

First-principles and experimental characterization of the electronic and optical properties of CaS and CaO

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ABSTRACT

Doped alkaline-earth chalcogenides are interesting photoluminescent materials for opto-electronic applications. It is crucial to have an extended knowledge about the undoped bulk CaS and CaO since all the excited state properties of the doped material heavily depend on it. In this work we investigate the structural parameters, electronic band structures, macroscopic dielectric constants and absorption spectra for CaS and CaO compounds. Their quasi-particle band structure in the *GW* approximation yields a value of 4.28 eV and 6.02 eV for the indirect theoretical particle gap of CaS and CaO, respectively. The imaginary part of the macroscopic dielectric function $\varepsilon(\omega)$ is computed including excitonic effects through the Bethe–Salpeter equation. The onset of absorption is within 0.1 eV of the experimental one and the calculated spectrum shows a qualitative agreement with experiment. Our computed exciton binding energies are 0.27 eV and 0.40 eV for CaS and CaO, respectively.

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1. Introduction

The calcium chalcogenides are technologically important as luminescent materials when doped with rare-earth ions. They can be used for efficient cathode-ray tube phosphors, radiation dosimetry, fast high-resolution optically stimulated luminescence imaging and infrared sensitive devices [1,2]. Alkaline-earth sulfides such as CaS and SrS activated with Eu^{2+} can be used for multi-color thin film electroluminescence [3] and as conversion phosphors for white light-emitting diodes.

In this paper we lead a combined experimental and theoretical study of CaS and CaO, focused on electronic and optical properties. The electronic properties of $\text{II}_a\text{--VI}_b$ compounds have been little studied due to serious difficulties in growing single crystals from these refractory compounds. Kaneko et al. [4] tackled this issue and measured the reflectivity spectra of alkaline-earth chalcogenide at 77 K using synchrotron radiation in the region 4–40 eV and later Kaneko and Koda [5] measured reflection and luminescence spectra of the same compounds but at 2 K and in a smaller energy window.

There has been previous related theoretical work. Let us mention in particular the theoretical study by Dadsetani and Doosti [6] using full potential linearized augmented plane wave (FP-

LAPW) calculation within Density Functional Theory (DFT) using the generalized gradient approximation (GGA). They have investigated the optical properties of calcium mono chalcogenide CaX ($X = \text{O}, \text{S}, \text{Se}$ and Te) within the Random Phase Approximation (RPA). The issue of predicting a direct or indirect band gap for CaS and CaO has been discussed in this reference, as well as in the references therein. In the present study, we use more refined tools to examine optical properties of CaS and CaO, and we provide also an experimental absorption spectrum for CaS. Before this study of optical properties, we present *ab initio* calculations of structural properties for CaS and CaO within the DFT framework. Then, electronic band structures for these two materials are computed using the many-body perturbation theory *GW* approximation [7], that is of higher accuracy than DFT-GGA for that purpose. Absorption spectra are computed using the Bethe–Salpeter Equation (BSE) [8] and compared with experiment. The BSE, that includes excitonic effects, also outperforms the RPA. We obtain exciton binding energies of 0.27 eV and 0.40 eV for CaS and CaO, respectively. Such binding energies seem much larger than the ones reported by Kaneko and Koda [5].

2. Experimental

Since the band gap of CaO is higher than 6 eV, the optical absorption edge of CaO could not be determined experimentally

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given the available equipment. Therefore, only CaS samples were analyzed experimentally.

Diffuse reflectance measurements on the powders were performed in the wavelength range 200–800 nm using a Varian Cary 500 spectrometer equipped with an internal integrating sphere, using BaSO₄ as a reference. Reflectance values were converted to absorption data using the Kubelka–Munk function. Undoped CaS was obtained from CERAC (99.99% purity).

