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RESEARCH ARTICLE

A first principles study on structural, dynamical, and mechanical stability of newly predicted delafossite $HCoO_2$ at high pressure

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Abstract
Cobalt oxyhydroxide ($HCoO_2$), which belongs to the heterogenite mineral family, exists in two hexagonal polytypes (2H) and rhombohedral (3R). Here, we investigate the high pressure behaviour of both polytypes of $HCoO_2$ using state-of-the-art first principles calculations-based density functional theory. We have used both local density approximation (LDA) and generalised gradient approximation (GGA) for exchange correlation functional. For the calculation of electronic band structures, we have also used the on-site Coulomb interaction U term with LDA calculations and found improvement in results. The obtained ground state properties for both polytypes agree well with experimental and previous theoretical data. The electronic band structure shows that both phases are semiconductor with an indirect band gap in the ran\ge of 2.01–2.06 eV. The pressure-dependent phonon dispersion curves and elastic constants depict the instability of 2H and 3R phases around 35 and 40 GPa, respectively. The O-H distance gradually decreases for both phases with pressure and results into the less compressibility in z-direction. The theoretically calculated pressure-dependent Raman spectra of 2H-$HCoO_2$ show the peak broadening nature of E_{2g} mode with pressure whereas in the case of 3R-$HCoO_{2,}$ the A_{1g} mode disappears beyond 45 GPa pressure. This indicates the existence of phase transition beginning around this pressure, which is driven by the shear modulus. A detailed analysis of the mode compatibility in the case of 2H polytypes is also reported. The phonon mode evolution with pressure is also analysed.

KEYWORDS
delafossite, electronic properties, heterogenite, phonon, Raman spectra

1 | INTRODUCTION

In the past few decades, materials with delafossite-type structure have attracted a great deal of interest due to their potential applications in optoelectronic, electronic, dye sensitized solar cell, rechargeable battery electrodes, catalysis in hydrogen evolution, electrochemistry, and thermoelectricity.[1–9] Delafossites are p-type wide band gap layered structural materials, with general chemical configurations of ABO_2 and are characterised by the

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Comparative *ab initio* study of the structural, electronic, dynamical, and optical properties of group-I based $CuMO_2$ (M = H, Li, Na, K, Rb)

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ABSTRACT

Despite similar chemical compositions, the $CuMO_2$ (M = H, Li, Na, K, Rb) compounds show remarkably distinct structural, electronic, dynamical, and optical properties. Different alkali atoms have a significant influence on their electronic, dynamical, and optical behavior. By means of first principles based density functional theory calculations, we explore the universality of electronic characteristics, dynamical stability, and optical properties of these compounds. The electronic band structures, vibrational frequencies, and optical properties are deeply connected with the atomic radius of the alkali atoms. The electronic bandgap of $CuMO_2$ (M = H, Li, Na, K, Rb) lies within the range of 0.5–1.0 eV bringing them in the group of low bandgap p-type semiconductors. We found a significant increase in the bandgap and p–d hybridization as going from H to Rb. Partial density of states revealed strong metal–oxygen (Cu–O) overlap due to the strong p–d hybridization. The phonon dispersion curves obtained for these compounds confirm the dynamical stability as there is no imaginary frequency throughout the Brillouin zone. The static dielectric constants and refractive index fall within the range of 8.0–12.91 and 1.98–3.55, respectively, suggesting the usefulness of scrutinized compounds in non-linear optical devices. The optical properties depict that the alkali atoms based delafossites can serve as promising candidates for highly efficient optical devices within a broad range from visible to ultraviolet light of electromagnetic spectra.

I. INTRODUCTION

Optoelectronic devices that are useful in invisible electronics, functional windows, small circuits, and dye sensitized solar cells (DSSCs) are the basic building blocks of modern technology,[1,2] thanks to the highly efficient metal oxide semiconductors that make these technologies quite possible.[1,3] However, it is still challenging to develop highly efficient optoelectronic devices due to the lack of high conducting p-type semiconductors. Most of the semiconductors, such as In_2O_3, ZnO, SnO_2, and $CuWO_4$,[4–7] are n-type, despite being known that the highly efficient optoelectronic devices require both n- and p-type semiconductors to be used in junction devices.[8] However, the low electrical conductivity in p-type semiconductors limits the technology. In metal oxide semiconductors, the p-type conductivity mainly originates from the holes that are localized around oxygen atoms due to its strong electronegativity.[9] In these p-type semiconductors, the O-2p orbitals lie far below the valence orbitals of metallic atoms that lead to the formation of a deep acceptor level by the holes.[10] These holes require high energy to overcome a large barrier height to migrate within the crystal lattice, resulting in poor conductivity and low hole mobility. The localized holes also result in high hole effective mass reflecting the less dispersive valence band maximum (VBM).[11,12] To overcome these problems, Kawazoe *et al.*[8] introduced a “degree of covalency” in metal–oxygen bonding of $CuAlO_2$ delafossite. To induce the formation of an extended valence band structure, the valence band edge should be modified by mixing orbitals of appropriate counter cations that have energy-filled levels comparable to

Electronic Properties and Stability Criteria of Rhombohedral $HCoO_2$

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Abstract. In this work density functional theory within the frame work of local density and gernalized gradient approximation have carried out to investigate the structural, electronic, elastic, mechanical and phonon properties of cobalt oxy-hydroxide ($HCoO_2$). The Hubbard U corrections are included to correctly predict the essential properties of this compound. Optimized structural parameters and electronic band structure have very good agreement with available experimental and other theoretical data. The calculated phonon dispersion curves and elastic constants respectively reveal the dynamical and mechanical stability of this compound at normal conditions. Hubbard U parameter also used to calculate electronic band structure, which significantly improves the band structure of this compound.

