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Band structure and dielectric properties of orthorhombic $SrZrO_3$

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Abstract

Ab initio density functional theory has been used to study the electronic band structure, $k = 0$ (zone center) vibrational modes, and dielectric properties of the crystalline high-κ perovskite oxide $SrZrO_3$. The frequencies of the $k = 0$ normal modes are computed by the linear response technique and then grouped according to their symmetry. The dielectric intensity of each IR-active mode has been determined. It is found that the calculated orientationally averaged static dielectric constant $\varepsilon^0 = 21.49$ is in good agreement with experiment.

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Keywords: A. $SrZrO_3$; D. Band structure; D. Dielectric constant; D. Phonon modes

1. Introduction

Strontium zirconate ($SrZrO_3$) belongs to the perovskite family with the general formula ABO_3 and has an orthorhombic structure at room temperature with space group *Pbnm* [1]. Perovskite oxides are important materials for various functional devices. $SrZrO_3$-based perovskite oxides have been studied for their high-temperature protonic conductivity [2], which makes them potential candidates for electrolytes in some novel electrochemical devices such as solid oxide fuel cells and hydrogen sensors.

Besides, $SrZrO_3$ has many characteristics which are suitable for high voltage and high reliability capacitor applications. It has high dielectric constant, high breakdown strength and low leakage current density. It has a large optical gap of $\approx$5.6 eV [3]. Recently, $SrZrO_3$ has been experimentally investigated as a possible candidate material for high-κ gate dielectrics [4,5].

The purpose of the present work is to investigate theoretically the electronic band structure and the electronic as well as the lattice contribution to the dielectric constant of orthorhombic $SrZrO_3$. We first check that the relaxed structural parameters are consistent with previous experimental work [1]. Using density functional perturbation theory, the frequencies of $k = 0$ (zone center) normal modes are computed and then grouped according to their symmetry. The dielectric intensities of IR-active modes are also determined. It is found that the modes at 229.8 cm^{-1}, 236.3 cm^{-1} and 269.7 cm^{-1} have the highest contribution to the dielectric constant along the x, y and z directions, respectively. The calculated orientationally averaged static dielectric constant is in reasonable agreement with experimental data.

The paper is organized as follows. Section 2 describes technical aspects of the calculations. Section 3 presents the results, including the electronic band structure, phonon normal modes, and the electronic and lattice contributions to the static dielectric tensor. Section 4 concludes the paper.

2. Technical aspects

Crystalline $SrZrO_3$ has been studied via ab initio calculations within density functional theory [6] to determine the structural parameters (as well as electronic band structure) and within density functional perturbation theory [7–10] to obtain the frequencies of normal modes and dielectric tensors, with the use of the ABINIT code [11]. The exchange-correlation energy is evaluated in the local density approximation [12] using Ceperley–Alder electron gas data [13]. The all-electron potentials are replaced by norm-conserving pseudopotentials [14,15].

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Table 1
The optimized lattice constants a, b, c (in Å) and atomic coordinates x, y, z (in fractional units of cell parameters) of $SrZrO_3$ compared with experimental values

Lattice constants			Calculated		Experimental [1]	
a			5.652		5.796	
b			5.664		5.817	
c			7.995		8.205	
	Atomic coordinates					
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sr	0.007	0.534	0.25	0.0040	0.5242	0.25
Zr	0	0	0	0	0	0
O(1)	−0.107	−0.036	0.25	−0.0687	−0.0133	0.25
O(2)	0.199	0.301	0.056	0.2154	0.2837	0.0363

The Sr $4p^6$, Sr $5s^2$, Zr $4s^2$, Zr $4p^6$, Zr $4d^2$, Zr $5s^2$, O $2s^2$, and O $2p^6$ levels are treated as valence states. The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 55 Ha. Integrals over the Brillouin zone were approximated by sums on a $3 \times 3 \times 2$ mesh of special k-points [16]. The structural parameters are obtained by optimizing lattice constants and atomic coordinates until all force components are below 10^{-2} eV/Å. The vibrational modes and effective dynamical charges, as well as the dielectric tensors, are calculated as linear-response derivatives [7–10].

3. Results

The orthorhombic phase of $SrZrO_3$ with space group *Pbnm* has four formula units per unit cell. The comparison of experimental and calculated structural parameters is given in Table 1.

