



# Impact of anion replacement on the optoelectronic and thermoelectric properties of $\text{CaMg}_2\text{X}_2$ , $\text{X} = (\text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi})$ compounds



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## ABSTRACT

The structural, electronic, optical and thermoelectric properties of ternary  $\text{CaMg}_2\text{X}_2$  ( $\text{X} = \text{N}, \text{P}, \text{As}, \text{Sb}$  and  $\text{Bi}$ ) compounds are investigated using all electrons full potential linearized augmented plane wave method. By using generalized gradient approximation (GGA), unit cell volumes of the compounds are optimized. For calculations of optical and electronic properties the modified Becke Johnson exchange potential is used along with the GGA. The direct energy band gap decreases by replacing the pnictogen elements, while indirect bandgap also decreases except for  $\text{CaMg}_2\text{As}_2$ . The optical properties show a prominent variation over the change of anion from N to Bi. There is inverse variation between refractive index and the band gap. The refractive indices of these compounds are high in the visible region and sharply decreased in the ultraviolet region. The thermoelectric properties are also studied using Boltzmann statistics through BoltzTrap code. A positive non-zero value of Seebeck coefficient shows a P-type semiconducting behavior of these compounds. High figure of merits (ZT) and optical conductivity peaks for all compounds reveal that they are good candidates for the thermo-electric and optoelectronics devices.

## 1. Introduction

In recent years, Nitrides and Oxynitrides have attracted substantial attention due to their important technological applications [1]. Nitrogen is stable under normal conditions and may react with selected elements with interesting properties to form different compounds [2]. Structural characterization as well as synthesis of  $\text{CaMg}_2\text{N}_2$ , have been reported in 1995 [3]. After six years, the structural characterization and synthesis of  $\text{CaMg}_2\text{N}_2$  was reported by Reckeweg and Disalvo [4]. They obtained  $\text{CaMg}_2\text{N}_2$  compound by the reaction of Ca and Mg with  $\text{NaN}_3$  at 1000 K, in the molar ratio 1:2:1 surrounded in welded Nb ampoules. The single crystals  $\text{CaMg}_2\text{N}_2$  were colorless plates with hexagonal shape and transparent. Although the electronic properties of the compounds could be investigated by experimental spectroscopic techniques [5,6], however, Orhan and co-workers [1] theoretically studied, the electronic and structural properties of  $\text{CaMg}_2\text{N}_2$  which is based on the FP-LAPW method. The structural, elastic, electronic, thermodynamic properties and chemical bonding of  $\text{CaMg}_2\text{N}_2$  have been studied using first-principles density functional theory (DFT). It shows striking elastic anisotropy, equilibrium structural parameters and a ductile behavior,

good in agreement with the experimental results. Under pressure effect, elastic constants and single-crystal were also predicted [7]. It is observed that  $\text{CaMg}_2\text{N}_2$  has a direct band gap and a transition to an indirect gap occurs at about 8.63 GPa.

N-type Zintl compounds show better thermoelectric (TE) performance as compare with P-type. Some of these Zintl materials hold nontoxic, low-cost, earth abundant and inexpensive elements such as  $\text{CaMg}_2\text{Sb}_2$  [8]. Iversen et al. [9] predicted that solid solution of both these phases show the crystal field splitting approximately zero with better electronic transport properties which may lead to high orbital degeneracy for  $\text{CaMg}_2\text{Sb}_2$  compound. Deformation mechanism and ideal shear strength of layered Zintl compounds  $\text{Mg}_3\text{Sb}_2$  for biaxial shear and pure shear deformations were determined by applying DFT. Due to the strong covalent Mg—Sb bond the breakage and softening of the ionic Mg—Sb bond, lead to dissimilar  $[\text{Mg}_2\text{Sb}_2]^{2-}$  substructures and sliding past each other for pure shear deformation. The buckling of the  $[\text{Mg}_2\text{Sb}_2]^{2-}$  substructure, which accounts for the decrease in the stress relaxation and rigidity in the structure, for biaxial shear deformation leads to the breakdown in the structure of  $\text{Mg}_3\text{Sb}_2$ . The stronger ionic Ca—Sb bond ( $\text{SFC} = 1.03 \text{ eV}/\text{\AA}^2$ ) than ionic Mg—Sb bond

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(SFC =  $0.59 \text{ eV}/\text{\AA}^2$ ), by Substituting the  $\text{Mg}^{2+}$  sheet structure with  $\text{Ca}^{2+}$ , resulting in a much higher ideal shear strength of 4.07 GPa in iso-structural  $\text{CaMg}_2\text{Sb}_2$  as compared to  $\text{Mg}_3\text{Sb}_2$  (1.99 GPa) [10].

