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Materials properties of magnesium and calcium hydroxides from first-principles calculations

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ABSTRACT

Recent experiments have revealed a good potential of applicability of multifunctional hydroxides $X(OH)_2$ (X = Mg and Ca) in optoelectronic devices and emphasized the lack of fundamental understanding of their materials properties. This work presents systematic study of ground state properties, electronic structure, dielectric and optical properties of the materials by first-principles calculations within PBE-GGA and range-separated hybrid functional schemes as well as by using GW approximation. The relevant HSE06 hybrid functional mixing parameters were determined from a self-consistent adjustment to the electronic dielectric constant ϵ_∞. We show that the overall performance of our adaptation of the HSE06 functional via implementation of the modified amount of the Fock exchange is nearly best for the ground state properties as compared to the other relevant methods of Hartree–Fock and density-functional theory. Structural stability of the crystalline $X(OH)_2$ hydroxides has been considered in static and dynamic aspects. The most important factors describing the bonding situation have been investigated, and a crystal-chemical integrity of the hydroxides has been analyzed. From electronic structure studies it was found that both materials are direct band gap insulators. Predictions for the fundamental band gaps were shown to be in the range of 7.7–8.3 eV for $Mg(OH)_2$ and 7.3–7.6 eV for $Ca(OH)_2$. The origin of the conduction and valence band states near the band edges has been studied in terms of orbital and site projected density of states as well as by comparison with the X-ray photoelectron spectroscopy measurements. It was shown that effective masses of carriers at the Γ-point in vicinity of the band extreme are strongly anisotropic and for the electrons are similar to those in the ZnO crystal. Optical properties of the bulk $X(OH)_2$ hydroxides have been investigated in terms of the real and imaginary parts of the optical dielectric function calculated in GW approximation. Electronic character of anisotropy of optical properties has been clarified.

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1. Introduction

Alkaline earth metal hydroxides $X(OH)_2$ (X = Mg, Ca) represent a fine example of multifunctional compounds having a widest range of technological and industrial applications. The elements compromising $X(OH)_2$ are widely available, low cost, and non-toxic. Hydrogen (H) and oxygen (O) are the most abundant elements in the universe. Because of the possibility of synthesis by inexpensive and green methods, these materials can be chemically tuned with the predesigned functional properties and, therefore, they hold very good promises for future applications, e.g., biomedicine, electronic device, solar energy, gas sensing, etc.

Along with calcium containing binary oxides and carbonates, portlandite $Ca(OH)_2$ is one of the most key inorganic materials in lime industries. In addition to the pivotal uses in building and engineering fields its functional properties are widely involved in a variety of applications, e.g., water treatment [1], dental therapy [2], etc. Brucite $Mg(OH)_2$ has also demonstrated similar effectiveness in waste water treatments [3–6] and a high antibacterial efficiency against several tested bacterial strains [7]. There is an interesting experience of employing $Mg(OH)_2$ as a precursor for magnesium oxide refractory ceramics [8], or as a flame retardant in various polymer compositions and smoke suppressants [8–10].

At the present time we can see a resurgence of scientific interest in $X(OH)_2$ studies caused by their potential for a possible applicability in optoelectronic devices [11]. Enhancement of electronic connectivity, reduction of the trapping/detrapping events, and

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suppression of charge recombination in the semiconductor/electrolyte interface of the dye-sensitized solar cells have been reported [12] for $Ca(OH)_2$. $Mg(OH)_2$ has been used as a buffer layer in CuInSe [13,14] cells and as a passivation layer in dye-sensitized [12,15–17] composite solar cells. The development of the $Mg(OH)_2$ films prepared with addition of certain amounts of C atoms have suggested a new type of rare-earth metal free transparent and conducting films possessing the following distinctive feature: [18] whilst the host material belongs to the group of wide-gap insulators and, correspondingly, is transparent to the visible light, these C-doped $Mg(OH)_2$ films in addition to conventional transmission $\sim 90\%$ measured in the wavelength range of 380–780 nm have demonstrated unconventional high electrical conductivity of $\sim$167 S/cm. For these applications a deep understanding of the materials properties is crucial. So far, in the focus were mainly structural, vibrational and chemical properties of $X(OH)_2$ [19–28]. Recent studies on the electronic structure were undertaken primarily to understand novel opto-electronic properties of $Mg(OH)_2$:C films [29]. The possible applications of the $X(OH)_2$ hydroxides in solid-state electronics requires firm knowledge of their fundamental physical properties, which is an important task at the moment. One of the actual issues is the determination of the fundamental band gap. Some information about it is available on thin films of $Mg(OH)_2$. Depending on the method of deposition and processing as well as characterization tools the experimentally measured values of the optical band gap demonstrate a large scatter in the results – from 5.17 eV [13], and 5.70 eV [30], to 7.0 eV [29]. To gain an insight into the processes responsible for suppressing the charge carrier recombination and surface states in solar cells, the full information on chemical bonding situation is very important. Various applications of the materials under consideration in optoelectronic devices require a general knowledge of the other parameters such as carrier effective masses, work function, and optical properties for the materials, which are not available in literature.

