Electronic and optical properties of pure and Ce^{3+}-doped CaS single crystals: a first-principles prediction

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This paper investigates the electronic and optical properties for pure and Ce^{3+}-doped CaS crystals by using the first-principles total energy calculations. The results show that CaS:Ce has a direct band gap of 2.16 eV, and the top of the valence band is determined by S $3p$ states and the bottom of the conduction band is determined by Ce $4f$ states, respectively. Our results validate that the yellow emission from CaS:Ce is produced by doped cerium and the green emission quenches at 12.5% cerium concentration. The Ce–S bond shows more covalent character than the Ca–S bond.

Keywords: CaS:Ce, density functional theory, electronic properties, optical properties
PACC: 7115H, 7125T, 7820D

1. Introduction

Wide band gap semiconductors attract an enormous technological interest both because of their potential use in devices capable of operating at high power level and high temperature and because of need for optical materials active in blue–green range. Furthermore, it is well known that rare-earth doped alkaline earth sulfide phosphors are efficient luminescent materials. During the last few decades many luminescence studies have been reported on sulfide compounds doped with rare-earth ions.[1−6] These sulfide compounds have been extensively studied as potential alternating current thin film electroluminescent phosphors because the rare-earth optical transitions are stable at high field.[7] A Ce ion was found to become efficient emission centres and exhibited a blue emission with high colour purity and stability. Vecht *et al.*[8,9] have reported that CaS:Ce powder type DC electroluminescent (EL) devices rival the best ZnS:Mn powder DC EL devices in brightness and efficiency. Two cathodoluminescence emission bands in the green (510 nm) and yellow (580 nm) regions were reported in 1969 and 1976 by Vij *et al.*[10,11] under photoexcitation when CaS:Ce phosphor contained 0.01–1.00% Ce. And they also found that the phosphor could give the brightest green emission at the concentrations of Ce ranging from 0.08% to 0.10%. Further, it was apparently found that for higher concentrations of Ce, the green emission quenches faster than the yellow emission. In 1984 Shanker *et al.*[12] reported the EL spectrum which consisted of a strong emission with a peak at 505 nm and a broad band with a peak at 570 nm due to $5d \rightarrow 4f$ transition of Ce^{3+} at 0.3 mol% Ce concentration. This EL spectrum agreed very well with the cathodoluminescence spectrum.[10,11] In 1990 Kim *et al.*[13] pointed out that the general features of the photoluminescence spectrum were almost identical up to 0.2 mol% cerium concentration in the CaS phosphor. At the same time, a peculiar change in the photoluminescence spectrum was observed that the green emission quenched when the concentrations of Ce exceeded l mol%. But Jia *et al.*[14] confirmed that the emission of CaS:Ce phosphor consisted of two green emission bands. It seems that this system needs more thorough investigation to understand the physical processes involved in its luminescence in view of its potential applications. So far, there is no theoretical study on the electronic and optical properties of CaS:Ce crystals. In possible approaches for theoretical calculation, first principle calculations have been very successful in predicting the electronic and optical properties of a number of alkali metal halides and alkaline earth chalcogenides.[15−18] Previously, we presented the study of structural and electronic properties for pure CaS.[19] In this work, structural, electronic, and optical properties of CaS:Ce material have been investigated by using the first-principles density

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functional calculations in order to reveal a complete understanding of the basically physical properties.