As can be seen from Table 1, the calculated lattice constants are in good agreement with the experimental data [1], but a little bit smaller. The underestimation results from the use of local density approximation within the density functional calculation. Only the coordinates of atoms occupying the Wyckoff position with free parameters are optimized in the structural relaxation. The coordinates of the Zr atom are fixed by space group number. As can be seen from Table 1, the optimized atomic coordinates are very close to the experimental values.

The energy band structure and density of states of the orthorhombic phase of $SrZrO_3$ are given in Fig. 1, where the zero of energy is chosen in such a way to coincide with the top of the valence band. The lower valence bands consist of two parts that are separated by a 0.5 eV gap. The lower part is composed of O 2s and Sr 4p semicore states, whereas the upper part is mainly due to Sr 4p with a few mixings with O 2s and O 2p states. The upper valence bands are mainly due to O 2p states with some mixings with Zr 4d states. The lower conduction bands consist of Zr 4d states with some mixings with O 2p states.

The maximum of the valence band is located at the U point and has O 2p character, whereas the conduction band minimum is at the Γ point and has Zr 4d character. The indirect band gap between the Γ and U points is 3.764 eV. However, the valence band is very flat, so the direct band gap at Γ is only slightly higher, 3.799 eV. As far as we know, there is no theoretical result on the electronic band structure of the orthorhombic phase of $SrZrO_3$ to compare with. A comparison of the present results can be made with the cubic phase of $SrZrO_3$, where density functional calculations within the local density approximation give an indirect band gap of 3.37 eV [17]. The present results thus indicate that the orthorhombic phase of $SrZrO_3$ has a bigger band gap than the cubic phase. The experimental value of the band gap of $SrZrO_3$ was determined as 5.6 eV, using optical conductivity analysis of the polycrystalline sample at room temperature [18].

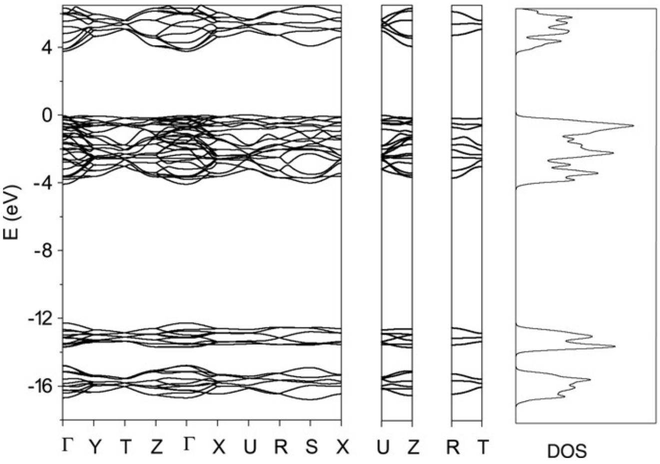

Fig. 1. Electronic band structure and density of states of the orthorhombic phase of $SrZrO_3$.

Now, we investigate the dielectric properties of orthorhombic $SrZrO_3$. The static dielectric tensor ε^0 can be separated into electronic ε^∞ and ionic $\varepsilon^{\text{ionic}}$ components: $\varepsilon^0 = \varepsilon^\infty + \varepsilon^{\text{ionic}}$. The ionic component is

$$\varepsilon^{\text{ionic}}_{\alpha\beta} = \frac{4\pi e^2}{\Omega} \sum_{\lambda} \frac{Z^*_{\lambda\alpha} Z^*_{\lambda\beta}}{\omega^2_\lambda} \tag{1}$$

where

$$Z^*_{\lambda\beta} = \sum_{i\beta} \frac{z^*_{i,\alpha\beta} \xi_{i,\lambda\beta}}{\sqrt{M_i}} \tag{2}$$

are the mode effective charge tensors. Here α and β label the Cartesian coordinates, e is the electron charge, Ω is the volume of the unit cell, ω_λ is the frequency of the λth IR-active phonon normal mode, $z^*_{i,\alpha\beta}$ the effective charge tensor of atom i, and $\xi_{i,\lambda\beta}$ is the eigendisplacement of atom i in phonon mode λ.

The squares of phonon frequencies at $k = 0$ (zone center) can be obtained as eigenvalues of the dynamical matrix

$$D^{\alpha\beta}_{ij} = \frac{\Phi^{\alpha\beta}_{ij}}{\sqrt{M_i M_j}}. \tag{3}$$

The force constant matrix $\Phi^{\alpha\beta}_{ij}$ can be expressed as a sum of an analytical and a non-analytical part [19]. The analytical part can be obtained by calculating all the Hellmann–Feynman forces (F^α_i) caused by displacing each ion in each possible