# Electronic and optical properties of magnesium and calcium hydroxides: The role of covalency and many-body effects

Smagul Zh. Karazhanov

*Department for Solar Energy, Institute for Energy Technology, NO-2027 Kjeller, Norway*

Aleksandr Pishtshev

*Institute of Physics, University of Tartu, 510411 Tartu, Estonia*

M. Klopov

*Department of Physics, Tallinn University of Technology, 19086 Tallinn, Estonia*

**Abstract**

Magnesium and calcium hydroxides $X(\mathrm{OH})_2$ ($X$=Mg, Ca) are the multifunctional materials that have many important applications in industry, technology and research. In solid state electronics, the emerging applications of these compounds are related to photovoltaic devices. In the present paper we review electronic properties of $X(\mathrm{OH})_2$, band gaps, work function, features of chemical bonding, and discuss theoretically predicted exciton effects.

*Keywords:* magnesium hydroxide, brucite, calcium hydroxide, lime, crystal structure, electronic structure, chemical bonding, optical properties, exciton

*Email addresses:* smagulk@ife.no (Smagul Zh. Karazhanov), aleksandr.pishtshev@ut.ee (Aleksandr Pishtshev), mihhail.klopov@ttu.ee (M. Klopov)

## 1. Introduction

Recent advances in chemical technology combined with modern quantum mechanical methods allow one to predict and construct materials possessing many desired properties such as electronic, mechanical, optical, thermal, or others, which are principally important for different technological applications. However, the design of a novel multifunctional material requires numerous efforts, and the corresponding production costs are often connected with high investment risks. On the other hand, compounds which have abundance in nature might be considered as attractive from technological and economical points of view. Functionality of the compounds can be extended by doping with different types of impurities [1, 2]. The compounds (or most of them) can be related to the class of multifunctional materials because they are typically endowed with different sets of properties depending mainly on the naturally occurring composition of elements and the specific features of chemical bonding. In the present paper, the focus is made on the case of relatively simple alkaline-earth hydroxides $X(\mathrm{OH})_2$ ($X$=Mg and Ca), which are interesting in the context of multifunctionality because they exhibit a variety of useful properties. It is worthy of note that the elements composing $X(\mathrm{OH})_2$ are widely available, low cost and non-toxic; magnesium is the eighth and calcium is the fifth most abundant elements in the earths crust. Their price is much lower than the price of indium and tin, and close to that of zinc. It is also well known that hydrogen, and oxygen are the most abundant elements in the universe.

The multifunctional hydroxides $X(\mathrm{OH})_2$ have found a wide range of applications in medicine, environment, and electronic technology. Studies of these materials have already been the topic for extensive scientific research. Portlandite $\mathrm{Ca(OH)_2}$ is one of the most important inorganic materials in lime industries. In addition to the significant usage in building and engineering fields its functional properties are widely implemented in a variety of applications; the primers range from water treatment methods [3] to dental therapy [4]. Brucite $\mathrm{Mg(OH)_2}$ has also demonstrated similar effectiveness in waste water treatments [5–8] and a high antibacterial efficiency against several tested bacterial strains [9]. There is an interesting experience of employing $\mathrm{Mg(OH)_2}$ as a precursor for magnesium oxide refractory ceramics [10], or as a flame retardant in various polymer compositions and smoke suppressants [10–12].

## 2. Applications in solar cells

$X(OH)_2$ is the emerging material for solar cell applications. It has been employed for a surface modification of $TiO_2$ nanoparticles, which is one of the promising strategies in improving energy conversion efficiency. For examples, coating the $TiO_2$ nanoparticles with a metal oxide has enhanced the conversion efficiency of the cell. It was reported [13, 14] that a coating of $TiO_2$ by $Mg(OH)_2$ has improved open circuit voltage of dye-sensitized solar cell. Suppression of charge carrier recombination at the interface of the dye-sensitized solar cells has been reported [15] for $Ca(OH)_2$. $Mg(OH)_2$ has been used as a buffer layer in CuInSe [16, 17] cells and as a passivation layer in dye-sensitized [13–15, 18] composite solar cells.