2. Calculational method

The calculations were performed by using the plane-wave pseudopotential method based on density functional theory (DFT) with the generalized gradient approximation (GGA) in the scheme of revised Perdew–Burke–Ernzerhof.[20] Also, we use the on-site Coulomb interaction U∼6 eV for the description of correlation effects in localized f bands for Ce in the local-density approximation (LDA) computational scheme in the calculation of electronic and optical properties. The ion–electron interaction was modeled by Norm-conserving pseudopotentials.[21] A plane-wave cutoff energy of 700 eV was employed throughout the calculation. For the sampling of the Brillouin zone, the electronic structures and optical properties use $5 \times 5 \times 2$ and $7 \times 7 \times 5$ k-point grids, respectively, generated according to the Monkhorst–Pack scheme. The charge densities were converged to 2×10^{-6} eV/atom in the self-consistent calculation. The CaS:Ce supercell ($1 \times 1 \times 2$) containing 16 atoms (eight Ca atoms and eight S atoms) by substituting a Ca atom located in (0.5, 0.5, 0.5) with a Ce atom with the doping concentrations of 12.5% was used and the calculated lattice constant[19] was adopted. Each supercell contained only one Ce atom in order to avoid the interaction of doping atoms. In the optimisation process, the energy change, maximum force, maximum stress, and maximum displacement tolerances were set as 2×10^{-5} eV/atom, 0.05 eV/Å, 0.1 GPa, and 0.002 Å (1 Å=0.1 nm), respectively. In our calculation, the scissor operators on both the electronic structure and optical properties were not considered. The optical transition calculation without the gap correction can actually give better agreement in the peak positions than those with gap correction.[22−30]

3. Results and discussion

3.1. Electronic structure

Figure 1 shows the perspective views of the CaS:Ce structure. Our calculated structural parameters are listed in Table 1 along with comparison of available experimental values.[31,32] The results show that the CaS:Ce structure expands slightly in comparison with the pure CaS crystal, which is natural because the large cation Ce replaces the smaller cation Ca. The trend is consistent with our previous calculation on MgS:Ce.[33] So far there exists not an experimental measurement, which can be used to compare with our theoretical predictions.

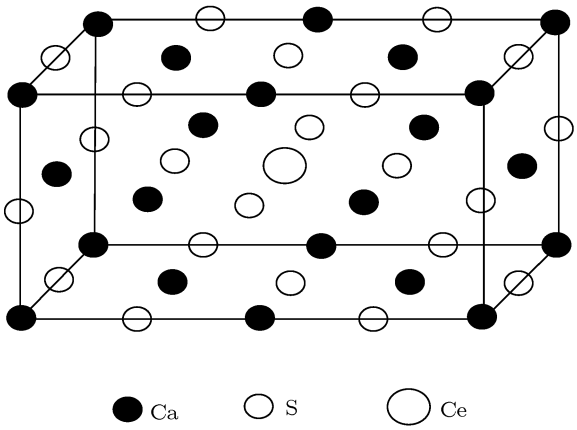


Fig. 1. Crystalline structure of the CaS:Ce crystal.

Table 1. Calculated and experimental structural properties of pure CaS and CaS:Ce.

	lattice constant a/Å	
	Calc.	Exp.
CaS	5.701	5.689[32] 5.696[31]
CaS:Ce	5.737	

The energy band structures are calculated for CaS and CaS:Ce along the high-symmetry directions in the Brillouin zone, as shown in Fig. 2, and the total density of states (TDOS) and the partial DOS (PDOS) are plotted in Fig. 3.

For pure CaS, the top of the valence band (VB) is mainly composed of S 3p states. The bottom of the conduction band (CB) is dominated by Ca 3d states, it is obvious that there is a strong hybridization of the Ca 4s and 3d with the S 3p states (Fig. 3). The result is consistent with the previous study.[34,35] The CaS presents an indirect band gap of 2.37 eV along $G-X$ line of the Brillouin zone, which is in excellent agreement with the other theoretical calculations,[34,36] but is less than the experimental value.[37,38] The underestimated band gap can be due to the choice of exchange–correlation energy.