INTRODUCTION

In the past few years materials with delafossite structures have attracted great interest due to their potential applications in optoelectronics, electronics oxy-hydroxide ($HCoO_2$), and suggested that the heterogenite minerals also belong to delafossite structures. and thin electric devices arising from their remarkable and varied properties such as tunable band gap, magnetic properties and high thermoelectric power[1]. Delafossites with a general formula ABO_2, where A is monovalent cations (Cu, Ag, Au, Pd, Pt) and B is trivalent cations (Al, Fe, Ge, In, Cr, Co) are layered structured materials with p-type semiconducting behaviour. These layered materials exist either in hexagonal (P63/mmc) or rhombohedral (R3m) structure based on the stacking sequence of anions[1-2]. Recently Burlet et al.[3] studied the heterogenite cobalt Furthermore, the $HCoO_2$ has shown considerable interests due to its unique physical and chemical properties such as catalysis for hydrogen evolution, electrochemistry, gas sensing and supercapacitor applications[4-6]. However, studies of cobalt oxides and its derived compounds mainly focused on its storage mechanism and capacitance applications[6], the first principles calculations of chen et al. reported the relative stabilities of crystalline cobalt oxides and hydroxides like CoO, $Co(OH)_2$, Co_3O_4, CoO(OH) and CoO_2 in electrochemical environment[7]. In the present work we investigated the structural electronic, elastic and phonon properties of 3R-$HCoO_2$ (R3m) using first principles calculations based density functional theory. The particularly aim of the present study is to investigate the electronic, mechanical and dynamical stabilities of rhombohedral $HCoO_2$ at normal conditions.

COMPUTATIONAL METHOD

All calculations in the present study were performed using first principles calculations based on density functional theory (DFT) with a plane wave pseudopotential method as implanted in Quantum espresso code[8]. We employed local density approximation (LDA) and generalized gradient approximation (GGA) using the scheme of

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Electronic and Optical Properties of Ferromagnetic $CuCrO_2$, $AgCrO_2$ and $AuCrO_2$

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Abstract. The structural, electronic, magnetic and optical properties of ferromagnetic states of $CuCrO_2$, $AgCrO_2$ and $AuCrO_2$ have been investigated by the state-of-the-art first principles calculations based on density functional theory. The optimized lattice parameters and electronic band gap agree well with the experimental and other theoretical data for $CuCrO_2$ and $AgCrO_2$. There is no reported data available for $AuCrO_2$. The spin polarized electronic density of states (DOS) with the majority and minority spin depicts a semiconducting nature of these compounds, with decreasing band gap going from Cu to Ag and Au. Spin polarized density of states shows the magnetic behavior of these compounds. The dielectric constants show significant anisotropy of these compounds in the component of polarization direction. The major peaks in dielectric constants reveal absorption of UV light of solar spectrum which confirms its applications in optical devices.

INTRODUCTION

In recent years the studies of delafossite type structures are not only limited for cu based oxides, the Ag and Au based oxides have started gaining much attention as well. The band gap of Ag and Au based compounds is lower than Cu based compounds which indicate its use as efficient photovoltaic devices [1, 2]. Furthermore, the new Ag and Au based delafossite compounds show good conductivity together with the transparency in contrast to the most studied $CuAlO_2$ and other p type delafossites. [3, 4]. Recent studies show that the $CuCrO_2$ is a p-type transparent conducting oxides (TCOs) with the conductivity in the range of 1-12 S cm^{-1} and transparency can be increased by increasing temperature [5, 6]. The multiferroic, geometrical frustrated $CuCrO_2$ type delafossite is an imported material in this family, due to its tunable electronic, optical and magnetic properties. The ferromagnetic materials are very useful in spintronic devices [7]. Besides, $AgCrO_2$ is an important magnetic material which shows unique properties in various fields. Cerqueira *et al.* [4] carried out a survey of new compounds configured (Cu, Ag, Au) MO_2 (M represents the transition metals) by merging calculations and global structure predictions and obtained 45 new stable phases out of which some are p-type transparent conductors. Further, Ag and Au based compounds are proved as a p-type semiconductor useful as TCOs. The $CuCrO_2$ and $AgCrO_2$ have shown simultaneously the magnetic and ferroelectric orders [8]. These systems also possess an outstanding tunability of the ferroelectric polarization by the magnetic field. Moreover, spin induced ferroelectricity reported in $AgCrO_2$ delafossites [9]. However, Au based delafossite is not yet reported. Therefore, it is important to study its hidden properties as well as it is a subject of interest to compare the properties of these three delafossites oxides. The aim of this study is to identify the desirable properties for which the delafossite is known i.e. the electronic, magnetic and optical properties.

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Computational Insights into the Electronic and Optical Properties of Newly Predicted Delafossite CuFO2

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Abstract. The structural, electronic, and optical properties of halogen based delafossite $CuFO_2$ has been investigated using first principles calculations based density functional theory (DFT). The crystal structure of $CuFO_2$ belongs to the orthorhombic crystal symmetry with $C222_1$ space group. The electronic band structure of $CuFO_2$ confirms its semiconducting nature with 0.9 eV indirect band gap. Partial densities of states (PDOS) reveal the significant mixing of Cu (3d) and O (2p) orbitals. The major peak of O (2p) near valence band maximum (VBM) confirms the de-localization of holes important for p-type conductivity. The imaginary dielectric constant and absorption coefficient suggest visible light absorption which is useful in photovoltaic applications.