As discussed below, excitons possessing large binding energy might exist in $X(OH)_2$ at room temperature. Once free electrons and holes are created in the material, they might be bound into excitons. Consequently, concentration of free electrons and holes in $X(OH)_2$ might be much smaller than that of excitons. Although the excitons are neutral, they can indirectly influence on charge carrier concentration by dissociation and annihilation as well as by modulating the charge state of impurities, which will also infouence on electrical current transport. There is no work estimating relation of concentration of excitons to that of free charge carriers and diffusion coefficient of excitons.

Recently, an exciting property of carbon doped $Mg(OH)_2$ films was reported in Refs. [1, 19]. It was demonstrated that such modified material is not only transparent in visible range of sunlight, but it is also electrically well conducting with conductivity of $\sim$167 S/cm. Note that $Mg(OH)_2$ itself is a wide band gap insulator. However, upon doping by C impurity, $Mg(OH)_2$, in addition to being transparent to sunlight, becomes electrically well conducting. This finding is expected to broaden the applications of $Mg(OH)_2$ in photovoltaic devices, smart windows, and other semiconductor devices.

## 3. Properties

### *3.1. Structural properties*

Structural, morphological, and vibrational properties of $X(OH)_2$ are the most systematically studied ones (see, e.g., Refs. [20–28]). Both magnesium and calcium hydroxides possess trigonal structure of space group $P\bar{3}m1$, no. 164, with one formula unit per the unit cell [29–32]. No other polymorphs of $Mg(OH)_2$ and $Ca(OH)_2$ have been reported in literature [33, 34].

### *3.2. Band parameters*

Implementation of $X(\mathrm{OH})_2$ in solar cells and other semiconductor devices requires an understanding of its fundamental physical and chemical properties. One of the important materials parameters to know is the band gap $E_g$. There is no systematic study of this parameter for $X(\mathrm{OH})_2$ performed for more or less pure compound at low temperatures. The existing experimental data have been obtained for $\mathrm{Mg(OH)_2}$ synthesized by chemical method and the measurements have been performed at room temperature. The obtained band gaps have a large scatter: 5.17 eV for the thin film samples [16], 5.70 eV for for $\mathrm{Mg(OH)_2}$ nanodisks [35] and about 7.6 eV [36] for the bulk. Theoretically estimated band gaps are predicted to be in the range of 7.7-8.3 eV for $\mathrm{Mg(OH)_2}$ and 7.3-7.6 eV for $\mathrm{Ca(OH)_2}$ [37].

Knowledge of effective masses is also important for characterization of charge carrier transport through the $X(\mathrm{OH})_2$ layer. There are no experimental data related to their measurements. Based on the electronic structure studies theoretical calculations have been performed [37]. Analysis showed that the conduction band effective masses are about 0.13 $m_0$ for $\mathrm{Mg(OH)_2}$ (in the unit of the free-electron mass ($m_0$ )) and 0.18 $m_0$ for $\mathrm{Ca(OH)_2}$. These masses are close to the 0.24 $m_0$ for ZnO [38]. The hole masses at the valence band maximum are 3.06 $m_0$ for $\mathrm{Mg(OH)_2}$ and 0.44 $m_0$ for $\mathrm{Ca(OH)_2}$, which are quite different than the mass 2.74 $m_0$ for ZnO.

Work function of electrons (WF) for $X(\mathrm{OH})_2$ is one of the important parameters, which is very sensitive to surface properties such as thermionic emission, photoemission, catalysis, etc. [39]. There are no experimental investigations of WF for the $X(\mathrm{OH})_2$ materials. Theoretical estimates based on *ab initio* studies [37] show 4.46 eV for $\mathrm{Mg(OH)_2}$ and 4.78 eV for $\mathrm{Ca(OH)_2}$, respectively.

### *3.3. Chemical bonding: the role of covalency*

The most interesting aspect of chemical design in $\mathrm{Mg(OH)_2}$ and $\mathrm{Ca(OH)_2}$ hydroxides is that a rich behavior of these materials are based mainly on two principal factors; both of them are associated with the hydroxyl anions $(\mathrm{OH})^-$. The first factor of structure-specific nature is connected with a layered complexity of the bulk along $c$ axes: it is determined by the hexagonal close packing of the hydroxide anions in the crystal lattice [34]. The second factor is that the three-body structural $X{-}\mathrm{O}{-}\mathrm{H}$ block consisting of the almost fully oxidized metal cation and $(\mathrm{OH})^-$ anion is responsible for a common chemical stability in terms of a spatial localization of the electronic

charge [37]. That is, the oxygen playing the role of a principal oxidizer forms the bridging site that balances electron-poor and electron-reach areas in such a way to maintain a structural stability via consistent matching ionic and covalent chemical interactions. At the macroscopic level, in terms of crystal sublatticies this implies that by incorporating a directional covalent bonding into a host framing the hydroxyl anion redistributes the valence electron density to give rise to a sufficient rigidness of $Mg^{2+}$ and $Ca^{2+}$ cationic orderings, which become electrostatically connected with the anionic sublattice of the hydroxyl ions.