3. Calculation method

The calculation of structural properties in this work is based on DFT [9] using the Trouiller–Martins type of pseudopotentials [11] and a plane-wave basis set. The valence electrons treated explicitly in the *ab initio* calculation are 3s² 3p⁶4s²3d⁰, 2s²2p⁴ and 3s² 3p⁴4s⁰3d⁰ for the calcium, oxygen and sulfur pseudopotentials, respectively. The calcium and sulfur ones are atomic pseudopotentials with semi-core states created with a multi-reference scheme from the APE software [10]. The unoccupied d orbitals are included to increase the flexibility of the basis and allow for a closer reproduction of all-electron results. The electronic band structure of both pseudopotentials have been computed for the pure calcium and sulfur as well as CaS materials and lead to a very close reproduction of the bandstructure with respect to their all-electron counterpart: an average of less than 80 meV difference was found on the occupied and the first 8 unoccupied bands.¹ The all-electron calculations have been made using the ELK software: <http://elk.sourceforge.net>.

In order to be converged within 0.5 mHa per atom a kinetic-energy cut-off of the plane-wave basis set of 45 and 38 Hartree was needed for CaS and CaO compounds, respectively. The CaS and CaO both required a 8 × 8 × 8 Monkhorst–Pack sampling [12] of the Brillouin zone. The Perdew–Wang [13] functional form of the local density approximation (LDA) was used to describe the exchange–correlation potential.

The correct inclusion of excited states in an electronic band structure relies on a many-body scheme in the quasi-particle picture. The computation was made within the one-shot G₀W₀ approximation [7] using the Godby–Needs plasmon-pole model [14] for the dielectric function. An extrapolar approximation was used to make the convergence against the number of bands much faster [15]. This extrapolar approximation assumes that all the states above the last state that we took into account have the same energy.

An extrapolar energy of 2.0 Hartree reduced by a factor 3 the number of empty states required for a convergence within 0.1% of the gap value both for screening and self-energy calculations.

For CaS it was required to take 100 bands (200 bands for CaO) into account in the calculation of the screening and 200 bands (the same for CaO) in the computation of the self-energy for a convergence to 1.0 meV for the direct bandgap.

The required kinetic energy cut-off for the dielectric matrix to converge the inverse dielectric matrix within 0.01% of the dielectric constant and within 1.0 meV of the direct bandgap was 10 Hartree (14 Hartree for CaO). A 8 × 8 × 8 Monkhorst–Pack *k*-point grid led to a maximum energy difference of 0.05 eV for high symmetry points.

The quasi-particle electronic band structure on a denser *k*-point grid along high symmetry points was obtained by an interpolation using Wannier functions [20]. This approach is significantly better than the usual method of just using a constant scissor-shift for all unoccupied bands.

The imaginary part of the macroscopic dielectric function $\epsilon(\omega)$ is computed including excitonic effects (electron–hole interaction)

through the solution of the BSE [8] in the Tamm–Dancoff approximation [16]. The same wavevector grid as for the quasi-particle calculation was used for the excitonic calculation. The kinetic-energy cut-off for the dielectric matrix to converge the dielectric function within 50 meV was 4 Hartree and 5 Hartree for CaS and CaO, respectively. The relative convergence below 1% of the absorption spectrum required to take explicitly into account the six top valence bands and the 12 first conduction bands for CaS. For CaO the four top valence bands and the 10 first conduction bands were needed. The convergence of the *k*-point sampling is crucial for BSE calculations and an average over 64 BSE calculation on a 10 × 10 × 10 *k*-point grid was required to converge every value below 1% for the peak position and 8% for the peak height. For CaO the calculations were converged below 0.1% for the peak position and 5% for the peak height using an average over 64 BSE calculations on 12 × 12 × 12 *k*-point grids.

All the first-principles calculations in this work were performed using the Abinit software [17].

4. Results

The lattice parameters of CaS and CaO were calculated after structural relaxation in DFT-LDA to be 5.567 Å and 4.711 Å respectively. These values match the experimental lattice parameters of 5.690 Å [18] and 4.803 Å [19]. The maximal relative error is below 2%.