INTRODUCTION

The energy crisis and environmental concerns have raised research towards the innovative technologies which can provide renewable energy sources. Being clean energy source the solar cells have the great potential to satisfy the present energy need [1]. The present photovoltaic (PV) devices depend on the conventional silicon based solar cells made of p/n junctions to effective thin film technologies [2]. Furthermore, the attention goes on dye-sensitized solar cells (DSSC) for the cost-effective alternative to solid-state photovoltaic solar cells. DSSCs still attract great attention due to their lightweight, transparency, flexibility and best performance at diffuse and low-intensity light, which make them suitable for portable and indoor applications [3]. However, the photo conversion efficiency (PCE) of DSSCs is very low. In order to overcome the efficiency drawback in DSSCs, tandem solar cells have been proposed [4,5]. The tandem solar cells are n-DSSCs coupled with p-type semiconductor sensitized with a dye for the absorption of larger portion of solar spectrum. Indeed, the actual application of tandem cells is however troubled for the limited efficiencies of the p-type DSSCs compared to their n-type counterparts [6].The Nickel Oxide (NiO) due to its low cost and easy manipulation is the best known material in p-type semiconductors. [7]. Unfortunately, NiO shows low electrical conductivity, low hole mobility and high valence band edge potential resulting in a too low photocathode open circuit potential (VOC) [8]. The development of new efficient p-DSSC as alternative to NiO is a basic need of photovoltaic industries.

Copper based delafossites with formula $CuMO_2$ (M = Al, Cr, Ga, Fe) [9] are the best alternative of NiO as p-type semiconductors. Nattestad et al. [10] reported that the $CuAlO_2$ has high VOC compared to NiO. In addition the valence band (VB) edge position of $CuAlO_2$ is found lower compared to NiO [11]. Several works show that the efficiency of these materials in p-DSSCs can be further improved by doping them with a divalent cation at the M site [12]. Another way to improve the efficiency of these materials is the manipulation of M^{III} cations with divalent or trivalent cations. To achieve high efficiency in delafossites, researchers are trying to predict the different compositions and different phases of delafossite oxides due to available essential wide range of band gap present in

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Predicting the stable rhodium based chalcopyrites with remarkable optical properties

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ABSTRACT

The ternary chalcopyrite compounds and related structures are well known for their noteworthy electronic and optical properties. The interaction between monovalent and trivalent atoms has a significant influence on their electronic as well as optical behavior. In the present work, a density functional theory based first-principles calculation is performed to investigate the structural, electronic, lattice dynamical, and optical properties of rhombohedral $CuRhX_2$ (X = S, Se, Te) compounds. The electronic band structure of these compounds depicts semiconducting nature with an indirect bandgap of 1.8, 1.17, and 0.75 eV for $CuRhS_2$, $CuRhSe_2$, and $CuRhTe_2$, respectively. There is a greater hole mobility and p-type conductivity in these compounds due to strong p-d hybridization. The phonon dispersion curves of these compounds confirm their dynamical stability as there is no imaginary frequency for any of the phonon modes in the entire Brillouin zone (BZ). Furthermore, we discuss mode compatibility at the zone center of the BZ and other high symmetry points of the BZ. The Raman spectra of $CuRhX_2$ demonstrate two Raman active modes, namely, the E_g and A_{1g}. The frequency of Raman active modes E_g and A_{1g} decreases due to the increase in Rh–X bond length. The static dielectric constants fall in the range of 8.7–10.4. The absorption coefficient of these compounds is in the range of 1.5–2.0 eV depending upon the ionic radii of chalcogen atoms. Thus, it can be deduced that these systems can be efficiently used in solar energy converters in the UV as well as in the visible region.

I. INTRODUCTION

In the past few decades, materials with delafossite structures have been widely explored in optoelectronic industries due to their wide range of electronic and optical properties.[1,2] Their remarkable optical transparency in the visible region has been extensively used in display screens, solar cells, smart windows, etc.[3–5] Additionally, their utilization as transparent conducting oxides (TCOs) can replace conventional n-type conducting materials in transparent optoelectronic applications. In this respect, the discovery of p-type conductivity in delafossite $CuAlO_2$ is of great importance as all technologically relevant transparent conducting oxides such as In_2O_3 and ZnO are n-type semiconductors.[6,7] However, the $CuAlO_2$ or other p-type TCOs suffer from poor conductivity and insufficient transparency for technological applications.[8,9] The major obstacle in identifying good p-type TCOs is the robust localization of holes at the valence band edge of most oxides. The 2p orbitals of the oxygen (O) in metal oxide semiconductors are the main channel of transportation of the localized holes at the valence band maxima (VBM).[10] This does not only imply the difficulties in hole doping but also results in large hole effective mass responsible for low hole mobility. In the search for obtaining materials with more delocalized holes, delafossites have been extensively explored in the past few years. Motivated by the great structure-property relationship in the delafossite family, Hosono[11] proposed some guidelines for obtaining a large bandgap as well as dispersive VBM in p-type TCOs. The closed *d* shell of *A* cations and the presence of p-d hybridization in ABO_2 metal oxides make them excellent optoelectronic materials. Following Hosono's[11] guidelines, the discovery of p-type conductivity in $CuAlO_2$ is initiated by the

