Computational Condensed Matter xxx (2017) 1–8

Contents lists available at ScienceDirect

Computational Condensed Matter

journal homepage: http://ees.elsevier.com/cocom/default.asp

First principles study of electronic, phonon and elastic properties of rock-salt-phase MTe (M = Mg, Ca, Sr, Ba)

Yanrong Ren

School of Biological and Chemical Engineering, Chongqing University of Education, Chongqing, 400067, PR China

ARTICLE INFO

Article history:
Received 13 March 2017
Received in revised form
23 May 2017
Accepted 23 May 2017
Available online xxx

Keywords:
Electronic band
Phonon
Elastic properties
Rock-salt-phase
ELF

ABSTRACT

There has been recent concerted effort in searching for clean and effective energy conversion materials. Herein we report on a new series of MTe (M = Mg, Ca, Sr, Ba) compounds with NaCl-like crystal structures that may be potential thermoelectric material and photocatalytically produce H_2 materials. Our density-functional theory results for the equilibrium structural parameters are consistent with experimental values and other theoretical data. Electronic calculations show that MTe (M = Mg, Ca, Sr, Ba) possess characteristic multi-valley band structures. The band gap of MgTe is much smaller than those of MTe (M = Ca, Sr, Ba). Phonon calculations indicate that MTe (M = Mg, Ca, Sr, Ba) are ionic crystals and dynamically stable. The theoretical lattice thermal conductivity values are also evaluated based on phonon dispersion without using any empirical parameters. Mechanical analysis shows that MTe (M = Mg, Ca, Sr, Ba) have small bulk moduli and Young's moduli.

1. Introduction

There has been recent and significantly growing interest in energy conversion materials, such as thermoelectric and photocatalytic materials [1–3]. Research in these areas has led to the discovery of a variety of important chalcogen compounds. Materials with a suitable band gap (>1.8 eV) can be appropriate candidate photocatalytic materials [4]. In particular, In_2S_3 and $ZnIn_2S_4$ provide efficient photocatalytic degradation of dye under ultraviolet light irradiation [5]. Ba_2ZnSe_3 and Ag_2S show high performance photocatalytic activity under irradiation with visible light [6,7]. Compared with wide band-gap photocatalytic materials, narrow band gap and binary compounds, such as SnSe, PbTe, In_4Se_3, and La_3Te_4, give excellent thermoelectric transport performance [8–11]. However, finding materials with higher energy conversion efficiencies still remains desirable.

The isostructural binary tellurides MTe (M = Mg, Ca, Sr, Ba) were studied based on their structural transitions. MgTe is known to exist in four crystalline phases: rock salt, zincblende, wurtzite, and nickel arsenide [12]. Theoretical calculations indicate that the NiAs-type is the ground-state phase and the rock-salt phase has the highest energy. In comparison, CaTe, SrTe, and BaTe are known to transition from a rock-salt structure to a CsCl-like structure [13–15]. The pressure induced in the structure transformation for CaTe, SrTe, and BaTe are 350 kbar, 120 kbar, and 40 kbar, respectively. In addition to the work carried out on the structure, we also note that the electronic band structures of MTe (M = Mg, Ca, Sr, Ba) in the rock-salt phase have been investigated [16]. However, the electronic, dynamical and mechanical properties are poorly understood in the literature. This is far from ideal when one considers that a large number of physical properties of solids depend on their phonon and electronic properties, such as specific heat, thermal conduction, and fermi surface, to name a few.

In this work we used the projector augmented wave (PAW) method with a generalized gradient approximation (GGA) to systematically study the electronic band structures, phonon dispersion, and mechanical properties of rock-salt-phase MTe (M = Mg, Ca, Sr, Ba). Further, the elastic and theoretical thermal conductivities are also evaluated. The aim of this work is to provide a prediction of potential new photocatalytic and thermoelectric materials of rock-salt-phase MTe (M = Mg, Ca, Sr, Ba) based on the results of density functional theory (DFT) calculations.

