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Systematic study of the elastic, optoelectronic, and thermoelectric behavior of MRh_2O_4 (M = Zn, Cd) based on first principles calculations

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ABSTRACT

In the present study, we performed first principles total energy calculations to explore the electronic, elastic, optical, and thermoelectric behavior of MRh_2O_4(M = Zn, Cd) spinel oxides. We employed Perdew–Burke–Ernzerhof-sol as well as the modified Becke and Johnson potential to compute the elastic, optoelectronic, and thermoelectric behavior of MRh_2O_4(M = Zn, Cd). The optical behavior was investigated by calculating the complex dielectric constant, refractive index, optical reflectivity, absorption coefficient, and optical conductivity. All of the optical parameters indicated a shift to lower energies as the atomic size increased from Zn to Cd, thereby suggesting potential applications of the spinel oxides in optoelectronic device. Moreover, the thermoelectric properties of MRh_2O_4(M = Zn, Cd) spinel oxides were computed in terms of the electrical conductivity (σ), Seebeck coefficient (S), thermal conductivity (k), and power factor (σS^2) using the BoltzTraP code.

1. Introduction

MRh_2O_4 (M = Zn, Cd) oxides are wide band gap semiconductors, which makes them transparent materials and they have applications in various devices. MRh_2O_4 (M = Zn, Cd) oxides are utilized as transparent conducting oxides (TCOs) in optoelectronic devices because they are transparent to the visible and infrared regions, and thus they have applications in flat panel displays and solar cells [1]. These TCOs can be utilized in various catalytic reactions due to their useful characteristics, such as high resistance to chemical alterations, high melting temperature, and high strength [2]. Therefore, they also have useful applications in processes involving cracking, dehydration, hydrogenation, and dehydrogenation [3]. In particular, $MgAl_2O_4$ is a well-known TCO material [4]. Determining the electronic and optical properties of materials is very important for exploring the suitability of TCOs for various applications, particularly TCO materials with better transparency and conductivity, where these characteristics can be quantified precisely using electronic structure computation methods in order to detect the novel or enhanced characteristic of these materials.

The electronic and optical properties of TCOs have been investigated in experimental [5–8] and theoretical [9–14] studies in recent years. MRh_2O_4 (M = Zn, Cd) are major TCO materials but there have been few investigations of their mechanical, optical, and thermoelectric properties. Both compounds ($ZnRh_2O_4$ and $CdRh_2O_4$) have a spinel structure with the Fd-3m space group [15]. The electronic structure of $ZnRh_2O_4$ was studied by Mizoguchi et al. [8] who showed that $ZnRh_2O_4$ is a normal spinel with a p-type wide band gap semiconductor ($E_g \sim 2.1$ eV). The presence of rhodium in the catalytic response is associated with the formation of rhodium oxides. Clarifying the mechanism of rhodium oxide formation is essential for understanding the catalytic process [16]. The solid-state chemistry of rhodium oxide is important for its attractive electronic and magnetic properties [17]. The spinel oxides of rhodium have a broader band gap than those in perovskites. Therefore, these oxides have possible applications in transparent oxide semiconductors [18], solar cells, and flat panel displays, including liquid crystal displays and organic light emitting diodes [19,20].

Many experimental investigations have also explored the band structures of these spinels. The electronic and optical properties of the

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$ZnRh_2O_4$ spinel structure were studied by Singh et al. [21] based on density functional theory (DFT) calculations, where the band gap was calculated as ~1.2 eV, which was determined according to the calculated optical conductivities. The band structure of $ZnRh_2O_4$ was studied by Mansourian-Hadavi et al. [22] using the local density approximation with strong Coulomb correlations (LDA + U) method [23,24], and they determined that a hole polaron state is formed. Nagaraja et al. [25] studied $ZnRh_2O_4$ using the generalized gradient approximation with strong Coulomb correlations (GGA + U) method, where they confirmed the exact Koopmans behavior of the functional, and observed that the hole polaron state is unstable [26].

In the present study, we investigated the electronic, mechanical, optical, and thermoelectric properties of MRh_2O_4 (M = Zn, Cd) compounds based on first principles calculations. The ground state electronic, mechanical, and optical properties were examined to assess their potential technological applications. The thermoelectric properties of these compounds were studied within the temperature range of 200–800 K. The main aim of this study was to improve the band gap calculated for MRh_2O_4 (M = Zn, Cd) by applying the modified Becke and Johnson (mBJ) potential [27] and to compute the realistic thermoelectric properties.

2. Calculation methods

The full-potential linearized augmented plane wave method [28] was used to perform the DFT calculations. The Perdew–Burke–Ernzerhof (PBE)-sol [29] potential was optimized to analyze the structural parameters. The GGA was treated as the exchange correlation functional by solving the Kohn–Sham equations. The GGA functional is well known for undervaluing the energy gaps in DFT calculations, so the electronic, optical, and thermoelectric properties of MRh_2O_4 (M = Zn, Cd) were computed using the mBJ local (spin) density approximation functional [27]. The plane wave cut-off in the interstitial area was investigated by setting $R_{MT} \times K_{max} = 8$ for the muffin-tin model of the crystal potential. The maximum value allowed for wave function expansion was 10 inside the atomic sphere. To execute the self-consistent calculations, the $10 \times 10 \times 10$ k-mesh was permitted to terminate when the change in the total energy between two successive cycles was below 10^{-4} Ry. The BoltzTrap code [30] was utilized to compute the thermoelectric properties where the normal Boltzmann kinetic transport theory and steady band approach were applied. This estimation was based on the smoothed Fourier interpolation to ensure the logical appearance of the bands. The relaxation time was allowed to be continual in the BoltzTrap code because it could not originate from the band structure [30].