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Full Length Article

Two-dimensional delafossite cobalt oxyhydroxide as a toxic gas sensor

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ABSTRACT

To the chain of development of 2D materials, recently synthesized ultrathin cobalt oxy-hydroxide (CoOOH) nano sheets gain potential interest due to its structural, electronic and other properties. We have studied the interaction mechanism of two toxic gases hydrogen peroxide (H_2O_2) and ammonia (NH_3) adsorbed over 2D CoOOH to understand the role of 2D CoOOH as a toxic gas sensor. We employ first principles based dispersion corrected density functional calculations to study the sensing behavior of 2D CoOOH towards H_2O_2 and NH_3 by calculating adsorption energy, electronic band structure, density of states (DOS) and work function. The electronic band structure, DOS and work function of 2D CoOOH are modulated after adsorption of H_2O_2 and NH_3 molecules. Adsorption of gas molecules confirms the sensing behavior of 2D CoOOH towards these molecules and depicts its use in a sensing device. The full phonon dispersion curves and phonon density of states reveal the dynamical stability of 2D CoOOH. The calculated adsorption energy of H_2O_2 and NH_3 molecules is −0.532 and −0.460 eV respectively which indicates the strong physisorption of these gases over 2D CoOOH. The ultrafast recovery time of 1239 and 1203 ns respectively were found for H_2O_2 and NH_3 on 2D CoOOH. The work function which is 6.29 eV found for 2D CoOOH, decreases to 5.63 eV for H_2O_2 as it follows the reduction process on 2D CoOOH, and increases to 6.44 eV for NH_3 molecules as it acts as oxidation gas on CoOOH. Our study reveals that the 2D CoOOH can be a better sensor for the H_2O_2 and NH_3 gases than some traditional two-dimensional materials.

1. Introduction

Two dimensional (2D) materials have become a dynamic area of research in nanotechnology due to their applications in next generation electronic and energy conversion devices [1–4]. The development of two-dimensional (2D) materials has further extended to several 2D materials like h-BN [5,6], transition metal dichalcogenides [7], silicene [8,9], germanene [8,10], etc, after the discovery of graphene [1,2]. The search of new 2D materials is a progressive approach to find properties like graphene in other materials. A new class of 2D materials such as phosphorene and phosphorene-like group-IV monochalcogenides are utilized as toxic gas sensors [11]. Materials like Ti_2CO_2, Sc_2CO_2 have been studied and found to be potential candidates for NH_3 and SO_2 gas sensing [12,13]. In the series of 2D materials, oxides from transition metals as earth abundant substitutes show the potential applications similar to graphene [14,15]. In particular, layered hydroxides/oxyhydroxides is a promising new class of 2D materials which is currently being experimentally investigated for their structural and electro catalytic activities [16]. Recent experimental study shows that the exfoliated single layer oxyhydroxide (MoOOH) sheets of Co, Fe and Ni, have high catalytic activities and electrochemical sensing [17,18]. Amongst these layered oxyhydroxide CoOOH is a multifunctional p-type semiconductor and has attracted much attention in the fields of catalysis [19], magnets, electrochemical devices, Li-ion batteries, supercapacitors, and gas sensors [20–22]. One of the unique applications of CoOOH nanostructures is a non-enzymatic sensor for biomolecule detection [23]. The enzymatic sensors possess high selectivity but have some limitations such as instability, complicated modification process and critical micro environmental factors. These limitations favor the development of non-enzymatic electrochemical sensors with simple modification procedures and good stability. Non-enzymatic sensors offer high sensitivity, long term stability, a resistance to thermal implications, a low cost, simple and reproducible fabrication method and a renewed approach to their design and development [24–26].

Lee et al. [27] have experimentally investigated the CoOOH nanosheet as a non-enzymatic sensor. Despite their studies on CoOOH, a systematic and atomic level theoretical description of the stability of 2D CoOOH and its adsorption mechanism is still awaited. Motivated with this fact we investigate this new 2D material to be used as a toxic gas sensor under the frame work of density functional theory.

The H_2O_2 is an important biochemical gas molecule with great significance in many areas like food manufacturing [28], chemical

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Peculiar Electronics and Optical Properties of OxychalcogenidesCuRhOX (X= S, Se, Te): A First Principles Investigation

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Abstract. We report the structural, electronics and optical properties of oxychalcogenide compounds CuRhOX (X= S, Se, Te) using state-of-the-art density functional theory (DFT). The structural geometry of these oxychalcogenides is same as the delafossite compounds. The electronic band structures reveal the semiconducting nature with an indirect band gap of 1.06, 0.90 and 0.69 eV for CuRhOS, CuRhOSe and CuRhOTe respectively. The partial density of states (PDOS) depicts the major contribution of O-2p and X-2p states near the valence band maximum (VBM). The dielectric constants and optical absorption spectra show the strong optical absorption in visible region indicating their potential applications in optoelectronics.

INTRODUCTION

Delafossite type materials have been recognized as a p-type semiconducting material with a special ability to be a conductor and transparent to visible light [1]. This unique combination of transparency and conductivity makes them suitable in optical and photovoltaic industries. In recent years the fabrication of highly efficient optoelectronic devices seems to be very difficult due to low electrical conductivity of p-type semiconductors as compared to n-type [2,3]. The low electrical conductivity in p-type delafossite oxides is attributed to the low carrier concentration and localization of the holes. To overcome these obstacles several approaches have been adopted by the researchers [4]. One of the effective approaches is the chemical modulation of the valence band. In this series, further investigations are devoted to the replacement of oxygen atoms by nitrogen and chalcogen (S, Se, Te) atoms [5,6]. These approaches are not sufficient to overcome the barrier of low electrical conductivity in p-type semiconductors. The mixed phase of delafossite compounds in which oxygen and chalcogenide atoms alternatively share the same position may be the effective approach to get the enhanced conductivity. This is the unexplored area in this field and a very few studies are reported for this type of compounds [7]. In the present work, we apply the same method for the new Rh based delafossite by replacing one oxygen atom by S, Se and Te atoms respectively. In the oxide based delafossite family the $CuRhO_2$ is a prominent compound and very useful in photovoltaic and catalytic activity [8]. Herein, we utilized the state-of-the-art density functional theory (DFT) calculations to study the structural, electronic, and optical properties of the CuRhOX (X= S, Se, Te) compounds. The absorption coefficient of CuRhOX compound reveals the strong optical absorption in visible region indicating its usefulness in photovoltaicapplications.