2. Computational methods

The initial crystal structures of MTe (M = Mg, Ca, Sr and Ba) were optimized using the Vienna ab initio simulation package (VASP) using DFT [17,18]. The Perdew Burke Ernzerhof (PBE) GGA [19] and PAW potentials of Blöchl, as implemented by Kresse and Joubert,

---

E-mail address: cqueryr@126.com.

http://dx.doi.org/10.1016/j.cocom.2017.05.004

Please cite this article in press as: Y. Ren, First principles study of electronic, phonon and elastic properties of rock-salt-phase MTe (M = Mg, Ca, Sr, Ba), Computational Condensed Matter (2017), http://dx.doi.org/10.1016/j.cocom.2017.05.004

were used [20,21]. Plane waves were included up to the kinetic energy cutoff of 800 eV. For the Brillouin zone integration, an 11 × 11 × 11 Monkhorst-Pack special k-point grid was applied [22]. The stopping criterion for any electronic self-consistent interactions was convergence of the total energy to within 10^{-6} eV. The calculations were performed by allowing both atomic positions and lattice parameters to find the most stable lattice configuration. The lattice structure is considered to be at equilibrium when the Hellmann-Feynman force on each ion is less than 0.001 eVÅ^{-1}. The band energies, E_k, were computed on a discrete k mesh along the high-symmetry directions, i.e., from the Brillouin zone center with coordinates W (0.5, 0.25, 0.75) to the L point (0.5, 0.5, 0.5), G point (0.0, 0.0, 0.0), X point (0.5, 0.0, 0.5), W point (0.5, 0.25, 0.75), and K point (0.375, 0.375, 0.375) in units of 2π/a, 2π/b, and 2π/c.

The lattice dynamics of MTe (M = Mg, Ca, Sr and Ba) were investigated using the frozen phonon method implemented in the Phonopy package [23]. Interactions between ions and electrons were described by the all-electron PAW method, with plane waves up to a cutoff energy of 600 eV. Supercells of dimensions 2 × 2 × 2 were used for MTe (M = Mg, Ca, Sr and Ba). High-symmetry points in the Brillouin zone [A(1/2, 0, 0), G(0, 0, 0), B(0, 1/2, 0), D(1/2,1/2,0), G(0, 0, 0), C(0, 0, 1/2)] were considered in our phonon dispersion and Grüneisen parameter calculations. The lattice thermal conductivities were calculated based on the Debye-Callaway formalism [24–26].

Elastic constants were calculated using the CASTEP (Cambridge Serial Total Energy Package) and VASP simulation programs [27]. The bulk modulus, B, and shear modulus, G, were obtained from the calculated elastic constants, C_{ij}. The Young's modulus, Y, and Poisson's ratio were also obtained.

3. Results and discussion

3.1. Crystal structure of rock-salt-phase compounds MTe (M = Mg, Ca, Sr and Ba)

MTe (M = Mg, Ca, Sr and Ba) contain a rock-salt phase (NaCl-type) with four formula units in one unit cell (space group Fm-3m) [12] (Fig. 1). They contain four alkaline earth atoms and four Te atoms, where the alkaline earth and Te atoms occupy the Wyckoff sites 4b (1/2, 1/2, 1/2) and 4a (0, 0, 0), respectively. Except for MgTe, the initial models used for optimization employed single-crystal diffraction data housed in the ICSD. The rock-salt phase of MgTe has not previously been reported, and, therefore, experimental data for this crystal structure could not be used to formulate a model for this work. Previous calculations have indicated that MgTe possesses four different phases: rock salt, zincblende, wurtzite (WZ), and NiAs-type. The NiAs-type is the ground-state phase. Here, for the calculation of MgTe, we employ the CaTe structure as the initial model and substitute Mg atoms for the Ca atoms.