Another key issue that should be addressed is the stability of the material. Among unique features the hydroxides commonly exhibit the layered structure seems to be the major factor that not only governs, at the macroscopic level, different properties of these materials, but also develops effective relations between the existing chemical interactions. The suggestion that these interactions, being active simultaneously, are connected via the simplest functional group – OH^- hydroxyl anion, directs essential attention to the issues of an interplay between ionicity and covalency such as (i) understanding how covalency is involved within the charge transfer process, and (ii) identifying how it affects the basic electronic properties of the ionic crystalline systems. A straight involvement of covalency in the activation of the electronic subsystem follows directly from an analysis of the Honjo et al. experiments [18] on $Mg(OH)_2$:C films, whereas the interplay of the ionic and covalent interactions can be seen from experimental studies [13,14,17] that demonstrate the possibilities of accommodation of lattice constants and band offsets in composite solar cells with a buffer layer of $Mg(OH)_2$.

The present work thus aims to give a first-principles outlook that quantifies structure-bonding-properties relationships for the $X(OH)_2$ hydroxides in terms of calculations by the density-functional theory (DFT) with emphasis on studying structural stability, features of electronic structure, mechanical and optical properties. Because of the absence of the detail theoretical studies that could serve as a guide for the electron subsystem, we will focus on the points that are principally important for the knowledge of key parameters and mechanisms underlying the specific physical properties of the hydroxides and that can contribute to the development of semiconductor devices using these compounds as the host or secondary materials. Since little information is presented about real electronic structure of the hydroxides in scientific literature, the other problem addressed in our work has a rather academic character; recent progress in numerical DFT methods has allowed us via performing accurate DFT calculations to update significantly theoretical description of the fundamental electronic and optical properties of these compounds.

2. Methods and computational details

2.1. Methodological aspects

For ionic-covalent materials usually one starts electronic structures calculations that can output theoretical predictions of the important properties such as band gap values, the band picture, density of states by using traditional local density approximation (LDA) or semilocal generalized gradient approximation (GGA) to DFT. For improvement of the description of the electronic states built of Kohn–Sham virtual orbitals one can decide between two possibilities: either to use computationally accessible hybrid functionals, which deal with a specified fraction of the Fock exchange, or to employ the powerful theoretical tool such as the many-body Hedin's GW approximation [31]. As both ways give the great adjustment of the results obtained on the base of LDA and GGA functionals, in the present work we apply numerical procedures based on HSE06 hybrid functional [32–34] within the frameworks of which we describe the crystal structure and determine electronic and dielectric properties of the $X(OH)_2$ hydroxides.

Since exchange effects (as an integral part of electron–electron interactions) appear to be especially significant in the wide-gap ion-covalent materials, the problem of how to describe the electronic structure in terms of single-particle states depends on an inherent potential of the hybrid functional to model effectively the full (x, x')- and ω-dependent electron interactions in terms of the exact Fock exchange. According to Refs. [35,36] a useful way of making such treatment within first-principles electronic structure methods is a consideration of the non-local hybrid functional as an approximation to the true electron self-energy $\Sigma(x, x'; \omega)$, which provides theoretical constructs that map efficiently to typical elements of the hybrid functional like as follows [36]: $\Sigma(x, x'; \omega)$ is projected into the direct sum of two principal terms – the first corresponds to a statically screened non-local exchange in which the amount of the exchange is driven by the inverse electronic dielectric constant ϵ_∞^{-1} and the second is identified with the static and local part of the hybrid functional; the quasi-particle equation followed from such construction corresponds to the generalized Kohn–Sham equation that can be self-consistently solved for a hybrid functional. The main benefit that was originally gained in this context is that determination of the fraction a of the Fock exchange in the one-parameter hybrid functional $V_{xc} = aV_x^F + (1-a)V_x^{GGA} + V_c^{GGA}$ in terms of the relation [35,37–40] $a = \epsilon_\infty^{-1}$ provides [39] a single-particle description of electronic states of an ion-covalent insulating system, much more accurate as compared to results recorded by conventional DFT-based calculations on the base of LDA or GGA. Moreover, the proper solutions of the generalized Kohn–Sham equation with the hybrid functional such as the eigenvectors and eigenvalues can be further used as a first starting point to evaluate various material properties of the physical system.

From a pragmatic point of view, note that while hybrid functional based approach may be subjected to some discussion concerning the certain amount of the exchange contribution, which appears to be a system-dependent parameter, this issue is quite well amenable to first-principles procedure that, with the goal of clearing that bottleneck, can evaluate a physical range of a via ϵ_∞^{-1} without relying on experimental input. To this end, the present

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