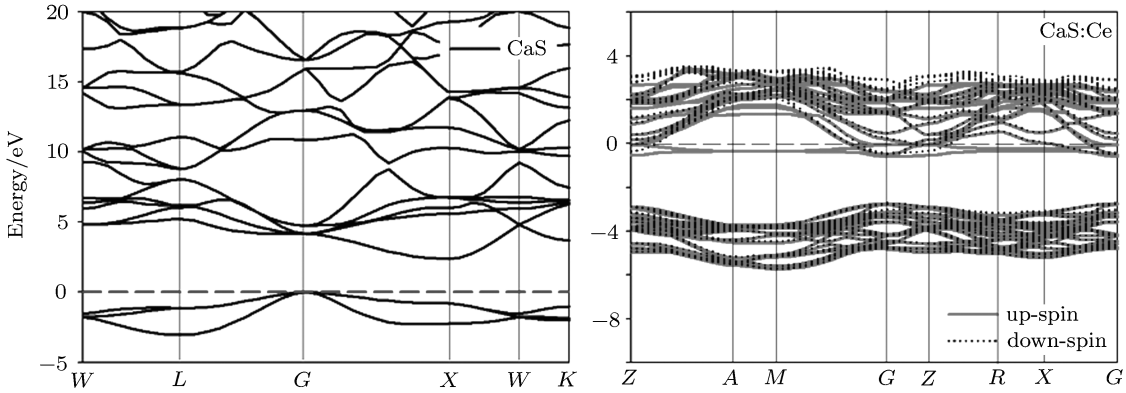


Fig. 2. Band structure of CaS and CaS:Ce. The position of the Fermi level is set to be 0 eV.