As follows from electron counting considerations the distribution of valence electrons (formal charges) in the $X{-}O{-}H$ block gives the charges consistent with the Lewis structure in which the octet rule is fulfilled. This corresponds to the standard arrangements of the electronic pairs of the $O^{2-}$ ion in $OH^{-}$: one bond pair and three lone pairs.

Analysis of electron partitioning schemes (Fig. 1) in terms of electron localization function (ELF) shows [37] that the electron-reach areas belong mainly to the anionic subsystem of $X(OH)_2$ where two regions of strong localization of valence electrons can be revealed. The first one is a vertically oriented distribution of shared electron pairs which is associated with $s$-$p_z$ hybridization that governs covalent $H{-}O$ bonding along $c$ axis. The other is arranged in $ab$-plane and corresponds to a manifold of non-bonding lone-pairs associated with the occupied $2p_x$, $2p_y$ oxygen orbitals. The theoretical calculations indicate [37] that electronic states formed by these pairs contribute into the top of the valence band, while the occupied $2p_z$ oxygen electronic states (related to the covalent $H{-}O$ bond) are significantly repelled toward lower energies. Such nonplanar separation of the overall electron density with respect to bonding and nonbonding regions, when states of $s - p_z$ hybridized electrons lie lower than those corresponding to highest occupied $2p_x, 2p_y$-type orbitals of oxygen, will lead to a strong anisotropy of the electronic and optical properties. Moreover, calculations of electronic partitions within the unit cell space have shown that about 78% and 67% of the cell volume in $Mg(OH)_2$ and $Ca(OH)_2$, respectively, is allocated to the arrangement of valence electron pairs supplied by the oxygen of $(OH)^{-}$ anion. This allows us to predict the dominant role of the oxygen valence orbitals in electronic responses of these materials.

