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First-principles calculations on the pressure induced zircon-type to scheelite-type phase transition of $CaCrO_4$

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Abstract

The zircon-type and scheelite-type $CaCrO_4$ are investigated by first-principles calculations based on density-functional theory. The calculated zircon-type lattice parameters and the oxygen positions are in agreement with the experimental results and those of scheelite-type structure are studied for the first time in this work. The theoretical phase transition pressure of $CaCrO_4$ from zircon phase to scheelite phase is about 5.8 GPa, which is consistent with the experimental observation. From the density of states and the electronic band structures, $CaCrO_4$ is an insulator with a direct band gap (2.16 eV) for zircon-type structure and an indirect band gap (1.98 eV) for scheelite-type structure. The bulk moduli of the two phases are evaluated from the Murnaghan equation fit to the total energies as a function of the unit cell volume.

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Keywords: D. First principle calculations; D. Phase transition; E. High pressure

1. Introduction

In thermally activated electrochemical cells, $CaCrO_4$ has been used as a cathode material for a long time [1,2]. In the system of Ca–Cr–O, $CaCrO_4$ is an intermediate compound used in many industrial processes [3,4]. In 1996, Weber et al. studied the crystal structure of $CaCrO_4$ and confirmed that the compound $CaCrO_4$ has a tetragonal zircon-type structure with space group $I41/amd$ from single-crystal X-ray data [5]. Most recently, Long et al. [6] reported the evidence of pressure-induced structural phase transition at about 6 GPa in $CaCrO_4$ through Raman scattering studies and they presumed that the structural transition was from a zircon-type ($I41/amd$) ambient phase to a scheelite-type ($I41/a$) high-pressure phase. In this work, we study the zircon-type and scheelite-type structures of $CaCrO_4$ by first-principles calculations. The lattice parameters, optimized atom positions, bulk modulus, density of states and band structures of the two phases are all investigated. It is predicted theoretically that the phase transition pressure of $CaCrO_4$ from zircon phase to scheelite phase is about 5.8 GPa and both phases are insulators.

2. Method of calculation

We make use of the Vienna pachage WIEN2K [7] for all our calculations. This is a full-potential linearized augmented plane waves (LAPW) method within the density functional theory (DFT) [8]. We used the generalized gradient approximation (GGA) proposed in 1996 by Perdew, Burke, and Ernzerhof (PBE96) [9]. Relativistic effects are taken into account in the scalar approximation. Muffin-tin (MT) sphere radii of 1.8, 1.6 and 1.5 bohr were used for Ca, Cr and O atoms, respectively. The valence wave functions inside the MT spheres were expanded into spherical harmonics up to $l=10$ and $R_{mt}K_{max}$ were taken to be 9.0. We used 1000 k-points in the Brillouin zone for the zircon-type structure and 1500 k-points for the scheelite-type structure. The self-consistent calculations were considered to be converged only when the integrated magnitude of the charge density difference between input and output, $\int |\rho_n(\vec{r}) - \rho_{n-1}(\vec{r})| d\vec{r}$ was less than 0.00001.

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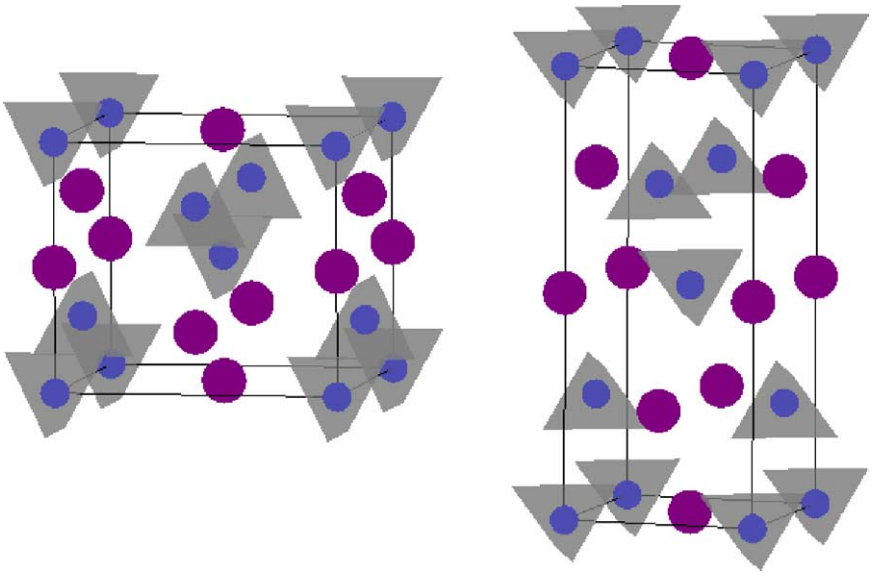

Fig. 1. The crystal structure of zironc-type and scheelite-type $CaCrO_4$, highlighting the Cr–O tetrahedron coordination. The left is zircon-type structure and the right is the scheelite-type structure. The larger solid ball is Ca, the smaller one is Cr, while the oxygen atom is at the vertices without drawing.