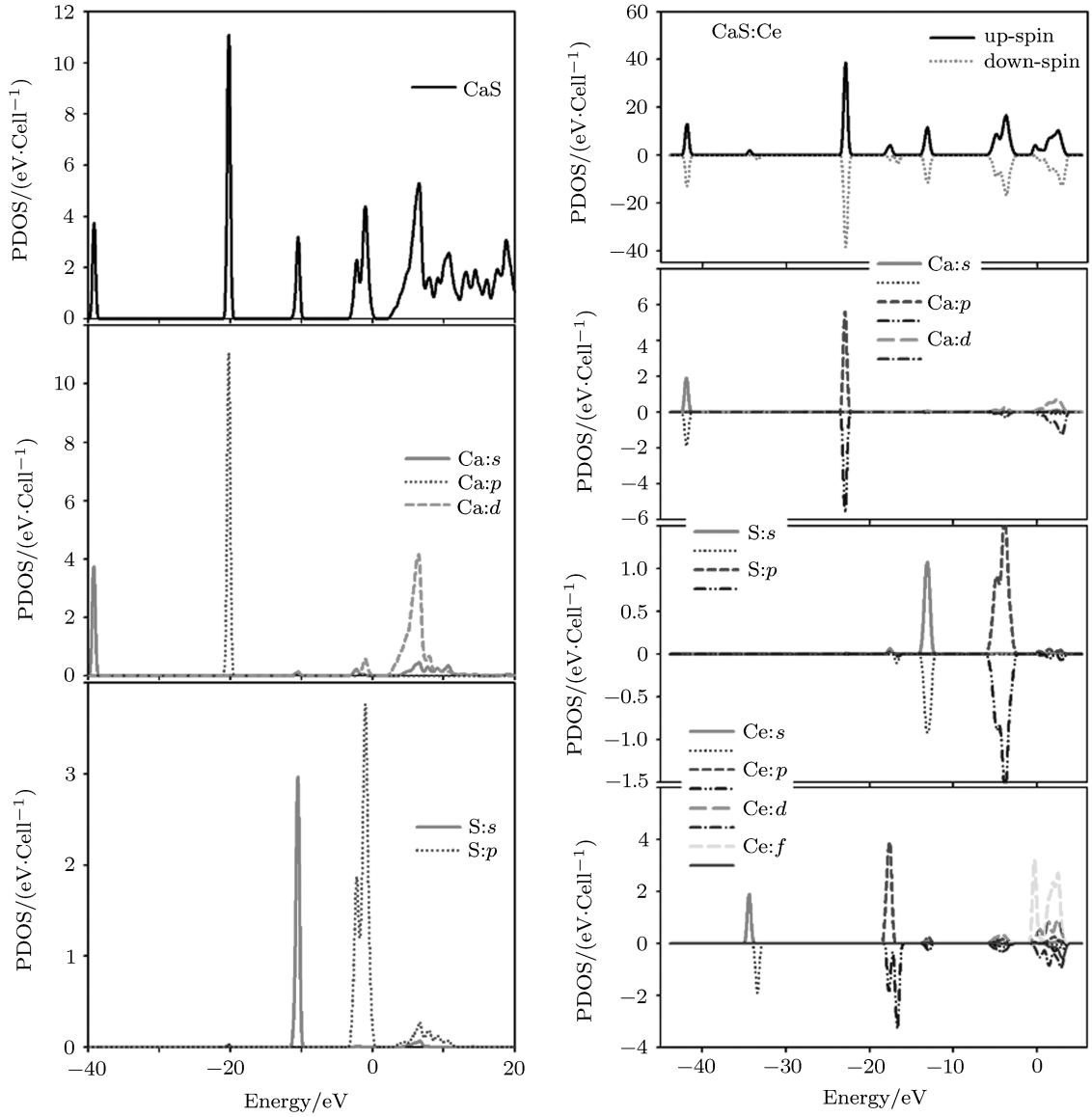


Fig. 3. Total DOS (TDOS) and PDOS of CaS and CaS:Ce.

In contrast, for CaS:Ce, the uppermost VB mainly consists of the S $3p$ states, the lowest CB is dominated by Ce $4f$ states, and presents a direct band gap of 2.16 eV at the G point corresponding to an absorption edge of 572 nm, which is in excellent agreement with the experimental observed emission peak at about 570 nm.[10−13] Our result is also consistent with the measurement made by Kim *et al.*[13] that the green emission quenched and the emission of this new luminescence centre shifted to the longer-wavelength region as the concentration of cerium increased and exceeded 1 mol%. However, there are no experimental data available so far to verify the calculated energy band of CaS:Ce. The band structure shows more compact and slightly shifts to low energy band throughout the region of the VB and CB, which suggests that Ce incorporation causes stronger interaction between cation and anion. This phenomenon is consistent with our DOS calculation. The Ce $4f$ and $5d$ states have appeared in the bottom of the CB ranged from about -1 to 5 eV, and there is large Ce $4f$ and little Ce $5d$ states moving across the Fermi level due to the use of LSDA+U. The large asymmetry of Ce $4f$ states is a strong indication of local magnetic moment, we calculated the magnetic moments to be 6.2×10^6 Pa for Ce. There also exists a strong hybridization interaction between Ce $4f$ and Ca $3d$ states, ranging from -0.30 to 4 eV. Meanwhile S $3s$ and $3p$ states weaken evidently in the top of the VB region due to Ce incorporation, indicate more electrons transfer to Ce $5d$ and $4f$ states from S $3s$ and $3p$ states.

To better understand the bonding behaviour of CaS:Ce, a calculation of the Mulliken charge population was performed, which is shown in Table 2.

Table 2. Mulliken charge population of CaS:Ce.

species	s	p	d	f	total/e	charge/e
Ca_1	2.27	6.00	0.74	0	9.01	0.99
Ca_{2-5}	2.25	6.00	0.78	0	9.03	0.97
Ca_6	2.27	6.00	0.79	0	9.05	0.95
Ca_7	2.23	6.00	0.75	0	8.98	1.02
S_{1-2}	1.86	5.07	0	0	6.92	–0.92
S_{3-4}	1.87	5.12	0	0	6.99	–0.99
S_{5-6}	1.87	5.14	0	0	7.02	–1.02
S_{7-8}	1.84	4.96	0	0	6.80	–0.80
Ce	2.25	6.54	1.57	1.02	11.37	0.63

The charge transfers from Ce to S are about $0.63e$. The bond order analysis shows that the Ce–S bond has values of 0.29 and 0.68, while the Ca–S bond has more variable bond order values of 0.11, 0.17, 0.21, 0.30, 0.33, 0.34 and 0.35, depending on the coordination environment in the CaS:Ce structure. The closer to 1 of the bond order is, the more covalent character the bond has. Therefore, the Ce–S bond shows more covalent character than the Ca–S bond.

