Journal of Solid State Chemistry 258 (2018) 358–375

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Modification of band gaps and optoelectronic properties of binary calcium chalcogenides by means of doping of magnesium atom(s) in rock-salt phase- a first principle based theoretical initiative

Bimal Debnath[a], Utpal Sarkar[a,b], Manish Debbarma[a], Rahul Bhattacharjee[a,c], Surya Chattopadhyaya[a,*]

[a] Department of Physics, Tripura University, Suryamaninagar 799022, Tripura, India
[b] Department of Physics, Government Degree College, Kamalpur 799285, Tripura, India
[c] Department of Physics, Women's College, Agartala 799001, Tripura, India

ARTICLE INFO

Keywords:
Ternary alloys
FP-LAPW
TB-mBJ
Electronic properties
Optical properties

ABSTRACT

The band gaps and optoelectronic properties of binary calcium chalcogenide semiconductors have been modified theoretically by doping magnesium atom(s) into their respective rock-salt unit cells at some specific concentrations $x = 0.0$, 0.25, 0.50, 0.75 and 1.0 and confirmed such modifications by studying their structural, electronic and optical properties using DFT based FP-LAPW approach. The WC-GGA functional is used to calculate structural properties, while mBJ, B3LYP and WC-GGA are used for calculating electronic and optical properties. The concentration dependences of lattice parameter, bulk modulus and fundamental band gap for each alloy system exhibit nonlinearity. The atomic and orbital origin of different electronic states in the band structure of each compound are explored from its density of states (DOS). The microscopic origin of band gap bowing for each of the alloy systems is explored in terms of volume deformation, charge exchange and structural relaxation. The chemical bonds between the constituent atoms in each compound are found as ionic in nature. Optical properties of each specimen are calculated from its computed spectra of dielectric function, refractive index, extinction coefficient, normal incidence reflectivity, optical conductivity, optical absorption and energy loss function. Several calculated results have been compared with available experimental and other theoretical data.

1. Introduction

The structural, electronic and various other physical properties of group II–VI alkali-earth calcium chalcogenides CaY and magnesium chalcogenides MgY (Y = S, Se and Te) have been the subject of a number of experimental as well as theoretical studies during last several decades. They form a very important closed-shell ionic system [1]. The calcium chalcogenides CaS, CaSe and CaTe crystallized in rock-salt (B1) structure under ambient conditions [2]. Several experimental research groups have reported that the calcium chalcogenides exhibit structural phase transition from sixfold-coordinated NaCl-type structure (B1) to the eightfold-coordinated CsCl-type structure (B2) and phenomenon of metallization under the application of high pressures [3–5]. Members of the calcium chalcogenide family are wide-indirect-band-gap semiconductors [6]. They are technologically important materials having wide applications in the areas of microelectronics and optoelectronics and are widely used as thermo-luminescent, photo-luminescent, phosphorescent and other optoelectronic materials [7,8]. They are technologically important phosphor materials with potential applications in the area of catalysis, thermo-luminescent devices, electroluminescence panels, cathode ray tubes, radiation dosimetry, fast-high-resolution optically stimulated luminescence imaging devices, infrared sensors etc. [1,2,5,7–11]. They are also used as host material for various applications ranging from photo and electro-luminescent thin films to magneto-optical devices, particularly in purple-blue emitting thin-film electro-luminescent (TFEL) device with high luminance, that are operating at high power level and at high temperatures [2,11,12].

In addition to these experimental studies related to their properties and applications, several other experimental studies have also been performed to explore various properties of CaS, CaSe and CaTe [13–22]. Moreover, several research groups have theoretically studied different aspect of diatomic CaS, CaSe and CaTe [23–58] using different DFT-based methodologies as well as considering variety of

---

[*] Corresponding author.
E-mail address: surya_ju@yahoo.com (S. Chattopadhyaya).

https://doi.org/10.1016/j.jssc.2017.10.028
Received 25 July 2017; Received in revised form 1 October 2017; Accepted 22 October 2017
0022-4596/ © 2017 Elsevier Inc. All rights reserved.

exchange-correlation potential schemes. The studies include calculations of structural, elastic, mechanical, vibrational, electronic, thermodynamic, linear and nonlinear optical properties as well as nature of chemical bonding, high-pressure structural (B1→B2) phase transition, metallization transition, structural stabilities under high pressure etc.

