

DFT LCAO and plane wave calculations of SrZrO₃

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The results of the density functional (DFT) LCAO and plane wave (PW) calculations of the electronic and structural properties of four known SrZrO₃ phases (Pm3m, I4/mcm, Cmcn and Pbnm) are presented and discussed. The calculated unit cell energies and relative stability of these phases agree well with the experimental sequence of SrZrO₃ phases as the temperature increases.

The lattice structure parameters optimized in the PW calculations for all four phases are in good agreement with the experimental neutron diffraction data. The LCAO and PW results for the electronic structure, density of states and chemical bonding in the cubic phase (Pm3m) are discussed in detail and compared with the results of previous PW calculations.

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Strontium zirconate SrZrO₃ is of interest because of possible applications in fuel cells, hydrogen gas sensors and steam electrolysis [1]. The powder neutron diffraction data suggest the following sequence of phase transitions in SrZrO₃: from the orthorhombic Pbnm to the orthorhombic Cmcn at 970 K, the tetragonal I4/mcm at 1100 K and lastly, to the cubic Pm3m at 1400 K [2]. The tetragonal phase has two formula units and orthorhombic phases have four formula units in the primitive cell. As far as we know, the only electronic structure calculation of SrZrO₃ [3] was performed for the cubic phase (with one formula unit in the primitive unit cell) using the DFT–LDA approximation and the plane wave (PW) basis set.

In this paper we present results of the first ab initio DFT calculations for all four phases of SrZrO₃ using both PW and LCAO (linear combination of atomic orbitals) basis sets. For the cubic phase we compare our results with those of previous PW calculations [3].

The structural parameter optimization was performed using DFT–PW calculations as implemented into the VASP computer code [4]. The Monkhorst–Pack [5] 8 × 8 × 8 set of special *k*-points was used in the Brillouin zone (BZ) sampling in the cubic phase, for other phases a number of special points was reduced in an inverse proportion to the primitive unit cell dimensions in a direct lattice, in order to provide approximately the same density of the

k-points in the BZ. The projector-augmented-wave (PAW) pseudopotentials [6] were used for the core–valence electron interactions and PBE–GGA density functional [7] was adopted. The relatively large energy cutoff of 600 eV was used in the PW calculations, in order to get a small finite sampling error. The comparison of experimental and calculated structural parameters for all phases is given in Tables 1 and 2. As it is well seen from Table 1, the calculated conventional (crystallographic) unit cell parameters are in good agreement with the experimental data [2] being a little bit larger. This results from the use of the GGA exchange–correlation functional in our calculations: typical LDA–DFT calculations (without GGA corrections) underestimate the lattice constants [1, 8]. The same is true for the atomic coordinates (Table 2). Only the coordinates of atoms occupying the Wyckoff positions with free parameters are optimized in the calculations and given here.

In the LCAO calculations we used the CRYSTAL-03 computer code [9] with small-core Hay–Wadt pseudopotentials [10] and the corresponding basis sets for Sr and Zr atoms, whereas O atom was treated as all-electron [11]. The DFT level and *k*-points sets were taken the same as in the PW calculations. In Table 3 the relative energies (per one formula unit) are given for the PW optimized structure, and for the LCAO, with both the experimental atomic structure and that optimized in the PW calculations. Both

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Table 1 Optimized and experimental lattice parameters a , b , and c (Å) for the conventional cells.

phase	Pm3m	I4/mcm	Cmcm				Pbnm		
parameter	a	a	c	a	b	c	a	b	c
expt. [2]	4.154	5.870	8.309	8.270	8.273	8.259	5.786	5.815	8.196
calculated	4.196	5.935	8.393	8.266	8.368	8.318	5.847	5.911	8.295

Table 2 Optimized and experimental coordinates of the atoms* (in fractional units of the conventional cell parameters).

phase	atom	calculated			expt. [2]		
		x	y	z	x	y	z
I4/mcm	O(2)	0.250	0.750	0.000	0.265	0.765	0.000
Cmcm	Sr(1)	0.000	0.989	0.250	0.000	0.993	0.250
	Sr(2)	0.000	0.495	0.250	0.000	0.490	0.250
	O(1)	0.290	0.000	0.000	0.269	0.000	0.000
	O(2)	0.000	0.214	0.048	0.000	0.230	0.041
	O(3)	0.300	0.255	0.250	0.286	0.252	0.250
Pbnm	Sr(1)	0.007	0.533	0.250	0.003	0.526	0.250
	O(1)	0.923	0.979	0.250	0.927	0.982	0.250
	O(2)	0.213	0.287	0.041	0.217	0.284	0.035

* Only for Wyckoff positions of the irreducible atoms with free internal parameters (coordinates of the other atoms are fixed by space group number). The Zr atom occupies position (0.25, 0.25, 0) in Cmcm phase and position (0, 0, 0) in other phases.

LCAO and PW results agree with the experimental sequence of the SrZrO₃ phases: the most stable turn out two orthorhombic phases, whereas the tetragonal and cubic high temperature phases are close in energy.