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Structural, Electronic and Dynamical Properties of Curium Monopnictides: Density Functional Calculations

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The structural, electronic, dynamical and thermodynamical properties of CmX (X = N, P, As, Sb, and Bi) compounds are studied using first principles calculations within density functional theory. The Perdew–Burke–Ernzerhof spin polarized generalized gradient approximation and Perdew–Wang (PW) spin polarized local density approximation as the exchange correlational functionals are used in these calculations. There is a good agreement between the present and previously reported data. The calculated electronic density of states suggests that the curium monopnictides are metallic in nature, which is consistent with earlier studies. The significant values of magnetic moment suggest their magnetic nature. The phonon dispersion curves and phonon density of states are also calculated, which depict the dynamical stability of these compounds. There is a significant separation between the optical and acoustical phonon branches. The temperature dependence of the thermodynamical functions are also calculated and discussed. Internal energy and vibrational contribution to the Helmholtz free energy increases and decreases, respectively, with temperature. The entropy increases with temperature. The specific heat at constant volume and Debye temperature obey Debye theory. The temperature variation of the considered thermodynamical functions is in line with those of other crystalline solids.

Key words: Density functional theory, structural and electronic properties, phonon dispersion curve, thermodynamical properties

INTRODUCTION

During the last few decades, the rare-earth monopnictides have attracted considerable interest due to their diverse structural, magnetic, transport and vibrational properties.[1–21] Like most of the actinide compounds curium monopnictides CmX (X: N, P, As, Sb, and Bi) crystallize in NaCl type (B1) structure at ambient conditions with space group Fm3 m (225)[12–14] and transform to CsCl type (B2) structure with space group Pm3 m (221) at high pressure.[12,14,15,22] The tracks along the B1 → B2 phase transition under pressure; electronic and mechanical properties have been widely reported for CmX.[12–15] Rached et al.[12] have studied the structural phase transition and elastic properties of curium monobismuthides (CmBi) together with the uranium monobismuthides (UBi) at high pressure using the full potential linear muffin tin orbital (FP-LMTO) method within local density approximation (LDA) for the exchange correlation (XC) potential. These authors found good agreement with the only available theoretical result at that time[22] and the experimental result[7] on structural data, but the phase transition pressure was almost half of the experimental value. Singh et al.[14] have studied the pressure induced phase transition and spin polarized electronic structure of five curium pnictides (CmX: X = N, P, As, Sb, and Bi) using self-consistent tight binding linear muffin tin orbital

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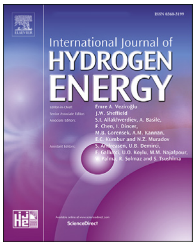

Catalytic activity and underlying atomic rearrangement in monolayer CoOOH towards HER and OER

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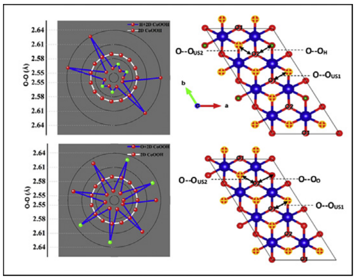
HIGHLIGHTS

- Activity of 2D CoOOH investigated for HER and OER via DFT calculations.
- Interplanar O–O separation on adsorption of H/O on pristine 2D CoOOH.
- Adsorption of H and O atom turns 2D CoOOH into metallic.
- 2D CoOOH is a potential candidate for better HER activity as compared to OER.

GRAPHICAL ABSTRACT



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ABSTRACT

For efficient hydrogen and oxygen production, design and synthesis of cost-effective, stable and active materials are inevitable. In this work, the catalytic activity of 2D CoOOH towards hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) has been investigated using first principles calculations based on density functional theory. The adatom induced structural rearrangement have been investigated from structural parameters as well as charge redistribution in 2D CoOOH. The preferred site for hydrogen and oxygen adsorption were found to be the top site of oxygen atom of 2D CoOOH. The catalytic activity of HER and OER towards 2D CoOOH was studied by calculating the Gibbs free energy. Our study revealed that the 2D CoOOH serve better as a catalyst for HER than OER with adsorption energy of −0.45 and −3.68 eV respectively suggesting its efficient use for hydrogen production. We further investigated the changes in electronic properties of 2D CoOOH on adsorption of hydrogen and oxygen atom.

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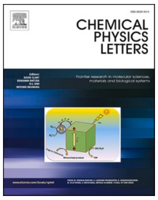

Research paper

Two dimensional hexagonal GaOOH: A promising ultrawide bandgap semiconductor for smart optoelectronic applications

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ABSTRACT

First-principles based density functional theory (DFT) calculations with the HSE functional are performed to predict a new two dimensional (2D) hexagonal GaOOH (h-GaOOH). Thermodynamical and dynamical stabilities are confirmed by calculating the formation energy and phonon dispersion curves respectively. Absence of imaginary phonon modes throughout the Brillouin zone depicts the dynamical stability of 2D h-GaOOH. The electronic band structure shows an indirect band gap of 4.4 eV. The dielectric constants and absorption coefficients show the optical transparency in the visible and near UV region, which makes this material a promising candidate for UV transparent conductors and solar-blind photo-detectors.

1. Introduction

Ultra wide band gap (UWBG) semiconductor oxides ($E_g > 3eV$) hold their specific place in the category of semiconductor materials for solid-state semiconductor-based technology, owing to their diverse material properties, cost-effective, easily tuneable conductivity, extremely high breakdown field and distinctive optoelectronic properties [1]. These multifunctional UWBG semiconductor oxide-based technologies enabling the huge span of energy and optoelectronic applications in high-performance power semiconductor devices and deep-UV range optoelectronics to overpass the standard wide-band-gap (WBG) transparent semiconductor oxides (TSO) (such as ZnO, SnO_2, or In_2O_3) near the UV region (~3.5 eV).