The electronic band structure calculated at the experimental lattice parameter within the GW approximation for CaS is shown in Fig. 1. The calculations have been performed on a 8 × 8 × 8 Monkhorst–Pack grid and interpolated using Wannier functions [20] to give the final electronic band structure along the traditional highest symmetry points of the rock salt structure.

The direct Γ – Γ band gap is 5.567 eV, the direct X–X gap is 5.133 eV and the indirect Γ –X one is 4.279 eV. These values are compared with the experimental ones in Table 1.

The electronic band structure in the quasi-particle picture within the GW approximation for CaO is shown in Fig. 2.

The direct Γ – Γ band gap is 6.528 eV, the direct X–X gap is 6.463 eV and the indirect Γ –X gap is 6.016 eV. These values are also compared with the experimental ones in Table 1.

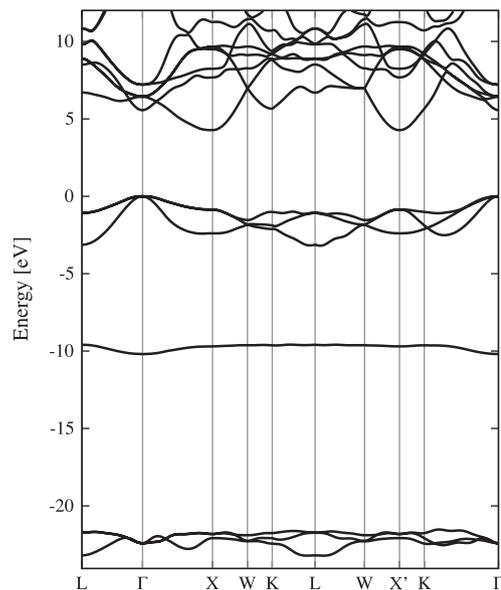


Fig. 1. Quasi-particle electronic band structure of CaS using Wannier interpolation.

¹ The difference on the unoccupied states of FCC bulk sulfur is larger (340 meV) but the FCC configuration is non-physical.

Table 1

(Upper): Theoretical band gaps using the G_0W_0 approximation as well as experimental band gaps energies of CaS and CaO compounds (determined at 2 K). (Middle): The theoretical absorption energies (using the BSE formalism) as well as the experimental absorption energies (determined from reflection spectra) at 2 K except for [22] and our result where it was at 300 K. (Lower): Theoretical dielectric constants are obtained using BSE and the experimental ones from single crystal normal incidence reflection spectra.

	Band-gaps (eV)		
	$E_g(X_c-\Gamma_v)$	$E_g(X)$	$E_g(\Gamma)$
CaS (this work)	4.279	5.133	5.567
(exp.)	4.434 [5]	5.343 [5]	5.8 [5]
CaO (this work)	6.016	6.463	6.528
(FP-LMTO)	6.01 [21]	-	-
(G_0W_0)	6.0 [25]	-	-
(scGW)	7.6 [25]	-	-
(exp.)	7.0 [21]	6.875 [5]	-
Absorption energies (eV)			
	$E(X_c-\Gamma_v)$	$E(X)$	$E(\Gamma)$
CaS (this work, th.)	-	4.86	-
(this work, exp.)	-	4.98	-
(RPA)	-	4.47 [6]	-
(exp.)	-	5.27 [5]	5.74 [5]
(exp.)	-	5.41 [4]	-
CaO (this work)	-	6.06	-
(RPA)	-	6.19 [6]	-
(exp.)	-	6.81 [5]	-
(exp.)	-	6.79 [22]	7.03 [22]
(exp.)	-	7.24 [4]	-
Dielectric constant			
	ϵ_∞		
CaS (this work)	4.80		
(exp.)	4.15 [23]		
CaO (this work)	3.33		
(exp.)	3.33 [24]		