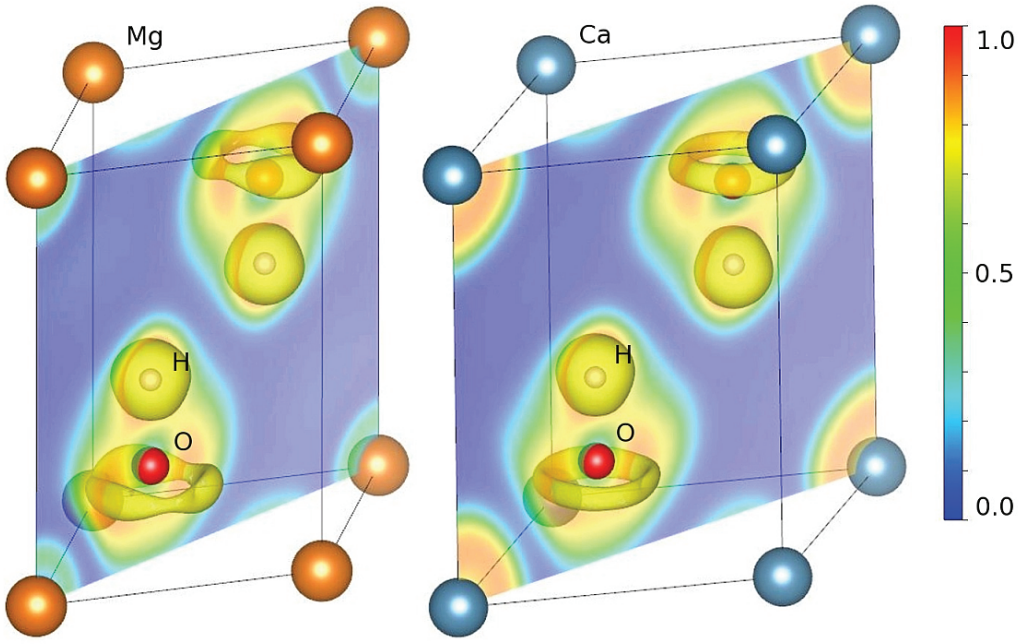


Figure 1: Representation of the valence ELF for $Mg(OH)_2$ (left) and $Ca(OH)_2$ (right) in (110) cut plane involving additional ELF isosurfaces for the hydroxyl anion evaluated at ELF= 0.87. The character of the regularity of the torus-shaped topology is determined by the minimization of electron-pair repulsion; this makes spatial arrangement of all three lone-pairs (the nonbonded domains) around the negative oxygen ion symmetrically localized in the $a - b$ plane. (Graphic illustration of this figure was made using the VESTA program[40]).

### *3.4. Excitons*

It is well-established in a description of electronic responses common to ion-covalent materials that the contribution of many-body effects is directly determined by the degree of electronic charge localization [41, 42]. In this context, the multifunctional $X(OH)_2$ are unique materials where the many-body effects should play crucial role in their optical properties. These properties definitely have important implication for different applications of the materials in optoelectronic devices [16–18]. Importance of the many-body effects in $X(OH)_2$ becomes evident upon studies of the macroscopic dielectric constant $\epsilon_\infty$, which serves as one of the important parameters characterizing how strong is the Coulomb interaction between an electron and a hole as well as how large is the exciton binding energy $E_b$. As it is well known, $\epsilon_\infty = 11.7$

Ref. [43] for Si with $E_b = 14.7$ meV Ref. [44], $\epsilon_\infty = 7.9$ Ref. [45] for ZnO with $E_b = 59$ meV Ref. [46], which means that excitons can exist at low temperatures in Si and at the room temperature in ZnO. Our theoretical studies [47] have shown that $\epsilon_\infty = 2.35$ for $Mg(OH)_2$ and $\epsilon_\infty = 2.33$ for $Ca(OH)_2$. Consequently, exciton binding energy in $X(OH)_2$ is expected to be larger than that in ZnO. Theoretical studies of Ref. [47] by using the *ab initio* calculations with the HSE06 hybrid functional [48–50] and GW approximation [51] combined with numerical solution of the Bethe-Salpeter equation [42, 52–55] (GW-BSE) predicted the possibility of existence of diverse number of excitonic states in the $X(OH)_2$ hydroxides. The excitons possessing large binding energy of 0.46 eV for $Mg(OH)_2$ and 0.85 eV $Ca(OH)_2$ have been reported. They have been identified to be related to a strong localization of the hole and electron to oxygen $2p_x, 2p_y$ occupied states as well as to oxygen and metal $s$ empty states, respectively. The corresponding model of the strongly localized excitons is schematically presented in Fig. 2.

A spectral peak near band edge corresponding to strongly localized excitons have been observed experimentally [16] in transmittance spectra of $Mg(OH)_2$, samples of which were prepared by chemical bath deposition method. This peak corresponds to exciton binding energy of 0.53 eV, which is slightly larger than the theoretically predicted value. The discrepancy between theory and experiment of about 13 % is evidently connected with the fact that the measurements have been performed at room temperature, while the calculated GW-BSE results were obtained for $T = 0$ K.

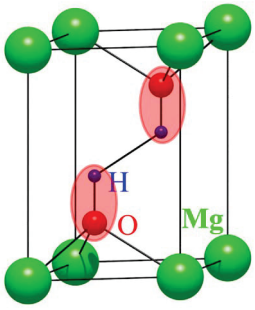


Figure 2: (Color online) Schematic presentation of excitons possessing large binding energy and located in the covalent sublattice of $Mg(OH)_2$.

## 4. Conclusion

We have provided a short review of applications of multifunctional $X(\mathrm{OH})_2$ ($X$=Mg, Ca) in photovoltaic devices as well as latest studies of electronic structure of these materials. The materials possess unique optoelectronic properties, can be synthesized by industrially viable methods, and consists of abundant and non-toxic elements. Based on an analysis of the literature and results of our research work we think that the $\mathrm{Mg(OH)_2}$ have good potential for the use in fabricating optoelectronic and semiconductor devices.

## Acknowledgments

The work was supported by the European Union through the European Regional Development Fund (Centre of Excellence "Mesosystems: Theory and Applications", TK114) and by the Estonian Science Foundation (grant No 7296). Also this work has received financial and supercomputing support from the Research Council of Norway within the FME project (192839) and ISP NANOMAT project (181884).