Notwithstanding, to compare and distinguish the full potential of the nominee material in the sector of high power-electronic and optoelectronic industries, two factors need to be considered (1) materials should satisfy the criterion of Baliga's figure of merit (which ultimately depends strongly on the breakdown field, which increases nonlinearly with increasing bandgap) and (2) control over the n-type and p-type conductivities. Thus, the UWBG semiconductors exhibiting the band gap wider than 3.4 eV of GaN (for instance, AlGaN/AlN (6 eV), diamond (5.5 eV), Ga_2O_3 (4.9 eV), BN and II-IV-N (3.4 eV) materials $ZnGa_2O_4$ (5 eV)) lead the semiconductor industries in past few decades, [2]. With the availability of several UWBG semiconductor oxides, the fabrication of various configurations of boron nitride (BN) such as wurtzite (5.5 eV), zinc blend (4.3 eV) and hexagonal BN (6.08 eV) belong to the class of UWBG semiconductors and turns out to be the eye-catching materials in the field of UWBG [3,4]. Owing to the unique physical and chemical properties [5] in the form of 2D structure (e.g., the atomic flatness, mechanical robustness, absence of dangling bonds, and high thermal conductivity), 2D h-BN and its van der Waals heterostructures [6] are rapidly emerging field of UWBG semiconductors to expand its utilization fields. At the same time, comprehensive investigation of gallium oxide hydroxide (GaOOH) an UWBG semiconductor has surged in recent decades because of their appealing electronic and catalytic properties. It is an important precursor for the direct preparation of Ga_2O_3 (4.2–4.9 eV) and GaN (~3.4 eV) semiconductors and active in the UV zone for the degradation of methylene blue dye [7].

In materials science, the size, shape and confinement dominated fabrication methodologies have always drawn attention of researchers. These facts lead to the remarkable diverse properties of the compounds with the same compositions but different morphologies [8]. In view of that, several efforts have been made to fabricate GaOOH with different morphologies e.g. rod-like GaOOH nanoparticles (NPs) (hydrothermal treatment) [9], scroll-like cylindrical GaOOH NPs (sonochemical hydrolysis of Ga^{3+} ions) [10], spindle-like GaOOH NPs (laser ablation) [11], wire-like GaOOH NPs (microwave method) [12], crystalline α-GaOOH NPs (electrochemical oxidation) [13] and needle-like submicron tubular α-GaOOH (hydrothermal route-4.9 eV UWBG) [14] to explore their response towards optoelectronics to photocatalysis to biological applications. Huang et al. prepared the nanowires of GaOOH, γ-Ga_2O_3 and β-Ga_2O_3 with the 4.9 eV, 4.4 eV and 4.2 eV optical band

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Pressure Induced Hydrogen Order−Disorder Transition in β-Ni(OH)$_2$

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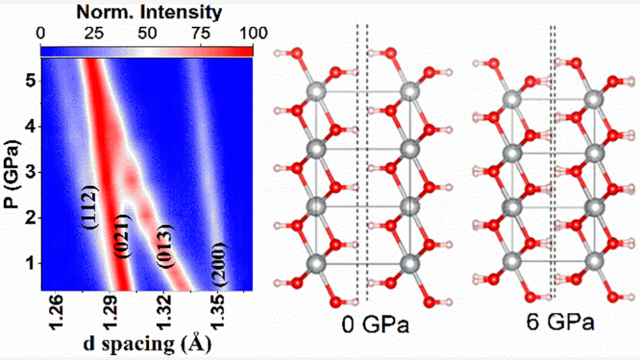

ABSTRACT: Here we address the challenging problem of pressure induced hydrogen sublattice disordering in layered hydroxides using synchrotron X-ray powder diffraction (XRPD) and first-principles calculations based on density functional theory (DFT) using β-Ni(OH)$_2$ as a model system. XRPD data demonstrate anomalous behaviors in some Bragg peaks. The shift in (003) and (013) peaks with pressure is large as compared to that of other Bragg peaks and these two peaks are not discernible above 5 GPa, similar to the characteristic observed in β-Co(OH)$_2$. The underlying changes within the structure were probed using DFT calculations on a $\sqrt{3} \times \sqrt{3} \times 1$ supercell of β-Ni(OH)$_2$. Structural relaxation yields a hydrogen disordered structure as the ground state for β-Ni(OH)$_2$ at pressures above 5 GPa. The disordered model also describes well the high pressure XRPD data. The hydrogen sublattice largely affects the electronic density of the (003) and (013) lattice planes thus permitting the development of a one-to-one correspondence of the anomalous behavior of these Bragg peaks with the hydrogen sublattice disordering. Further evidence of a possible structural rearrangement was obtained by the pressure dependence of the unit-cell volume (P vs V) as well as the ratio of the out-of-plane to in-plane lattice parameter (c/a). With the availability of a large number of data points with smaller pressure steps, the above two quantities are shown to behave differently below and above 2.5 GPa. The P vs V data are well described by a second order Birch−Murnaghan equation-of-state, whereas for c/a, a clear change in trend is observed for data above 2.5 GPa. The pressure response of β-Ni(OH)$_2$ is similar to that of Co(OH)$_2$ reported in our recent high pressure study, and therefore pressure induced hydrogen order−disorder transition may be a general characteristic of layered hydroxides.