In case of the members of magnesium chalcogenide family, it is experimentally observed that the binary MgS and MgSe crystallized in rock-salt (B1) structure [59,60]. On the other hand, MgTe crystallized in wurtzite (B4) phase [61–65] and exhibits a structural phase transition to nickel-arsenide (B8) phase under the application of high pressure [66]. On the other hand, several theoretical studies [67–70] have also been performed to investigate different properties of MgS, MgSe and MgTe considering different structures as their stable crystallographic phases. The studies were performed considering zinc-blende (B3) and rock-salt (B1) phases for both MgS and MgSe [67,68], nickel arsenide (B8) structure for MgTe [68], B1 structure for all the MgS, MgSe and MgTe [69] and B1, B3, B4, and B8 phases for each of the MgS, MgSe, and MgTe [70] as stable structures.

They are also wide-indirect-band-gap semiconductors in their rock-salt phase and they are technologically important materials having potential applications in optoelectronic and luminescent devices [9,13,71–77]. In addition to these experimental and theoretical studies on magnesium chalcogenides related to their structures, properties and applications, several other studies on their different physical properties have been performed experimentally [13,78–80] as well as optical properties in their B1 phase theoretically [24].

Formation of alloys by combining two or more different compounds having different structural, electronic and optical properties in their commensurate crystallographic phases is one of the efficient and easiest procedures in material science for fabrication of new materials having intermediate or completely different physical properties. Several studies to explore various physical properties of doped ternary alloys of CaS, CaSe and CaTe at different concentrations have been performed experimentally [81,82] as well as theoretically [83–91] so far. Also, several such studies on doped ternary alloys of MgS, MgSe and MgTe at different concentrations have been performed experimentally [92–96] as well as theoretically either considering their B1 [97–99] or B3 [100–106] phase. Therefore, alloying of these two types of respective chalcogenide compounds, performed by doping of magnesium atom(s) into the unit cells of CaS, CaSe and CaTe at different concentrations in B1 phase, would be an effective approach of preparation of a series of new ternary alloys having optoelectronic properties intermediate or completely different from their parent binary compounds. From extensive literature survey, we cannot find any experimental or theoretical study that had explored the structural, electronic and any other physical properties of rock-salt/zinc-blende Mg-doped calcium chalcogenide ternary alloys i.e. $Mg_xCa_{1-x}S$, $Mg_xCa_{1-x}Se$ and $Mg_xCa_{1-x}Te$.

In this article, we have taken a theoretical initiative to modify the optoelectronic properties of binary calcium chalcogenides by means of doping of Mg atom(s) into their unit cells in B1 phase. For this purpose, we have designed the unit cells of rock-salt binary compounds and ternary alloys under $Mg_xCa_{1-x}S$, $Mg_xCa_{1-x}Se$ and $Mg_xCa_{1-x}Te$ systems at some specific dopant concentrations x = 0.0, 0.25, 0.5, 0.75 and 1.0 and investigated the structural, electronic and optical properties using DFT based FP-LAPW approach. Though, such kind of studies have been performed theoretically with such wide range of dopant concentrations, it is not yet possible experimentally as the surface driving force becomes so strong at some of the concentrations that the impurities can no longer be incorporated into the crystal. Therefore, a few selected dopant concentrations are experimentally possible in semiconductors and it depends on the growth rate and the diffusion coefficient of the crystal [107]. Our theoretically reported various properties of these newly designed alloys may exhibit some useful and interesting properties, which would encourage the experimentalists to perform new experiments to observe. Moreover, they may also be helpful to researchers as well as designers to propose and fabricate special kind of new microelectronic and optoelectronic devices for their different potential applications.