## References

[1] T. Kuji, M. Chiba, T. Honjo, K. Kotoda, Patent TW200923974. Transparent conductive film and method for making same (2009).

[2] H. Shi, L. Chang, R. Jia, R. I. Eglitis, Ab initio calculations of hydroxyl impurities in caf2, J. Phys. Chem. C 116 (10) (2012) 6392–6400.

[3] T. Krüger, Sequestering carbon dioxide from the atmosphere by enhancing the capacity of the oceans to act as a carbon sink, `http://www.cquestrate.com/` (2008).

[4] C. Estrela, F. C. Pimenta, I. Y. Ito, L. L. Bammann, In vitro determination of direct antimicrobial effect of calcium hydroxide, J. Endod. 24 (1) (1998) 15–17.

[5] Q. Cao, F. Huang, Z. Zhuang, Z. Lin, A study of the potential application of nano-$\mathrm{Mg(OH)_2}$ in adsorbing low concentrations of uranyl tricarbonate from water, Nanoscale 4 (2012) 2423–2430.

[6] A. Gibson, M. Maniocha, White paper: The use of magnesium hydroxide slurry for biological treatment of municipal and industrial wastewater, Martin Marietta Magnesia Specialties, LLC (2004) 1–7.

[7] E. Ghali, W. Dietzel, K.-U. Kainer, General and localized corrosion of magnesium alloys: A critical review, J. Mater. Eng. Perform. 13 (1) (2004) 7–23.

[8] A. C. Snider, Hydration of magnesium oxide in the waste isolation pilot plant, Mat. Res. Soc. Symp. Proc. 757 (2003) II8.3.1–6.

[9] H. Dhaouadi, H. Chaabane, T. Fathi, $Mg(OH)_2$ nanorods synthesized by a facile hydrothermal method in the presence of ctab, Nano-Micro Lett. 3 (2011) 153–159.

[10] C. Henrist, J.-P. Mathieu, C. Vogels, A. Rulmont, R. Cloots, Morphological study of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution, J. Cryst. Growth 249 (1–2) (2003) 321 – 330.

[11] J. Jančář, J. Kučera, Yield behavior of polypropylene filled with $CaCO_3$ and $Mg(OH)_2$. I: "zero" interfacial adhesion, Polym. Eng. Sci. 30 (1990) 707–713.

[12] L. Shi, D. Li, J. Wang, S. Li, D. G. Evans, X. Duan, Synthesis, flame-retardant and smoke-suppressant properties of a borate-intercalated layered double hydroxide, Clays Clay Miner. 53 (3) (2005) 294–300.

[13] T. A. N. Peiris, S. Senthilarasu, K. G. U. Wijayantha, Enhanced performance of flexible dye-sensitized solar cells: Electrodeposition of $Mg(OH)_2$ on a nanocrystalline $TiO_2$ electrode, J. Phys. Chem. C 116 (1) (2012) 1211–1218.

[14] T. A. Nirmal Peiris, K. G. Upul Wijayantha, J. Garcia-Canadas, Insights into mechanical compression and the enhancement in performance by $Mg(OH)_2$ coating in flexible dye sensitized solar cells, Phys. Chem. Chem. Phys. 16 (2014) 2912–2919.

[15] Promotion of charge transport in low-temperature fabricated $TiO_2$ electrodes by curing-induced compression stress, Electroch. Acta 100 (0) (2013) 85–92.

[16] C.-H. Huang, Y.-L. Jan, W.-C. Lee, Investigation of Mg(OOH) films prepared by chemical bath deposition as buffer layers for $Cu(InGa)Se_2$ solar cells, J. Electrochem. Soc. 158 (9) (2011) H879–H888.

[17] H. Miyazaki, R. Mikami, A. Yamada, M. Konagai, Chemical-bath-deposited ZnO and $Mg(OH)_2$ buffer layer for $Cu(InGa)Se_2$ solar cells, Jpn. J. Appl. Phys., Part 1 45 (4A) (2006) 2618–2620.

[18] J.-H. Yum, S. Nakade, D.-Y. Kim, S. Yanagida, Improved performance in dye-sensitized solar cells employing $TiO_2$ photoelectrodes coated with metal hydroxides, J. Phys. Chem. B 110 (7) (2006) 3215–3219.

