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Lattice dynamics and thermodynamical study of yttrium monochalcogenides

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ABSTRACT

In this work we have investigated the structural, mechanical, electronic, phonon and thermodynamical properties of yttrium monochalcogenides (YX: X = S, Se and Te) in the rocksalt phase using state-of-the-art first principles density functional theory. The calculated results of optimized lattice parameters, elastic constants, and bulk modulus agree well with the available experimental and other theoretical values. The electronic band structure of the yttrium monochalcogenides reveals the metallic character of these compounds. The shear modulus, Young's modulus, Poisson's ratio and Lame's constants are calculated and discussed in detail. The calculated mechanical properties indicate that the considered yttrium monochalcogenides are brittle in nature. The Debye temperature of yttrium compounds is also calculated. The first time reported phonon dispersion curves and phonon density of states for YS, YSe and YTe calculated using *ab initio* first principles calculations shows that the B1 phase of YS, YSe and YTe is lattice dynamically stable at ambient conditions. The temperature dependence of thermodynamical properties on temperature is also calculated by using the quasi harmonic approximation and discussed. The variation of constant volume lattice-specific heat with temperature obeys the classical Dulong–Petit's law at high temperature, while at low-temperature it obeys the Debye's T^3 law.

1. Introduction

In the last few decades the studies on structural, mechanical, lattice dynamics and thermodynamical properties of rare earth (RE) compounds have received considerable attention of the condensed matter physicists, due to their complex electronic structure and unusual behavior of phonon modes [1–14]. Most of these compounds crystallize in the rocksalt (B1) structure at ambient condition and contain partially filled *f*-electron orbital. These *f*-electrons in the rare-earth ion are highly delocalized and interact strongly with the conduction band and *p* states of the neighboring anion.

The rock-salt structured yttrium monochalcogenides from the group of RE compounds are subject of current interest [14–25] particularly in the light of superconductivity with transition temperature around 2 K [17,18] in contrast to the 1 K [26] in the case of isovalent lanthanum monochalcogenides. Furthermore, these RE monochalcogenides have potential impact on important technological applications in yttrium based magnets due to higher resistance to demagnetization, and hence found in small motors, headphones, high-end magnetic pickups for guitars and related musical instruments. The phonon dispersion curves of yttrium sulfide (YS) show anomalous behavior such as softening of acoustic modes at L-point of the Brillouin zone [15,16,19,20], which has been correlated with the superconducting nature of YS due to the strong electron–phonon coupling at the rare-earth ion site arising from 4*f* to 5*d* hybridization [10,27–29]. A fundamental property related to the superconducting nature is the lattice dynamics, i.e. phonon spectrum and phonon modes of yttrium monochalcogenides. However, a systematic study on lattice dynamical properties for yttrium monochalcogenides is still lacking particularly using first principles *ab initio* calculations. In addition, a wide variety of physical properties of solids depend on their lattice-dynamical behavior, such as infrared, Raman, and neutron-diffraction spectra, specific heat, thermal expansion, heat conduction, resistivity of metals, superconductivity and the temperature dependence of optical spectra are just a few of them. As a matter of fact, their understanding in terms of phonons is considered to be one of the most convincing pieces of evidence for correctness of quantum picture of any solid. In recent past, Vaitheeswaran et al. [14] have

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performed the high pressure structural study on three yttrium monochalcogenides, YS, YSe and YTe using high pressure X-ray diffraction and first principles total energy calculations using the full potential linear muffin tin orbital (FP-LMTO) method and found that these compounds undergo a structural phase transition from NaCl (B1) to CsCl (B2) phase at 53, 36 and 14 GPa for YS, YSe and YTe, respectively in contrast to the experimental high pressure X-ray diffraction study where no signature of any phase transition was observed which might be due to the limited range of pressure up to which measurements were performed. However, their electronic band structure calculations show ionic and metallic nature in B1 and high pressure B2 phases, respectively. Seddik et al. [23] have performed the structural, elastic and high pressure properties of these monochalcogenides using full potential linearized augmented plane wave plus local orbitals method with the GGA approximation for the exchange correlation potential and predicted the B1–B2 type structural phase transition in YS, YSe and YTe, at pressures ~49, 28 and 11 GPa, respectively. However, both theoretical [14,23] and experimental results [14] predict the properties with noticeable difference. This embarks for a detailed theoretical study on these compounds. A second and important motive of the present study is to investigate the phonon properties of these compounds which can establish the connection between structural and phonon properties and yet to be reported.

In the present work we have performed a detailed theoretical study of structural, mechanical, electronic, lattice dynamical, and thermodynamical properties of yttrium monochalcogenides (YX; X = S, Se and Te) using first principles *ab initio* calculations. We have also estimated the Young's modulus, shear modulus, Poisson's ratio, anisotropy factor, sound velocities, Debye temperature and phonon properties of yttrium compounds. It is noteworthy that the phonon calculations for these compounds except YS [30–32] are reported for the first time. The rest of the paper is organized as follows. In Section 2, we present the detail description of the computational technique. The calculated lattice parameters, results from phonon dispersion curves, phonon density of states, band structures and thermodynamical properties are presented and discussed in Section 3. Finally, in Section 4, important conclusions are presented.