2. Computational details

In the present study, the structural, electronic and optical properties of the aforesaid binary compounds and their ternary alloys have been computed using the DFT [108,109] based FP-LAPW methodology [110], as implemented in the WIEN2K code [111,112]. The exchange-correlation potentials for structural properties are calculated considering the Wu-Cohen generalized gradient approximation (WC-GGA) [113] scheme. It is well established that Tran-Blaha modified Becke-Johnson (TB-mBJ) [114,115] orbital-independent and semi-local exchange-correlation potential scheme is capable to provide almost accurate electronic properties, maximum possible energy band gaps as well as correct band-dispersions compared to LDA and different versions of GGA schemes in case of semiconductors and insulators. Since our specimens are semiconductor in nature, we have computed the electronic properties of the aforesaid binary compounds and their ternary alloys using TB-mBJ scheme. Since the optical properties of a solid are directly related to its electronic properties, we have also used the TB-mBJ scheme for precise calculation of optical properties of the aforesaid binary compounds and their ternary alloys in the present study. In addition, we have computed their electronic and optical properties using to WC-GGA scheme [113] and a hybrid functional B3LYP [116–118] for comparison. A short description of the FP-LAPW methodology is given in Section-I of the Supplementary materials.

In the present computations, the maximum value of angular momentum for the wave function expansion inside the atomic spheres is restricted to $l_{max} = 10$. The wave function in the interstitial region are expanded in plane wave basis with a cut-off value $K_{max} = 8.0/R_{MT}$, where R_{MT} denotes the smallest muffin-tin radius and the K_{max} is the magnitude of the largest K-vector in the plane wave expansion. The potential and charge density Fourier expansion parameter G_{max} is taken as 16 $Ry^{1/2}$. The R_{MT} values are chosen in such a way to ensure non-overlapping atomic spheres and the total energy convergence. The R_{MT} values of Mg, Ca, S, Se and Te are taken as 2.3, 2.5, 2.2, 2.4 and 2.5 a.u., respectively. A mesh of 47 special k-points for the binary compounds and 125 k-points for the ternary alloys are used for the integration over the irreducible Brillouin zone (IBZ). Both the plane wave cutoff and the number of k-points are varied to ensure the convergence. The self-consistent field (SCF) calculations are repeated until the total energy convergence is less than 10^{-5} Ry.

It is necessary to design the unit cells of binary compounds and ternary alloys under each of the $Mg_xCa_{1-x}S$, $Mg_xCa_{1-x}Se$ and $Mg_xCa_{1-x}Te$ systems in order to initiate calculations of their different properties. The brief procedure of designing such unit cells are presented in Section-II of the Supplementary materials. In the present study, visualization of structures and some calculations have been performed using the graphic code XCrySDen [119].

3. Results and discussions

3.1. Structural properties

The calculations of structural properties of the rock-salt binary compounds and their ternary alloys under each of the $Mg_xCa_{1-x}S$, $Mg_xCa_{1-x}Se$ and $Mg_xCa_{1-x}Te$ systems at some selected compositions x = 0.0, 0.25, 0.50, 0.75 and 1.0 have been performed using the volume optimization process. The structural optimization of each of the designed unit cells of binary compounds and their ternary alloys have been performed by calculating the total energy for different volumes around the equilibrium unit cell volume (V_0). The optimized crystal structures of $Mg_xCa_{1-x}S$ alloys for x= 0.0, 0.25, 0.50, 0.75 and 1.0 are presented as Fig. S1(a–e), respectively, as prototype in the

Download English Version:

https://daneshyari.com/en/article/7757901

Download Persian Version:

https://daneshyari.com/article/7757901

Daneshyari.com