■ INTRODUCTION

High pressure studies on layer hydroxides serve as primary reference for understanding the behavior of complex hydrous minerals abundant in the earth's mantle and provide valuable information underlying various geophysical phenomena. Apart from geophysical implications, their unique structural configuration involving stacked layers incorporating hydroxyl groups gained much attention among researchers as it enables exploring various structural phenomena by manipulating the interlayer separation. The simplest prototype of layered hydroxides widely investigated belongs to the M(OH)$_2$ family [M = Mg, Ca, Co, Ni, etc], which are often referred to as brucite-type hydroxides. Even though they are structurally simple, their structures at ambient and high pressure conditions have been debated for long, questioning the preferred hydrogen sites and its effect on pressure response of the lattice. This ambiguity arose due to competing H−H repulsion and attractive hydrogen bonding in these materials. The widely accepted crystal structure of these M(OH)$_2$ is a CdI$_2$ structure in the P-3m1 space group with a metal atom at the 1a (0, 0, 0) Wyckoff position, while O and H atoms are at the 2d (1/3, 2/3, z) site. Under pressure, the interlayer separation of layers decreases and hydrogen atoms from opposite layers comes close to each other, thereby increasing the contribution of H−H repulsion to nonbonded atomic interactions. Since the distance cannot be reduced arbitrarily, at a critical interlayer separation, H−H repulsion destabilizes the initial structure.[1] Though this phenomenon sounds trivial, the structural changes driven by H−H repulsion exhibits large diversity among M(OH)$_2$ compounds.

High pressure spectroscopic[2−7] and crystallographic[4,5,8−10] studies of M(OH)$_2$ compounds showed that they exhibit complex structural phenomena such as structural frustration, sublattice (H-layer) amorphization,[11] and pressure-induced amorphization.[2,3,12] Ca(OH)$_2$ has been shown to undergo

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Exploring structural, electronic, and optical properties of the bismuth based palladium chalcopyrite

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ABSTRACT

The palladium (Pd) based delafossites unique class of layered conducting oxides with noticeable electronic properties, are enhancing the interest of material scientists to explore this noble material. In this article, the structural, electronic and optical properties of $PdBiS_2$ (PBS) chalcopyrite are studied using state-of-the-art density functional theory (DFT). The structural geometry of PBS is similar to the delafossite type oxides. The phonon dispersion curves (PDC) of PBS indicate its dynamical stability. The electronic band structure and density of states (DOS) reveal that the PBS compound is metallic in nature. The partial density of states (PDOS) indicates the major contribution of the Pd 3d and S 2p orbitals near the valence band maximum (VBM). The real and imaginary parts of the dielectric constant further confirm its metallic nature.

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1. Introduction

Delafossite type materials such as $PdCoO_2$, $PdCrO_2$, and $PdRhO_2$ are currently attracting much attention by the condensed matter and materials researchers due to their exotic and surprising physical properties [1–6]. The high electrical conductivity of Pd based delafossites among the group of oxides make them a promising candidate in various technological applications. The chemical formula for delafossite compound is $A^{+1}B^{+3}O_2$, which is associated with a family of ternary oxides (A = Cu, Ag, Pd, Pt; B = Cr, Fe, Rh, Bi, etc.) and can be visualized as a layered structure of A^{+1} cation, stacked between edge-shared octahedral layers of BO_6. These are perpendicularly connected forming a dumbbell-like structure (O-A-O), which generally crystallizes in either rhombohedral or hexagonal, marked as 3R ($R\overline{3}m$) and 2H (P63/mmc) respectively. They are being used for many technologically relevant applications [7–8]. Kawazoe et al. [9] reported low carrier concentration and localization of holes in $CuAlO_2$, which limits the p-type conductivity. To overcome these problems many approaches have been considered to enhance electrical conductivity in p-type semiconductors, for example, the substitution of chalcogens (S, Se, Te) and nitrogen at the place of oxygen [10–12]. In delafossites, the A-site cations are generally Ag or Cu and B-site cations are either a p-block metal or transition metal Al or Fe. Another class of this family includes the metallic compounds at A-site cations such as Pd or Pt, and the B-site cations contain post-transition metals Bi or In, shows the metallic nature [13–14]. Previously reported electrical conductivity at low temperature for these metallic compounds is the highest reported conductivity for any oxide materials i.e$1.3 \times 10^8 S/cm$ [15]. Recent studies showed that Pd based oxides and chalcogenides are stable and have diverse functional properties [16–19]. These motivated us to explore the bismuth-based palladium chalcopyrites. In this study, we have explored the bismuth (Bi) based $PdBiS_2$ (PBS) chalcopyrite to understand its electronic, vibrational and optical properties.

2. Computational methods

All calculations in the present work were performed using first-principles calculations based on density functional theory (DFT) [20]. We employed the plane-wave pseudopotential method implemented in the Quantum ESPRESSO code [21]. The Perdew–

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Bio-corrosion studies of Fe-based metallic glasses

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ABSTRACT

Fe-based metallic glasses are known for their high corrosion resistance. Also, the corrosion resistance of metallic glasses are greatly influenced by the alloying elements. In the present study, the bio-corrosion resistance of two Fe-based metallic glasses ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ and $Fe_{67}Co_{18}B_{14}Si_1$) has been studied. The bio-compatibility of these metallic glasses are studied in four simulated body fluids (SBFs), namely artificial saliva solution (ASS), phosphate-buffered saline solution (PBS), artificial blood plasma solution (ABP), and Hank's balanced saline solution (HBSS). Potentiodynamic polarization studies are performed on both the metallic glasses, for understanding their bio-compatibility.