[19] M. Chiba, D. Endo, K. Haruta, H. Kimura, H. Kiyota, Semiconductive properties of alternating mg/c multi-layer films with hydroxylation treatment, in: Symposium F Oxide Semiconductors and Thin Films, Vol. 1494 of MRS Proceedings, 2013, pp. 197–202.

[20] D. E. Haycock, M. Kasrai, C. J. Nicholls, D. S. Urch, The electronic structure of magnesium hydroxide (brucite) using x-ray emission, x-ray photoelectron, and auger spectroscopy, J. Chem. Soc., Dalton Trans. (1978) 1791–1796.

[21] Y. Zhu, G. Wu, Y.-H. Zhang, Q. Zhao, Growth and characterization of $Mg(OH)_2$ film on magnesium alloy az31, Appl. Surf. Sci. 257 (14) (2011) 6129 – 6137.

[22] K. Azuma, T. Oda, S. Tanaka, Vibration analysis of O−H stretching mode in $Mg(OH)_2$, $Ca(OH)_2$, LiOH, and NaOH by plane-wave pseudopotential DFT calculation, Comput. Theor. Chem. 963 (1) (2011) 215–220.

[23] P. Baranek, A. Lichanot, R. Orlando, R. Dovesi, Structural and vibrational properties of solid $Mg(OH)_2$ and $Ca(OH)_2$ performances of various hamiltonians, Chem. Phys. Lett. 340 (3-4) (2001) 362–369.

[24] B. Weckler, H. D. Lutz, Near-infrared spectra of M(OH)Cl (M = Ca, Cd, Sr), Zn(OH)F, $Cd(OH)_2$, $Sr(OH)_2$, and brucite-type hydroxides $M(OH)_2$ (M = Mg, Ca, Mn, Fe, Co, Ni, Cd), Spectrochim. Acta, Part A 52 (11) (1996) 1507–1513.

[25] H. D. Lutz, H. Müller, M. Schmidt, Lattice vibration spectra. part lxxxii. brucite-type hydroxides $M(OH)_2$ (M = Ca, Mn, Co, Fe, Cd) - IR and Raman spectra, neutron diffraction of $Fe(OH)_2$, J. Mol. Struct. 328 (0) (1994) 121–132.

[26] J. C. Owrutsky, N. H. Rosenbaum, L. M. Tack, R. J. Saykally, The vibration-rotation spectrum of the hydroxide anion ($OH^-$), J. Chem. Phys. 83 (10) (1985) 5338–5339.

[27] R. L. Frost, J. T. Kloprogge, Infrared emission spectroscopic study of brucite, Spectrochim. Acta, Part A 55 (11) (1999) 2195–2205.

[28] S. Raugei, P. L. Silvestrelli, M. Parrinello, Pressure-induced frustration and disorder in $Mg(OH)_2$ and $Ca(OH)_2$, Phys. Rev. Lett. 83 (1999) 2222–2225.

[29] L. Desgranges, G. Calvarin, G. Chevrier, Interlayer interactions in $Mg(OH)_2$: a neutron diffraction study of $Mg(OH)_2$, Acta Crystallogr., Sect. B: Struct. Sci. 52 (1) (1996) 82–86.

[30] M. Catti, G. Ferraris, S. Hull, A. Pavese, Static compression and H disorder in brucite, $Mg(OH)_2$, to 11 GPa: a powder neutron diffraction study, Phys. Chem. Miner. 22 (3) (1995) 200–206.

[31] L. Desgranges, D. Grebille, G. Calvarin, G. Chevrier, N. Floquet, J. C. Niepce, Hydrogen thermal motion in calcium hydroxide: $Ca(OH)_2$, Acta Crystallogr., Sect. B: Struct. Sci. 49 (5) (1993) 812–817.

[32] W. R. Busing, H. A. Levy, Neutron diffraction study of calcium hydroxide, J. Chem. Phys. 26 (3) (1957) 563–568.

[33] H. Oswald, R. Asper, Bivalent metal hydroxides, in: R. M. A. Lieth (Ed.), Preparation and Crystal Growth of Materials with Layered Structures, Vol. I of Physics and Chemistry of Materials with Layered Structures, Springer, 1977, pp. 71–140.