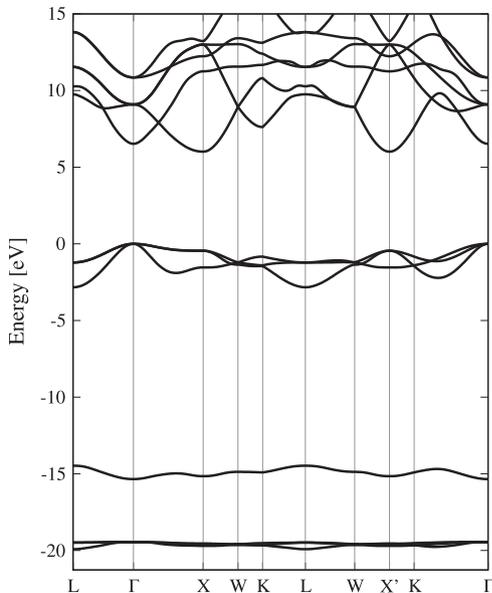


Fig. 2. Quasi-particle electronic band structure of CaO using Wannier interpolation.

In both cases G_0W_0 underestimates the gap with respect to experimental results. This effect, although not yet fully understood, is commonly accepted as well as the fact that self-consistent GW overestimates it [25].

The absorption spectrum can be computed from the imaginary part of the macroscopic dielectric function including excitonic effects through the Bethe–Salpeter equation. The imaginary part of

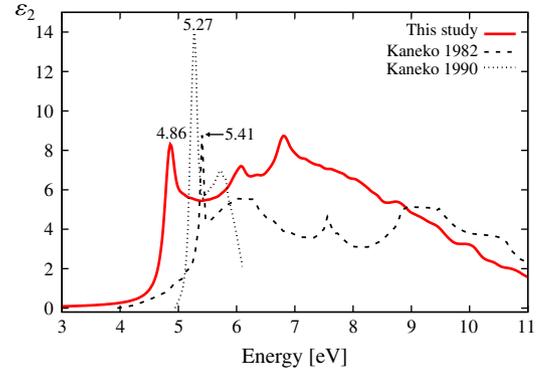


Fig. 3. Quasi-particle absorption spectra (i.e. the imaginary part of the dielectric constant ϵ_2) of CaS including excitonic effect. The spectra in dashed line is the experimental reference from synchrotron radiation at 77 K [4] and the spectra in dotted line is the imaginary part of the complex dielectric constant obtained from an experimental exciton reflection spectra at 2 K [5].

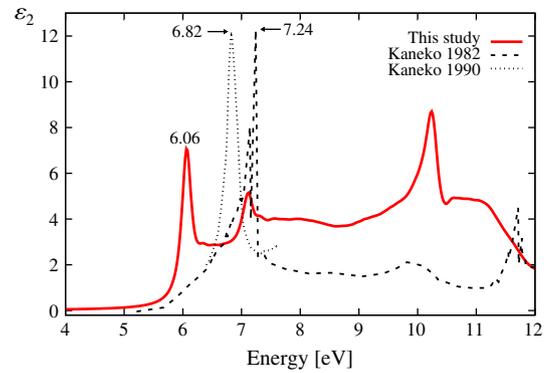


Fig. 4. Quasi-particle absorption spectra (i.e. the imaginary part of the dielectric constant ϵ_2) of CaO including excitonic effect. The spectra in dashed line is the experimental reference from synchrotron radiation at 77 K [4] and the spectra in dotted line is the imaginary part of the complex dielectric constant obtained from an experimental exciton reflection spectra at 2 K [5].

the macroscopic dielectric function ϵ_2 gives the spectrum at zero Kelvin, depicted in Fig. 3 for CaS and in Fig. 4 for CaO and is compared with two experimental spectra [4,5].

The experimental results point toward a lowering of the onset of absorption with decreasing temperature. One can infer that the experimental value at 0 K would be even closer to the theoretical one.

