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Theoretical Calculations on Electronic Structure and Optical Properties of Orthorhombic SrHfO$_3$ in Cmcm Space Group

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Abstract: Electronic structure and optical properties of Cmcm orthorhombic SrHfO$_3$ were computed, using the plane-wave ultrasoft pseudopotential technique based on the first-principles density functional theory (DFT). The equilibrium lattice parameters of orthorhombic SrHfO$_3$ are in good agreement with experimental values. The band structure, the densities of states (DOS) and charge densities of Cmcm orthorhombic SrHfO$_3$ have been obtained. The band structure shows that Cmcm orthorhombic SrHfO$_3$ has direct band gap. The charge densities of Cmcm orthorhombic SrHfO$_3$ indicate that bonding between Hf and O is mainly covalent whereas the bonding between Sr and O is mainly ionic. The complex dielectric function, refractive index and absorption coefficient of Cmcm orthorhombic SrHfO$_3$ have been predicted. The imaginary and real parts of the calculated complex dielectric function are close to the results of experimental measurements.

Key words: first-principles; electronic structure; optical properties; orthorhombic SrHfO$_3$ material

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Recently, ABO$_3$ perovskite materials are extensively studied due to their unusual ferroelectric, piezoelectric, dielectric, magnetic and electrochemical properties [1-11], which have many technological applications in the thermal barrier coatings [4,5], microwave ceramic resonators [6], optoelectronic materials [7,8], phosphor [9], and high-κ dielectric gate in MOSFET [10,11], etc. Among them, Hf-based SrHfO$_3$ perovskite oxide has attracted much attention because of its good electrical and physical properties such as high dielectric constant, large band gap, optimal band offsets and high melting temperature. Additionally, SrHfO$_3$ used as high-gate dielectric oxides for the next generation of CMOS devices have been studied both experimentally [11-13] and theoretically [14-16]. Previous theoretical studies focused mainly on the high temperature cubic phase of SrHfO$_3$ [15-19]. Nevertheless, SrHfO$_3$ adopts the Cmcm orthorhombic structure in a wide range of temperatures where its useful applications take place.

However, there are very few theoretical studies on the properties of orthorhombic SrHfO$_3$ [20, 21]. In order to fully take advantage of the properties of SrHfO$_3$ in applications of optoelectronic devices, the theoretical investigations of the electronic structure and the optical properties of orthorhombic SrHfO$_3$ are crucial. To the best of our knowledge, no systematical studies on the relations between electronic structure and optical properties of orthorhombic SrHfO$_3$ have been reported so far.

In the present paper, the first-principles calculations were used to study the electronic structure and the optical properties of Cmcm orthorhombic SrHfO$_3$. Current work was focused on investigating the relations between electronic structure and optical properties of Cmcm orthorhombic SrHfO$_3$ so as to clarify its mechanism of optical transitions.

1   Computation Methods

The calculations presented in this study were performed using the localized density approximation (LDA) with the Ceperley-Alder-Perdew-Zunger (CA-PZ) function [22] based on density functional theory (DFT) and implanted in CASTEP package [23]. The ionic cores were represented by ultrasoft pseudo-potentials for Hf, Sr and O atoms. The Sr 4s, 4p, 5s electrons, Hf 5p, 5d, 6s electrons and O 2s, 2p electrons were explicitly treated as valence electrons. The plane-wave cutoff energy was set to be 380 eV and the Brillouin-zone integration was performed over the 4×4×3 grid sizes using the Monkorst-Pack method [24] for structure optimization. This set of parameters assured the total energy convergence of 5.0×10^{-6} eV/atom, the maximum force of 0.1 eV/nm, the maximum stress of 0.02 GPa, and the maximum displacement of 5.0×10^{3} nm.

2   Results and Discussion

2.1   Structure optimization

Orthorhombic $SrHfO_3$ in Cmcm space group has the local symmetry of D_{2h}^{17}. The total energy of Cmcm orthorhombic $SrHfO_3$ was calculated at different volumes around the experimental volume. The calculated total energies were fitted to the Murnaghan[25] equation of state to obtain the equilibrium lattice constant. Fig.1 shows the energy-volume curves. In Fig.1, the lowest energy comes from the volume of 71.4×10^{-3} nm^3 and then the equilibrium lattice parameters of Cmcm orthorhombic $SrHfO_3$ can be obtained. Table 1 summarizes the calculated lattice constants of Cmcm orthorhombic $SrHfO_3$ as compared with other theoretical values[5,11,17,19] and experimental data[10,12,21]. It can be seen that our calculated results are in good agreement with the available experimental values[10,12].