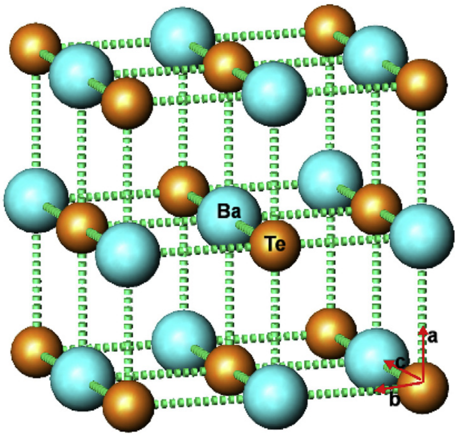

Fig. 1. The crystal structure of rock-salt-phase compounds MTe (M = Mg, Ca, Sr and Ba).

Table 1 shows the equilibrium lattice parameters of rock-salt-phase compounds MTe (M = Mg, Ca, Sr and Ba). Our results are in good agreement with experiment and other theoretical values. The optimized structural parameters are slightly larger than those of previous reports, which is likely caused by the GGA functional adopted in the present work. The relative errors in lattice parameters and unit cell volumes are small, which indicate that our results may be considered reasonable.

3.2. Electronic structure of rock-salt-phase compounds MTe (M = Mg, Ca, Sr and Ba)

The electronic band structures of MTe (M = Mg, Ca, Sr and Ba), calculated within the GGA functional, are presented in Figs. 2 and 3. The overall band profiles are found to be similar for each of the four compounds and are in agreement with those obtained by previous work. MTe (M = Mg, Ca, Sr and Ba) show indirect semiconductor behavior, where the top valence band is located at the G point and the lowest conduction band is located at the X point. Specifically, three valence orbital bands (two heavy bands and one light band) are degenerate at the G point and there is valence orbital degeneracy at the X or L points. The shape of this valence band is similar to that of n-type PbTe thermoelectric materials. The characteristic band dispersion is beneficial for optimizing the thermoelectric performance via band engineering. The calculated values of the band gap are given in Table 2 along with the experimental and theoretical values obtained previously.

The theoretical band gaps of MTe (M = Mg, Ca, Sr and Ba) are 0.35, 1.5, 1.6, and 1.6 eV, respectively. In general, our band gap results are in agreement with data available from previous works. The band gap of MgTe is smaller than that of the other compounds studied, and this might be caused by the smaller electronegativity difference between Mg and Te atoms. Compared with the band gaps obtained by experiment, the respective theoretical values are approximately 50% smaller. This is mainly due to the errors introduced by the GGA functional that underestimates the band gap. It is expected that a hybrid functional and quasiparticle calculation would bring the band gap values into closer agreement with the experimental results. The plots of total density of states (TDOS) and partial density of states (PDOS) for rock-salt-phase compounds MTe (M = Mg, Ca, Sr and Ba) are displayed in Fig. 3. The PDOS show that the M p-orbital and Te p-orbital hybrid dominate the valence band near the Fermi level. However, the conduction bands are

Table 1
Optimized cell constants of rock-salt-phase compounds MTe (M = Mg, Ca, Sr and Ba), and comparison to experimental and calculated values from previous works.

Specie	Space Group		*a*(Å)	*V*(Å^3)
MgTe	Fm-3m	Present	5.971	212.885
		Theory [12]	5.900	205.379
		error	1.2%	3.7%
CaTe	Fm-3m	Present	6.393	261.297
		Experiment [13]	6.345	255.444
		error	0.7%	2.3%
SrTe	Fm-3m	Present	6.725	304.197
		Experiment [13]	6.659	295.275
		error	1.0%	3.0%
BaTe	Fm-3m	Present	7.090	356.386
		Experiment [14]	7.005	343.736
		error	1.2%	3.7%

Please cite this article in press as: Y. Ren, First principles study of electronic, phonon and elastic properties of rock-salt-phase MTe (M = Mg, Ca, Sr, Ba), Computational Condensed Matter (2017), http://dx.doi.org/10.1016/j.cocom.2017.05.004