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1. Introduction

Metals and their alloys have been used as bio-implants for over a decade. The two major issues of using any material as bio-implant are: (a) ability of the material to resist corrosion in bio-fluids, and (b) the impact of corroded material on the human body. Corrosion of material inside the human body impairs the implant and also enables toxic elements to damage the nearby tissues of the implant. A good bio-compatible material must have poor susceptibility towards corrosion in bio-fluids along with no harmful after-effects of the corroded implant. The biocompatibility of implant material can be tested through potentiodynamic tests with different simulated bio-fluids as electrolyte. Many studies are available in the literature [1–5] for studying the biocompatibility of bio-implants such as stainless steel (316 L SS), metals and amorphous alloys (Ti-, Sr-, Zr-, Fe-based metallic glasses) in SBFs like saliva solution, Phosphate-Buffered Saline Solution (PBS), Hank's solution, etc. Zr- based metallic glasses are found to have better bio-compatibility as compared to 316L SS and Ti-6Al-4 V alloys [6–8]. The presence of elements like Ni or Be in any potential bio-implant is supposed to have a toxic effect on tissue functionality and cell growth [7–11]. However, the biocompatibility and non-toxic effects of $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ and $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ bulk metallic glasses (BMGs) have been proved by Schroers et al [12].

The strength and poor susceptibility of Fe based metallic glasses towards highly corrosive media like HCl, NaCl, H_2SO_4, etc, makes them a suitable candidate for engineering applications [13]. Fe-based metallic glasses also show good corrosion resistance even in bio-fluids [14], which makes them useful as bio-implants. In present work, the corrosion behavior of $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ and $Fe_{67}Co_{18}B_{14}Si_1$ metallic glasses is studied through the potentiodynamic polarization method under the influence of four SBFs.

2. Experimental

Amorphous ribbons of $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ and $Fe_{67}Co_{18}B_{14}Si_1$ metallic glasses were procured from Allied Corporation, USA. The metallic glass ribbons were prepared by single roller melt-spinning method. XRD and TEM were done to confirm the amorphous nature of glassy ribbons. The corrosion behavior of Fe-based metallic glasses was studied using potentiodynamic polarization technique. Gammry reference 600 potentiostats were used to carry out electrochemical polarization experiments using a typical three-electrode system. The operating parameters such as initial and final voltages are −0.5 V and 1.5 V respectively. The scan rate is set on 5 mV/sec, conditioning time, and initial delay is 60 sec. Sample exposure area is set to be 5 mm × 5 mm = 0.25 cm^2.

The tests were performed using the calomel electrode as reference, graphite electrode as a counter electrode and test sample as a working electrode. Four artificially synthesized body fluids, viz artificial saliva solution (ASS, pH 6.2), phosphate-buffered saline solution (PBS, pH 7.4), artificial blood plasma solution (ABP, pH

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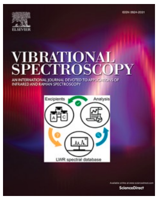

Probing Fano resonance, relaxor ferroelectricity, light scattering by orbital exchange-bond, orbitons by Raman spectroscopy, and their correlation with dielectric properties of pure and Fe^{3+} – Substituted calcium-copper-titanate

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ABSTRACT

Micro-Raman spectroscopy study on a slowly-cooled polycrystalline sample of $CaCu_3Ti_4O_{12}$ was conducted over a wide temperature and wavenumber ranges. The characteristic high-intensity peak observed first ever at ~ 2425 cm^{-1} is assigned to the scattering of light caused by fluctuation of orbital exchange-bond. The high-energy broad hump like Raman mode at ~ 2500 cm^{-1} bespeaks its origin from orbitons. The dielectric permittivity (ε') measurements are performed as a function of temperature and frequency. The negative permittivity ($T \leq 100$ K and $f \geq 1$ MHz) and slim polarization versus electric field loop indicative of relaxor ferroelectric behavior are observed. Besides, spectra reveal evidence of a Fano resonance. The reformed phenomenological model is proposed to interpret temperature and frequency-dependent dielectric permittivity ($\varepsilon'(T, f)$). The peculiarities manifest collective conjunction of electronic degrees of freedom, lattice degrees of freedom, and orbital degrees of freedom. The results are analyzed and discussed in the light of Raman spectral analysis of microwave-assisted and quenched samples of $CaCu_3Ti_4O_{12}$. The effect of Fe^{3+} - substitution on $\varepsilon'(T, f)$ spectral features for quadruple perovskite series, $CaCu_{3-x}Ti_{4-x}Fe_{2x}O_{12}$ (x = 0.1, 0.3, 0.5 and 0.7) is investigated and a correlation with Raman spectral profiles is established.

1. Introduction

Exactly two decades ago, Subramanian et al. [1] and Ramirez et al. [2] found the most phenomenal dielectric characteristics manifested by quadruple perovskite, calcium-copper-titanate ($CaCu_3Ti_4O_{12}$). It is observed that the dielectric permittivity (ε') shoots by a factor of 100 in a polycrystalline sample of $CaCu_3Ti_4O_{12}$ above ~ 90 K (at f = 1 kHz). The material demonstrates giant ε' of the order of ~ 10^4 at T =100 K. However, ε' is poorly temperature-dependent in the 100 K–320 K range. This sudden rise in ε' (T) is companioned by a wide peak in loss tangent, tan δ (T), curves. Further, this anomaly is heavily influenced by f, for f =100 Hz to 1 MHz, and the temperature at which such prodigious rise in ε' occurs shifted from ~ 70 K–220 K. Moreover, the magnitude and rate at which ε' rises with T also decrease with f [2]. Based on the analysis of temperature (T =5 K – 300 K) dependent Raman scattering spectra and low-frequency dielectric behavior, there occur exceedingly polarizable relaxation modes with typical gap energy of 28 meV [2]. However, it is ruled out that the mechanism (correlated alignment of the local dielectric dipoles) responsible for the huge ε' exhibited by ferroelectric materials is also accountable for the composition under investigation. Furthermore, it is concluded that $CaCu_3Ti_4O_{12}$ is not a charge density wave system. But the thermal variation of the integrated intensity of Raman scattering from the continuum is consistent with the ε'(T) variation, which advises the relationship between the Raman modes and dielectric permittivity. Since then many studies are carried out and different causes are proposed to explain these most exceptional

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