2.2   Electronic structure

The energy band structure of orthorhombic $SrHfO_3$ in Cmcm space group is shown in Fig.2. The Fermi level (E_F) is set to zero energy. It can be seen from Fig.2 that orthorhombic $SrHfO_3$ in Cmcm space group has direct band gap because the top valence and the bottom conduction are

found at the same G point. The calculated band gap of Cmcm orthorhombic $SrHfO_3$ is about 3.25 eV, which is in agreement with other calculational results (3.74 eV[14], 3.7 eV[18] and 3.2 eV[19]). Nevertheless, the calculated band gap is smaller than the experimental data of 6.1 eV[11] because of the well-known underestimation of conduction band state energies inabinitio calculations.

Fig.3 shows the total and the partial DOS of Cmcm orthorhombic $SrHfO_3$. As can be seen, there are three valence bands in the total DOS of Cmcm orthorhombic $SrHfO_3$. The lower valence bands from –32.7 eV to –31.7 eV are composed of Sr-s states. The middle valence bands from –17.1 eV to –13.1 eV are essentially dominated by Sr 4p and O 2s. The upper valence bands from –4.0 eV to –0.3 eV consist mainly of O 2p which shows a hybridization character with Hf 5d electrons. In addition, the unoccupied conduction bands from 4.2 eV to 10 eV are composed predominantly of Hf 5d which shows a hybridization character with O 2p and Sr 4p. Moreover, the s state of Sr atom and s, p states of Hf atom are also contributing to the conduction bands, but the values of densities of these states are quite small compared with Hf 5d states.

Fig.4 shows the charge densities in the (020) plane of Cmcm orthorhombic $SrHfO_3$. It is clear to see from Fig.4 that the bonding structure between Sr and O is mainly ionic for Cmcm orthorhombic $SrHfO_3$. Additionally, the bonding structure between Hf and O is mainly covalent due to Hf 5d and O 2p hybridization. These characteristics agree well with the results of previous analysis of DOS.

Table 1   Calculated lattice constants (*a*, *b* and *c*) of Cmcm orthorhombic $SrHfO_3$ as compared with the other calculational values and experimental data (nm)

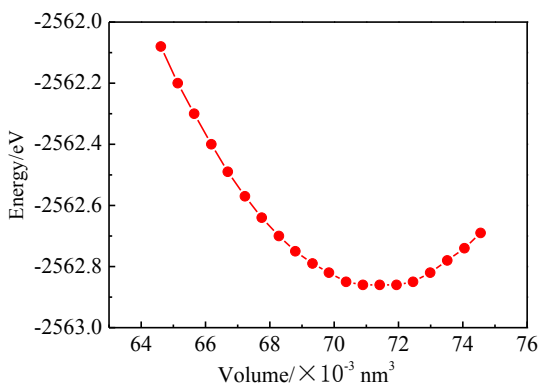| Constants	*a*	*b*	*c*
This work	0.821 24	0.832 35	0.831 07
Previous Calc.[11]	0.804 99	0.807 28	0.805 54
Expt.[12]	0.817 41(16)	0.819 74(12)	0.817 97(11)

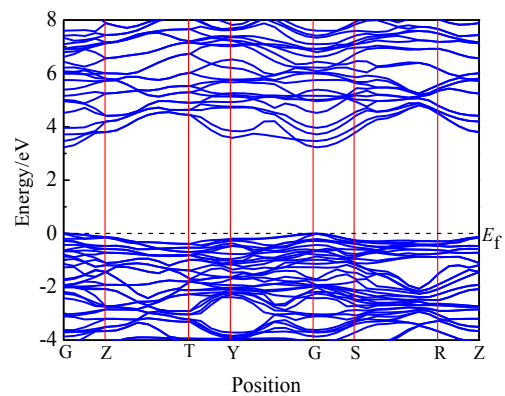Fig.1   Calculated total energies as a function of the cell volumes for Cmcm orthorhombic $SrHfO_3$

Fig.2   Band structure of Cmcm orthorhombic $SrHfO_3$ along with the high-symmetry points of the Brillouin zone