Table 3 Calculated relative energies of SrZrO₃ polymorphs.

phase	ΔE , eV		
	experimental geometry	optimized geometry	
	LCAO	LCAO	PW
Pm3m	0.000	0.000	0.000
I4/mcm	-0.040	0.002	0.004
Cmcm	-0.177	-0.252	-0.235
Pbnm	-0.241	-0.303	-0.274

Table 4 Averaged atomic charges (e) in SrZrO₃ polymorphs (optimized geometry).

charge	phase			
	Pm3m	I4/mcm	Cmcm	Pbnm
$q(\text{Sr})$	1.843	1.843	1.824	1.821
$q(\text{Zr})$	1.828	1.828	1.894	1.905
$q(\text{O})$	-1.224	-1.224	-1.239	-1.242

Figure 1 presents the band energy structure of the cubic phase as obtained in our LCAO calculations. The conduction band minimum is at the Γ point and the valence band maximum at the R point of the BZ, in agreement with the results of PW calculations [3]. Figure 2 shows the density of states (total and projected) for the upper valence and the low conduction bands. It is seen that the lower valence bands are composed of Sr 4p and O 2s states whereas the upper valence band is produced mainly by the O 2p-atomic orbitals. The Fermi level lies at -2.82 eV. The bottom of the conduction band consists of the Zr 4d orbitals, followed by the bands with Sr 4d character. The indirect band gap between the Γ and R points is 3.23 eV whereas the direct Γ - Γ gap 3.50 eV. These results of our LCAO calculations are close to the values of 3.37 eV and 3.62 eV, respectively, obtained in the PW calculations [3]. Note that the calculated direct energy gap is essentially smaller than the experimental value of 5.9 eV [12], which is well-known artifact of the DFT method [13]. The calculated band gap may be significantly improved using the hybrid DFT-Hartree-Fock functionals [14].

Table 4 presents a comparison of atomic charges in four SrZrO₃ phases, found in LCAO calculations using the Mulliken population analysis. It is seen that Sr in SrZrO₃ has practically fully ionic charge of +2e but a considerable covalency occurs between Zr and O atoms. This is in good agreement with the results of charge distribution in the cubic SrTiO₃ perovskite [14]. Also, we found that the charges in cubic and tetragonal phases completely coincide, whereas

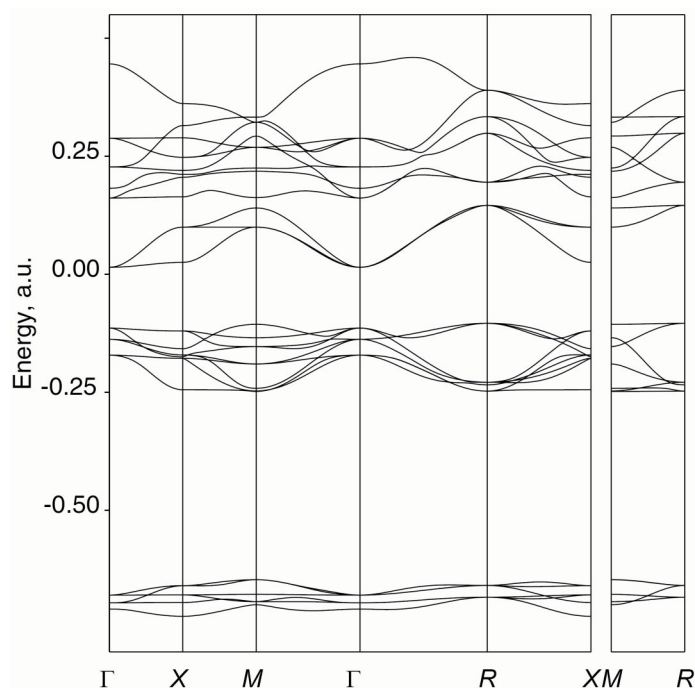


Figure 1 Band structure of the SrZrO₃ cubic phase.

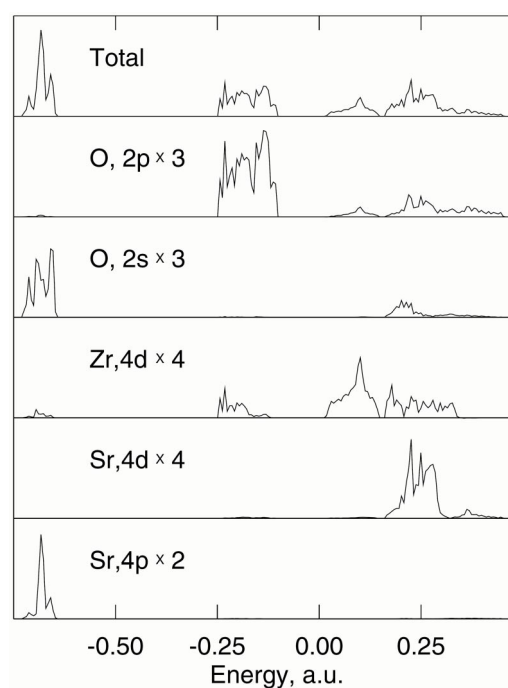


Figure 2 Density of states (total and projected).

the charge on Zr atoms in orthorhombic phase is slightly more positive.

The sequence of phase transitions in ABO₃ type oxides with the temperature increase could be described in terms of the nearest BO₆ octahedral tilts/rotations [2, 15, 16]. In our case orthorhombic structure with three rotations is changed by two rotations for Cmc_m and finally by one rotation for the tetragonal structure. The combination of three rotations produces the lowest-energy structure. The electrostatic energy is lowest for the lowest symmetry because of the inherent instability of the ideal corner shared octahedral network. To compensate the loss in Madelung energy, the repulsive energy should also be lowered, in order to achieve the equilibrium. Thermal expansion or entropy is the driving force for the octahedral tilts. Illustration of these ideas for the case of MgSiO₃ perovskite under high pressure was presented in Ref. [16].

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