The first absorption peak that will correspond to the $X-X$ direct transition is shifted towards lower energy by 0.27 eV due to excitonic effects (0.40 eV in the case of CaO). These values appear compatible with exciton binding energies in typical sulfide/oxides following Dorenbos' [26] rule of thumb $E_b = 0.08E_g(X)$ for optical gaps (in our case at the X k -point).

Such binding energies seem much larger than the ones reported in Ref. [5]. However, these values are not straightforwardly deduced from the experimental data: they rely on independent-particle theoretical band structure. We hypothesise that this discrepancy may come from the intrinsic limitations of the available theoretical tools in this reference, without explicit treatment of the excitons. Anyhow, for the rest of the spectrum, the experimental data and theoretical spectrum are in qualitative agreement, but quantitatively, there are significant differences.

The zero-frequency limit of the real part of the dielectric function corresponds to the electronic dielectric constant ϵ_∞ because the formalism only probes electronic degrees of freedom while vibrations of the lattice are not included. The electronic dielectric

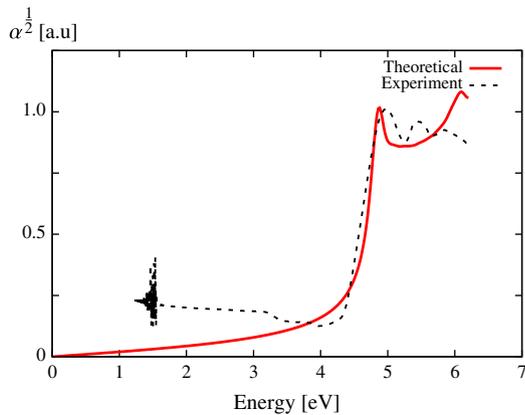


Fig. 5. The dashed line is the absorption spectrum $\alpha^{\frac{1}{2}}$ of CaS obtained from reflectance data and the full line is the theoretical *ab initio* counterpart (without the background noise) computed from the macroscopic dielectric function. They both are in arbitrary unit and the first peak has been chosen to match.

constant for CaS is relatively close to the experimental one (13.5%) of 4.15 [23] whereas the one calculated for CaO is in striking agreement with the experimental value of 3.33 [24].

The complex refractive index is defined as $n = \sqrt{\varepsilon_1 + i\varepsilon_2} = \nu + i\kappa$ and this is also equal to $n = \sqrt{R}e^{i\frac{\phi}{2}}$ with $R = \varepsilon_1^2 + \varepsilon_2^2$ and $\phi = \arctan \varepsilon_2/\varepsilon_1$.

The absorption coefficient is defined as:

$$\alpha = \frac{2\omega\kappa}{c} = \frac{2\omega\sqrt{R}\sin\frac{\phi}{2}}{c}. \quad (1)$$

From this equation and the Bethe–Salpeter macroscopic dielectric function we can compute the absorption function as depicted in Fig. 5. In comparison, we also show in Fig. 5 the experimental absorption spectrum of CaS at room temperature.

We can see that the absorption onsets of both spectra are very close. The actual value of the highest point of the absorption spectra is scaled to match in both spectra. After our theoretical and experimental analysis we suspect that Ref. [5] with an onset value of 5.27 eV is to be questioned.

5. Conclusions

First-principles analysis of CaS and CaO as well as experimental characterization of the CaS compound have been performed. Agreement is observed for the lattice parameter to within 1.2% using DFT with LDA. We confirm the indirect character of the band

gap between the X-point conduction band and the Γ -point valence band for both compounds. The onset of absorption for CaS is reproduced within 0.1 eV using many-body theories including excitonic effects through the Bethe–Salpeter equation. The electronic dielectric constant of 3.33 was matched by the calculation for CaO and the value of 4.15 was approached for CaS. The shape of CaS and CaO absorption spectra qualitatively (and to a certain extent quantitatively) match the experimental one. We report 0.27 eV and 0.40 eV for the exciton binding energies, respectively.

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