3.2. Optical properties

The optical properties of CaS and CaS:Ce is determined by the frequency-dependent dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + \mathrm{i}\,\varepsilon_2(\omega)$, which is mainly connected with the electronic structures. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function $\varepsilon(\omega)$ is calculated from the momentum matrix elements between the occupied and unoccupied electronic states and given by

$$\varepsilon_2 = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}|\langle\psi_k^{\mathrm{c}}|\hat{u}\cdot r\,|\psi_k^{\mathrm{v}}\rangle|^2\,\delta(E_k^{\mathrm{c}} - E_k^{\mathrm{v}} - E),$$

where ω is the light frequency, e is the electronic charge, ψ_k^{c} and ψ_k^{v} are the CB and VB wave functions at k, respectively. The real part is derived from the imaginary part $\varepsilon_2(\omega)$ by the Kramers–Kronig transformation. All other optical constants, such as the absorption spectrum, refractive index, and reflectivity, are derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.[39]

The calculated dielectric function of CaS and CaS:Ce are shown in Fig. 4. The peaks of the imaginary part of the dielectric function are related to the electron excitation. To pure CaS, the main peaks, as seen in Fig. 4, are 6.25, 11.67 and 26.57 eV, which is in excellent agreement with the theoretical results of about 6 and 11 eV ranged from 0–20 eV obtained by Shaukat *et al.*[40] and Ching *et al.*[36] For the three peaks, the strongly contributing regions of k space are much the same as those for the III–V materials.[41] The optical transition of the first two peaks is ascribed to the transition between S $3p$ in the highest VB and Ca $3d$ in the lowest CB. The third peak may be ascribed to the transition between S $3s$ in the VB and Ca $3d$ in the lowest CB. The first critical point of the dielectric function $\varepsilon_2(\omega)$ occurs at about 2.36 eV for CaS, this is attributed to the threshold for the direct optical transitions between the VB maximum and the first CB minimum, which is in excellent agreement with our calculated band gap value of 2.37 eV. After Ce incorporation, the optical transitions of 0.50, 5.41 and 25.56 eV are observed, which are lightly shifted to low energy range. However, the peak of 11.67 eV for CaS disappears. The 0.50 eV peak is associated with

transitions in the Ce^{3+} $5d \rightarrow 4f$ states. The 5.41 eV peak is associated with transitions in the S $3p \rightarrow$ Ce $5d$ states. The calculated static dielectric constant, $\varepsilon_1(0)$, is 5.49 for CaS, which is in good agreement with the experimental value of 4.24.[42] and the other theoretical values of 4.75[40] and 4.47,[36] however, Ce doping CaS leads to very large static dielectric constant value of 11.3, suggesting that CaS:Ce is a promising dielectric material.

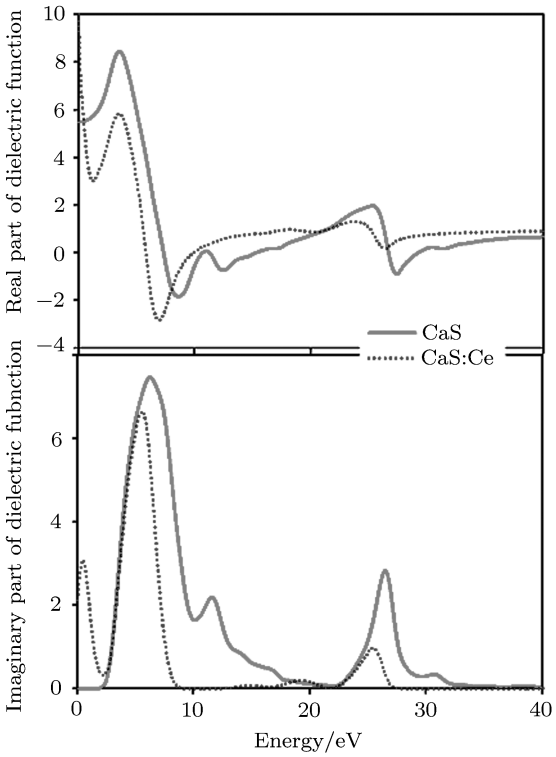


Fig. 4. The dielectric function of CaS and CaS:Ce.