3. Results and discussion

3.1. Structural and elastic behavior

We computed the equilibrium cubic lattice parameter (a_o) and bulk modulus (B_o) for MRh_2O_4 (M = Zn, Cd), where the plot of the total energy verses different lattice volumes fitted by the Murnaghan equation of state is shown in Fig. 1. The computed values shown in Table 1 demonstrate the excellent agreement between the experimental and theoretically calculated values. As expected, the value of the lattice constant increased when we replaced Zn with Cd, whereas the bulk modulus decreased, as shown in Table 1. This may be explained by the greater atomic radius of Cd (1.55 Å) compared with Zn (1.35 Å) making the structure less dense. Moreover, increasing the atomic size shifted the state closer to the Fermi level, which reduced the band gap for $CdRh_2O_4$ compared with that for $ZnRh_2O_4$. Due to the hybridization between the Rh *d*-states and O 2p-states [31], the ferroelectricity increased in MRh_2O_4. Thus, the compression of the states reduced the cubic lattice constant differences in terms of the magnitude of hybridization, thereby affecting the ferroelectricity.

Determining the elastic constants is very important for analyzing the

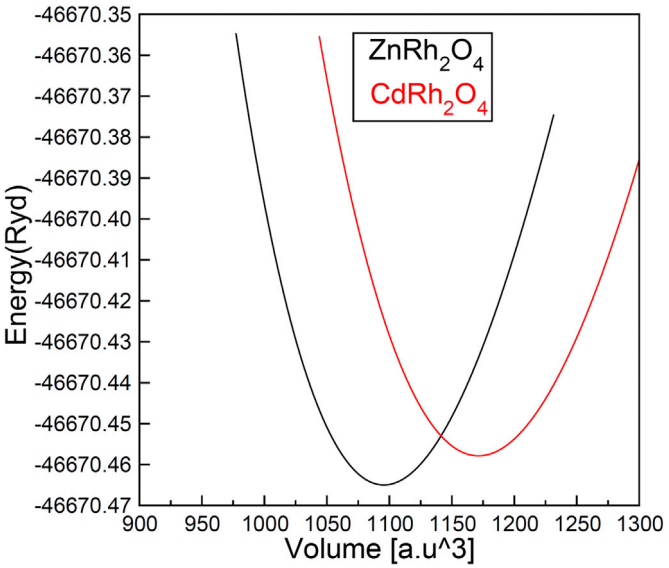

Fig. 1. Structural optimization in terms of total energy versus unit cell volume for $ZnRh_2O_4$ and $CdRh_2O_4$ by using PBEsol.

mechanical and dynamical properties of crystals. The elastic coefficients indicate how a material performs before and after stress is applied [32]. We performed ab-initio calculations to determine the elastic moduli C_{ij} with stress tensor mechanisms for insignificant strain. These constants are important for the understanding the properties of materials because they indicate their stiffness and stability. The technique used to estimate these coefficients was established by Charpin and executed using the Wien2k program [28], which has been employed in many previous studies [33]. It was necessary to compute three elastic parameters, C_{11}, C_{12}, and C_{44}, to assess their mechanical characteristics because the materials considered have cubic symmetry. Therefore, these coefficients were calculated using three equations. The generalized Hooke's law determines the associations between stresses (s) and strains (ε) to calculate the elastic moduli. The Born stability standards [34] describe the mechanical stability of cubic crystals. The bulk modulus was evaluated by energy minimization using the relation: $B = (1/3)(C_{11} + 2C_{12})$, and the almost equal values obtained are given in Table 1. The Voigt–Reuss–Hill [35,36] calculation of bulk and shear moduli showed that the compounds are mostly poly-crystalline. Thus, the moduli were obtained for cubic structures [37]. Furthermore, Young's modulus (E) and Poisson's ratio (ν) were calculated. The bulk modulus (B) and shear modulus (G) are associated with these values according to specific equations [38]. The elastic moduli calculated for MRh_2O_4 (M = Zn, Cd) are given in Table 1. Poisson's ratio was calculated among the elastic parameters to elucidate the forces in the materials. Poisson's ratio ν is in the range of 0.5 and 0.25 [39]. For MRh_2O_4, the value of ν was within the range of 0.25–0.5. Thus, the central inter-atom forces are fixed in these compounds. In addition, Poisson's ratio had a critical value of 0.26, which indicates whether a material is ductile or brittle. The computed ν values showed that all of the materials are ductile. Pugh's ratio (B/G) can be used to characterize the nature of a material where the critical value is 1.75. A compound is ductile when the value is above 1.75 and brittle when it is below this value. The B/G values obtained for $ZnRh_2O_4$ and $CdRh_2O_4$ were 2.608 and 2.362, respectively, as shown in Table 1, which indicates that they are ductile materials. The main characteristic of bond stretching or bending in cubic materials is designated by the Kleinman parameter (ζ). The values of bond bending and stretching are in the range of 0 and 1. We found that the prominent bond stretching terminated the bond bending for $ZnRh_2O_4$ and vice versa for $CdRh_2O_4$ [40]. The elastic anisotropy is important in engineering science because it provides insights into micro-cracks in materials [41]. We estimated the value of the anisotropy