By using powder of pure elements in necessary amounts and melted beneath an inert atmosphere, the compound  $\text{CaMg}_2\text{Bi}_2$  was synthesized. Characterization of sample by X-RAY Diffraction ensured the growth arrangement of  $\text{CaMg}_2\text{Bi}_2$  after synthesis. It shows the formation of  $\text{Mg}_3\text{Bi}_2$  and  $\text{Mg}_2\text{CaBi}_2$  species, though there is no such information of the compound  $\text{Ca}_3\text{Bi}_2$  [11].  $\text{CaMg}_2\text{Bi}_2$  single crystals was full-grown in Mg–Bi flux as well as their properties were characterized. It is a direct-gap semiconductor as predicted by the electronic structure calculation with a band gap of  $\sim 0.7 \text{ eV}$ . The charged-balanced crystals were also observed, with Hall career concentrations in the range of  $2 \times 10^{19}$  to  $5 \times 10^{19} \text{ cm}^{-3}$  and the lowest value resistivity ratio  $\leq 1.6$ , indicating significant defect scattering is observed for  $\text{CaMg}_2\text{Bi}_2$ . It possesses the highest Debye temperature and reasonable thermoelectric efficiency [12]. Shai and Co-workers have recently reported the thermoelectric properties of  $\text{CaMg}_2\text{Bi}_2$  122 phase. Improved performance was observed in the Bi-based 122 phase compared with Sb-based similar systems, for their Eu and Yb doped  $\text{CaMg}_2\text{Bi}_2$  samples with a record ZT value of 1.3 at 873 K [13]. The thermoelectric transport properties of  $\text{CaMg}_2\text{Bi}_2$ , were characterized between 2 and 650 K. Structure of  $\text{CaMg}_2\text{Bi}_2$  and  $\text{YbMg}_2\text{Bi}_2$  show similar behavior by Refinements of neutron powder diffraction, with flat lattice expansion and relative expansion in  $c$  being  $\sim 35\%$  larger than in  $a$  at 973 K [14]. New compounds  $\text{AMg}_2\text{B}_2$  ( $A = \text{Ca, Sr and Ba}$ ;  $B = \text{As, Sb and Bi}$ ) have been grown and structurally characterized by X-ray single crystal investigations. All compounds belong to the Zintl-phases, whereas they are trigonal and isotypic in anti- $\text{La}_2\text{O}_3(\text{Ce}_2\text{O}_2\text{S})$ -type [17].

In the present work,  $\text{CaMg}_2\text{X}_2$  ( $X = \text{N, P, As, Sb and Bi}$ ) compounds have been studied for the first time focusing on the whole series of the compounds using first principles technique of density functional theory (DFT). Impact of changing the anions from N to Bi is observed and compared with the available literature.

## 2. Computational details

Our calculations have been performed using the all electron full-potential linearized augmented plane wave (FP-LAPW) [18] applied in Wien2k code [19]. For account of exchange-correlation effects the results presented below were obtained using Tran-Blaha modified Becke-Johnson (TB-mBJ) [20] and Perdew–Burke–Ernzerhof (PBE) [21] <http://pubs.rsc.org/-/content/articlehtml/2017/cp/c7cp02513k-cit31>. The atomic positions were relaxed until the energy and the force converged to  $10^{-4} \text{ eV}$  and  $10^{-3} \text{ eV}/\text{\AA}$ , in that order. The numerical integration of Brillouin zone was performed using a  $10 \times 10 \times 10$  Monkhorst–Pack k-point sampling procedure for these compounds. The converged PBE wave functions were used as the starting points for the TB-mBJ calculations.