The calculated results on the absorption spectrum, reflectivity, and energy-loss spectrum are also shown in Fig. 5. It is clearly observed that the Ce incorporation induces the decreasing optical absorption over a large range of energy of 2 to 40 eV. Simultaneously, the optical absorption peaks are evidently shifted to low energy range, which is in excellent agreement with the result made by Kim *et al.*[13] that the emission of luminescence centre shifted to the longer-wavelength region as the concentration of cerium increased. This result is also in good agreement with the result by Vij *et al.*[11] that the green emission quenches faster than the yellow emission for higher concentrations of Ce. At about 10 eV, optical reflectivity presents a strong reflex peak in ultraviolet light regions. The energy-loss spectrum describes the energy loss of a fast electron traversing the material and is usually large at the plasma energy. A prominent peak is found at 10 eV, which corresponds to a rapid reduction in the reflectance. This process is associated with the transitions from the filled S $3p$ bands to empty CB.

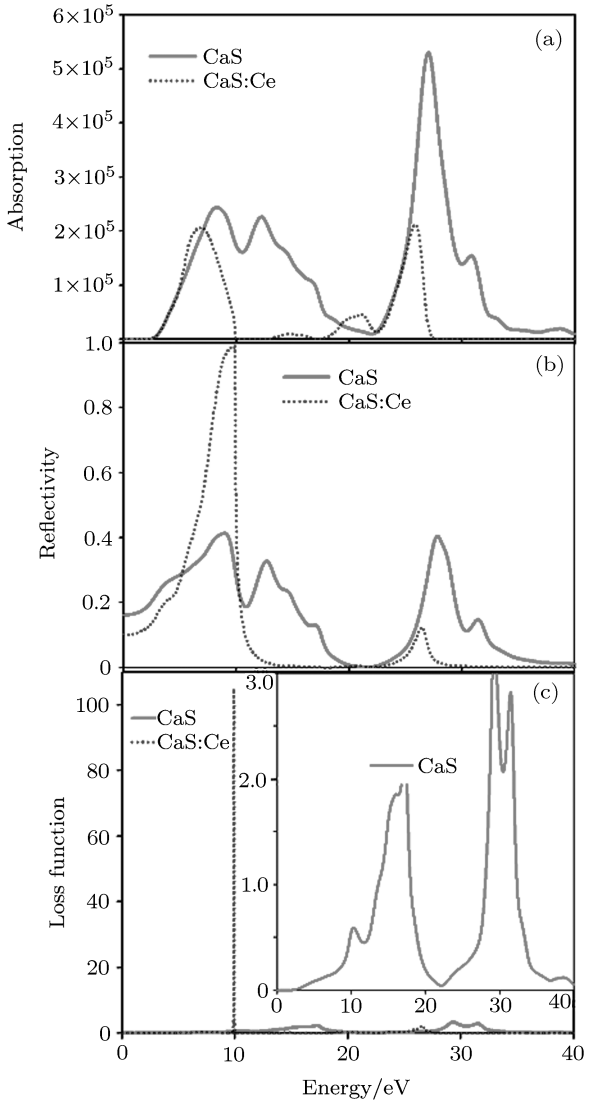


Fig. 5. Optical constants of CaS and CaS:Ce: (a) absorption spectrum; (b) reflectivity; (c) energy-loss spectrum.

4. Conclusion

In summary, we calculated the structural parameters, electronic and optical properties of CaS and CaS:Ce by means of the DFT within GGA. Our structural parameters of CaS are in good agreement with the experimental data. The electronic structures of CaS:Ce show that the top of the VB is determined by S $3p$ states, the bottom of the CB is determined by Ce $4f$ states. Furthermore, the Ce–S bond shows more covalent character than the Ca–S bond. Finally, the dielectric function, absorption spectrum, reflectivity, and energy-loss spectrum are obtained and discussed in detail.

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