[34] F. Freund, Highly ionic hydroxides: unexpected proton conductivity in $Mg(OH)_2$ and homologues, in: P. Colomban (Ed.), Proton conductors. Solids, membranes and gels - materials and devices, Vol. 2 of Chem. Solid State Mater., Cambridge University Press, 1992, Ch. 9, pp. 138–157.

[35] L. Kumari, W. Z. Li, C. H. Vannoy, R. M. Leblanc, D. Z. Wang, Synthesis, characterization and optical properties of $Mg(OH)_2$ micro-/nanostructure and its conversion to MgO, Ceramics International 35 (8) (2009) 3355–3364.

[36] T. Murakami, T. Honjo, T. Kuji, Dos calculation analysis of new transparent conductor $Mg(OH)_2$-C, Mater. Trans. 52 (8) (2011) 1689–1692.

[37] Pishtshev, A., Karazhanov, S. Zh., Klopov, M., Materials properties of magnesium and calcium hydroxides from first-principles calculations, Comput. Mater. Sci (2014) in Press.

[38] K. Hümmer, Interband magnetoreflection of ZnO, Phys. Status Solidi B 56 (1) (1973) 249–260.

[39] A. Subrahmanyam, S. Kumar, The Kelvin Probe for Surface Engineering: Fundamentals and Design, CRC Press, New Delhi, Chennai, Mumbai, Bengaluru, Kolkata, Thiruvananthapuram, Lucknow, 2010.

[40] K. Momma, F. Izumi, *VESTA3* for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Crystallogr. 44 (6) (2011) 1272–1276.

[41] Meskini, N., Hanke, W., Mattausch, H.J., Balkanski, M., Zouaghi, M., The absorption spectrum of a heteropolar crystal : the role of many-particle effects, J. Phys. France 45 (10) (1984) 1707–1715.

[42] M. Dvorak, S.-H. Wei, Z. Wu, Origin of the variation of exciton binding energy in semiconductors, Phys. Rev. Lett. 110 (2013) 016402.

[43] Dunlap, W. C., Watters, R. L., Direct measurement of the dielectric constants of silicon and germanium, Phys. Rev. 92 (1953) 1396–1397.

[44] K. L. Shaklee, R. E. Nahory, Valley-orbit splitting of free excitons: The absorption edge of si, Phys. Rev. Lett. 24 (1970) 942–945.

[45] H. Yoshikawa, S. Adachi, Optical constants of zno, Jpn. J. Appl. Phys. 36 (10) (1997) 6237.

[46] P. Y. Yu, M. Cardona, Fundamentals of Semiconductors, Springer, New York, 2005.

[47] Pishtshev, A., Karazhanov, S. Zh., Klopov, M., Excitons in $Mg(OH)_2$ and $Ca(OH)_2$ from *ab initio* calculations, Solid State Commun. 193 (0) (2014) 11–15.

[48] J. Heyd, G. E. Scuseria, M. Ernzerhof, Hybrid functionals based on a screened coulomb potential, J. Chem. Phys. 118 (18) (2003) 8207–8215.

[49] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, G. E. Scuseria, Influence of the exchange screening parameter on the performance of screened hybrid functionals, J. Chem. Phys. 125 (22) (2006) 224106.

[50] T. M. Henderson, J. Paier, G. E. Scuseria, Accurate treatment of solids with the HSE screened hybrid, Phys. Status Solidi B 248 (4) (2011) 767–774.

[51] L. Hedin, New method for calculating the one-particle Green's function with application to the electron-gas problem, Phys. Rev. 139 (1965) A796–A823.

[52] M. Rohlfing, S. G. Louie, Electron-hole excitations in semiconductors and insulators, Phys. Rev. Lett. 81 (1998) 2312–2315.

[53] L. X. Benedict, E. L. Shirley, R. B. Bohn, Optical absorption of insulators and the electron-hole interaction: An *Ab Initio* calculation, Phys. Rev. Lett. 80 (1998) 4514–4517.

[54] S. Albrecht, L. Reining, R. Del Sole, G. Onida, *Ab Initio* calculation of excitonic effects in the optical spectra of semiconductors, Phys. Rev. Lett. 80 (1998) 4510–4513.

[55] D. Y. Qiu, F. H. da Jornada, S. G. Louie, Optical spectrum of $MoS_2$: Many-body effects and diversity of exciton states, Phys. Rev. Lett. 111 (2013) 216805.