## 3. Results and discussion

### 3.1. Structural properties

$\text{CaMg}_2\text{X}_2$  has a trigonal structure with symmetry:  $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$  and space group  $P\bar{3}m1$  #164. The Ca usually occupy Wyckoff position 1b, while Mg and X (N, P, As, Sb and Bi) both occupy 2d position. The structural behavior of the compounds is determined by calculating its structural parameters. By volume optimization of the unit cell of  $\text{CaMg}_2\text{X}_2$ , the lattice parameters  $a(\text{\AA})$ ,  $c(\text{\AA})$ ,  $c/a$  ratio, pressure derivative ( $B'$ ), the bulk modulus  $B$  (GPa), volume and energy ( $V_0, E_0$ ) are obtained. Optimized structure is shown in Fig. 1, whereas optimization curve is shown in Fig. 2. The ground state energy of the unit cell is the lowest energy, and the volume related to this optimum energy is ground state volume. There is increase in  $a(\text{\AA})$  as we replace the anion from N to Bi which is clearly observed in the Table 1. It is due to the

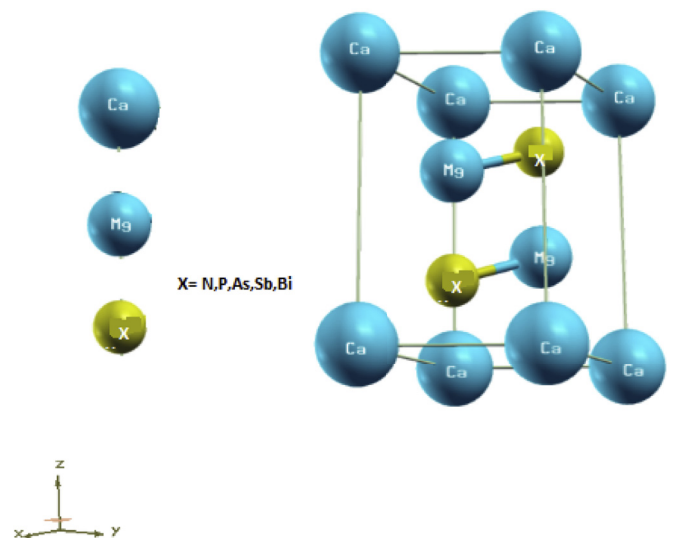


Fig. 1. Optimize structure of  $\text{CaMg}_2\text{X}_2$  compounds.

increase in atomic size of the anions when we move down in a group from N to Bi. The bulk modulus is a determination of crystal rigidity, thus larger values is for higher rigidity. The observed result suggest that  $\text{CaMg}_2\text{N}_2$  is harder than the rest of compounds in the group. As we move from N to Bi there is increase in unit cell volume, therefore  $B$  (GPa) decreased, which explain increase in a material compressibility, as we move from N to Bi. So, the calculated values are in good agreement with the other experimental and theoretical published work [1,3,4,12,14,17] for all the compounds except P based compound which was predicted for the first time so this data could be used for further experimental investigations of this compound.

### 3.2. Electronic properties

Band structure of  $\text{CaMg}_2\text{X}_2$  compounds are shown in Fig. 3. Our calculated bandgap values are in good agreement with the available recent experimental and theoretical published works [1,13–17]. The conduction band minimum (CBM) of  $\text{CaMg}_2\text{X}_2$  lies at the  $\Gamma$  point in both types while valence band maximum (VBM) lies at the  $\Gamma$ -point for direct band gap type and at M point for indirect band gap type. As may be seen from Table 2, alkaline earth element has much weaker dependence, and there is an obvious trend with the pnictogen elements. A clear regularity

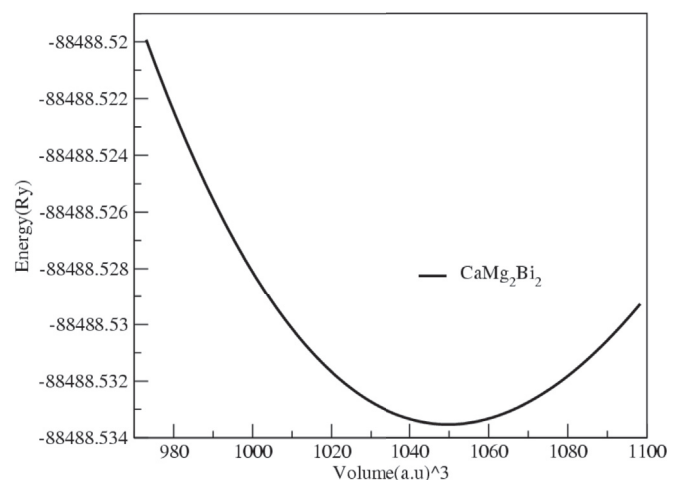


Fig. 2. The calculated total binding energy versus cell volume of  $\text{CaMg}_2\text{Bi}_2$  and the prototype for  $\text{CaMg}_2\text{X}_2$  compound.

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