2. Method of computation

The electronic structure calculations of yttrium monochalcogenides in B1 phase were performed using plane wave method as implemented in ABINIT code [33], within the framework of density functional theory. The electron–ion interactions were described through the use of Troullier and Martins type pseudo-potentials [34]. The exchange correlation was treated within generalized gradient approximation (GGA). A set of convergence tests was performed in order to correctly choose the mesh of $\boldsymbol{k}$-points and the cut-off kinetic energy plane waves to start the ground state calculations. In order to find an appropriate energy cutoff, the total energy was calculated as a function of the energy cutoff. The total energy converged near the energy cutoffs of 60, 80 and 70 Ha for YS, YSe and YTe, respectively. The number of sampling $\boldsymbol{k}$-points used in the Brillouin zone (BZ) summation of the electronic density and total energy was increased till the total energy converged to the desirable tolerance. The Brillouin zone was sampled by $6 \times 6 \times 6$ Monkhorst–Pack mesh of $\boldsymbol{k}$-points [35]. Convergence tests prove that the (BZ) sampling and the kinetic energy cutoffs were sufficient to guarantee an excellent convergence. The crystal structure and associated equilibrium lattice constants for all YX compounds have been obtained by minimizing the total energies as a function of lattice constant. The phonon dispersion curves of yttrium monochalcogenides were calculated using the density functional perturbation theory (DFPT) [36,37]. The convergence of the total energy of around 0.0001 Ha, the phonon frequencies by 4 cm^{-1} and the transition pressure by about 1 GPa were ensured.

The phonon density of states is an important dynamical property which is not only required to determine many of the allied properties of any solid but it also describes the success of any phonon calculations as its computation needs frequencies in the entire Brillouin zone and defined as [38,39]:

$$g(\omega) = \frac{1}{N}\int_{BZ}\sum_{j}\delta\left[\omega - \bar{\omega}_j(\bar{q})d\bar{q}\right] \quad (1)$$

where N is normalization constant, $g(\omega)\,d\omega$ is the ratio of the number of eigen states in the frequency interval $(\omega, \omega + d\omega)$ to the total number of eigen states and $\omega_j(q)$ are the phonon modes. Using phonon density of states obtained from Eq. (1), the phonon contributions to the internal energy E, Helmholtz free energy H, the constant volume specific heat C_v, and entropy S at temperature T can be calculated.

3. Results and discussion

3.1. Structural properties

The structural optimization for minimum total energy condition has been performed to obtain the ground state properties of three yttrium monochalcogenides, YS, YSe and YTe. The calculated total energy for all three compounds is fitted to third-order Birch–Murnaghan equation of state. This yields the lattice constant (a_0), bulk modulus (B_0) and first order pressure derivative of bulk modulus (B_0') which are listed in Table 1 along with the available experimental [14,18,40–44] and other theoretical data [11,12,23,15–20]. The lattice constant for these compounds follows the relation: YS > YSe > YTe, similar to the relation which is followed in the case of their chalcogen ion's radius. The calculated ground state lattice constants for all the three yttrium monochalcogenides are in overall good agreement with available measured and theoretical values.

3.2. Mechanical properties

Elastic properties of the materials reflect the response of the inter-atomic forces between the atoms concerned to an applied stress and thus are responsible for many solid state and related thermodynamical phenomenon such as equation of states, phonon spectra, specific heat, and Debye temperature. The elastic constants are very crucial tools to determine the relation between the strain of the material and applied stress. Since YX compounds are cubic, there are only three independent elastic constants, namely C_{11}, C_{12} and C_{44} for these compounds. The calculated value of elastic constants (C_{ij}) obtained using optimized parameters are listed in Table 2. One can observe that the calculated values of elastic constants increases as one moves from Te to S which supports the previous reports [14,23]. It is also noticed that the C_{11} is higher than C_{12} with C_{44} being the lowest for all the three compounds. This indicates that the velocity of a longitudinal wave in the [1 0 0] direction is much larger than the shear wave. Our calculated C_{11} and C_{12} are slightly higher and lower side, respectively than the available experimental and theoretical data [14,23]. The elastic constant C_{44} for YS is lower than the available data [14,23]. However, the present values are closer to the theoretical data of Ref. [14]. The present value of elastic constant C_{12} is closer to the experimental value for YSe and YTe while it is slightly higher for YS. We cannot make any comment as both available theoretical data show quite diversity. However, it is important to note that the present calculations predict $C_{12} - C_{44}$ positive in contrast to earlier