not been studied to the best of our knowledge. Also, it will be worthwhile to use another accurate ab initio method to study the electronic properties of these compounds which will provide a good basis for understanding the optical properties. To this end, in Section 2, we briefly present some details of the theoretical procedure used to obtain the band structure, density of states and optical properties. In Section 3, results of the calculations will be presented and compared with previous theoretical results as well as available experimental data. Conclusions are made in the next section.

## 2. Computational method

We have carried out self-consistent calculations for $AsNMg_3$ and $SbNMg_3$ cubic perovskites using a full-potential augmented plane wave plus local orbital (APW + lo) method [9]. In this calculational scheme, there are no shape approximations to the charge density or potential. Space is divided into two regions, a spherical muffin-tin (MT) around the nuclei in which the radial solutions of the Schrodinger equation and their energy derivatives are used as basis functions, and the interstitial region between the muffin-tins, in which the basis set consists of plane waves. Core states are treated fully relativistically while valence states and semi-core states are treated semi-relativistically (without spin-orbit coupling). The cut-off energy which defines

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0921-5107/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.mseb.2006.02.066

the separation between the core and valence states was set at −6.0 Ry. The sphere radii used were 2.0 a.u. for As, 2.2 a.u. for Sb, 1.6 and 1.8 a.u. for N and Mg, respectively. An APW plus local valence orbitals were used with the wave functions, the potentials and charge densities expanded in terms of spherical harmonics inside the muffin-tin spheres. The Brillouin zone integration was carried out by using the modified tetrahedron method [10] up to 286 $k$-points in the irreducible wedge of the simple cubic Brillouin zone. Well-converged solutions were obtained with $RK_{\max} = 8.0$ (where $R_{\mathrm{MT}}$ is the smallest of the muffin-tin radii and $K_{\max}$ is the plane wave cut-off) and $k$-point sampling was checked. Self-consistent calculations are considered to be converged when the total energy of the system is stable within $10^{-3}$ mRy. The structural calculations are based on the generalized gradient approximation (GGA) to the exchange-correlation of Perdew–Burke–Ernzerhof (PBE) [11] type and were repeated within the LDA [12] in order to estimate the sensitivity of the results to exchange-correlation.

For the calculation of the optical properties, which usually requires a dense mesh of uniformly distributed $k$-points, the Brillouin zone integration was performed using the tetrahedron method with 1540 $k$-points in the irreducible part of the Brillouin zone without broadening. The dielectric function ($\varepsilon(\omega)$) is known to describe the optical response of the medium at all photon energies.

Specifically, in this study, the imaginary part of the dielectric function $\varepsilon(\omega)$ is given as in Refs. [13,14] by

$$\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2\omega^2}\right)\sum_{i,j} \times \int_k \langle i|M|j\rangle^2 f_i(1-f_j)\delta(E_{j,\mathbf{k}} - E_{i,\mathbf{k}} - \omega)\mathrm{d}^3k \qquad (1)$$

where $M$ is the dipole matrix, $i$ and $j$ are the initial and final states respectively, $f_i$ the Fermi distribution function for the $i$-th state, and $E_i$ is the energy of electron in the $i$-th state with crystal wave vector $\mathbf{k}$.

The real part ($\varepsilon_1(\omega)$) of the dielectric function can be extracted from the imaginary part using the Kramers–Kronig relation in the form [15]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}P\int_0^{\infty}\frac{\omega'\varepsilon_2(\omega')\mathrm{d}\omega'}{\omega'^2 - \omega^2} \qquad (2)$$

where $P$ implies the principal value of the integral. The complex dielectric constant of a solid is given as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The knowledge of both the real and imaginary parts of the dielectric tensor allows the calculation of important optical functions such as the refractive index ($n$), extinction coefficient ($k$), energy loss function and reflectivity ($R$). In particular, the refractive index $n(\omega)$ can be calculated using the following expression [16]:

$$n(\omega) = \left\{\frac{\varepsilon_1(\omega)}{2} + \frac{\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}}{2}\right\}^{1/2}. \qquad (3)$$

At low frequency ($\omega$=0), Eq. (3) reduces to the following relation [16]:

$$n(0) = \varepsilon^{\frac{1}{2}}(0). \qquad (4)$$

It is well known that density functional calculations within the generalized gradient approximation (GGA) and local density approximation (LDA), tend to underestimate the energies of excitations [17]. This limitation of density functional theory (DFT) for excitations from the ground state is usually solved by employing the GW formalism [18,19]. However, if the $k$-dependence of the error in the excitation energies is negligible, the scissors approximation [20] can be used to correct the results of the density functional calculations of the dielectric function [21]. In this work, we have not applied the scissors approximation to our calculations of the dielectric function and hence, to the other optical properties, since the experimental data on which a reliable scissors approximation should be based are not available at the moment.

## 3. Results and discussions

We shall first briefly describe the electronic and bonding properties of $AsNMg_3$ and $SbNMg_3$ in order to adequately interpret their optical properties, to which interband transitions also contribute. For the determination of the equilibrium lattice constant and bulk modulus of each material, the total energy was calculated at different volumes. The equilibrium lattice constant, bulk modulus and its pressure derivative were determined by fitting the energy versus volume curve to the Murnaghan equation of state [22]. Table 1, gives the calculated values of the equilibrium lattice constant $a_0$, bulk modulus ($B_0$) and its pressure derivative ($B'$) for the materials as well as available results from other theoretical studies. The results show that the calculated values of the lattice constant are within about 1% of the experimental values for the compounds. The FP-LMTO results of Ref. [8] overestimates the experimental values more than our present calculations. We note however, that the values of our calculated bulk modulus are larger than the values obtained by Shein and Ivanovskii [8]. It is thought that their underestimation of $B_0$ may arise due to the overestimation of the lattice constants.

The electronic structure of $AsNMg_3$ and $SbNMg_3$ along the lines of high symmetry are displayed in Fig. 1. The electronic

Table 1
Calculated lattice constant ($a_0$(Å)), bulk modulus ($B_0$(GPa)) and pressure derivative ($B'$) compared with experimental data and previous works for $AsNMg_3$ and $SbNMg_3$

| Compound | Lattice constant, $a_0$(Å) | $B_0$ (GPa) | $B'$ |
|---|---|---|---|
| $AsNMg_3$ | | | |
| This work | 4.2423 | 85.14 | 4.23 |
| Others[a] | 4.33325 | 47.3 | 5.54 |
| Experimental[b] | 4.21704 | – | – |
| $SbNMg_3$ | | | |
| This work | 4.3815 | 76.39 | 3.93 |
| Others[a] | 4.47638 | 48.0 | 4.38 |
| Experimental[b] | 4.35161 | – | – |

[a] Ref. [8].
[b] Ref. [7].

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