3. Results and discussion

3.1. Structure properties and the phase transition

The conventional unit cells of zircon-type (space group *I*41/*amd*, NO. 141) and scheelite-type (space group *I*41/*a*, NO. 88) structures are body-centered tetragonal and contain four formula units. A primitive cell containing only two formula units can be defined. In order to illustrate the relative arrangement of cations clearly, we choose Cr positions as the origins of the unit cells, as shown in Fig. 1. In both structures, the Cr ions are tetrahedrally coordinated by O ions, but with different bond lengths and angles. In the zircon-type structure, the Ca and Cr atoms are located at (0,3/4,1/8) and (0,1/4,3/8) on the 4a and 4b Wyckoff sites, respectively. The O atoms occupy the 16h Wyckoff sites $(0,y_1,z_1)$, where y_1 and z_1 are internal parameters. In scheelite-type structure, Ca and Cr atoms are located at (0,1/4,5/8) and (0,1/4,1/8) on the 4b and 4a Wyckoff sites, respectively. The O atoms occupy the 16f Wyckoff sites (x_2,y_2,z_2), where x_2, y_2 and z_2 are internal parameters. Fig. 1 shows the two structures.

The zero-pressure structural parameters of zircon-type and scheelite-type $CaCrO_4$ are summarized in Table 1. The lattice parameters and the oxygen positions of scheelite phase are calculated for the first time. For zircon phase, our calculated lattice parameters is 1.5% larger than the experimental result of Weber et al. Calculations within the generalized gradient approximation (GGA) typically overestimate (0–3%) the lattice parameters. With overestimated lattice parameters, the bulk modulus is typically underestimated. The bulk modulus (B) was evaluated from the Murnaghan equation fit to the total energies as a function of the unit cell volume. The obtained bulk modulus is $B=81$ GPa for the zircon phase and $B=94$ GPa for the scheelite phase. The scheelite-phase bulk modulus is larger compared to that of the zircon phase and it reveals that scheelite phase is more difficult to compress than the zircon phase. This is reasonable since scheelite phase is the high-pressure phase which is more closely packed than the zircon phase.

Before calculating the total energy, we first optimize the c/a ratio as a function of unit cell volume. We found that when the unit cell volume varies the c/a ratio is almost fixed at 0.8703 in zircon phase and 2.3076 in scheelite phase. The total energy is

Table 1
The zero-pressure structure parameters of $CaCrO_4$ in zircon-type and scheelite-type structures: space group, lattice parameters, unit cell volume and atomic coordinates

$CaCrO_4$	Zircon-type structure	Scheelite-type structure	Ref.
Space group	*I*41/*amd* (NO. 141)	*I*41/*a* (NO. 88)	
Lattice parameters (Å)	$a=7.3278$, $c=6.3774$	$a=5.1146$, $c=11.8026$	This work
	$a=7.2222$, $c=6.2851$		[5]
Unit cell volume (Å^3)	342.4450	308.7458	This work
	327.8319		[5]
Atomic positions			
Ca	(0,3/4,1/8)	(0,1/4,5/8)	
Cr	(0,1/4,3/8)	(0,1/4,1/8)	
O	(0,0.57107,0.78357)	(0.25819,0.62550,0.54771)	This work
	(0,0.56944,0.78494)		[5]

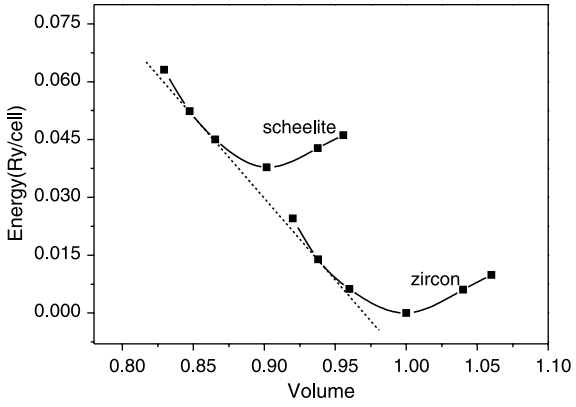

Fig. 2. Total energy as a function of unit cell volume for zircon phase and scheelite phase of $CaCrO_4$.

calculated as a function of unit cell volume for the optimized *c*/*a* ratio. The optimized volume is obtained with the minimum energy. With the optimized volume the oxygen coordinates are relaxed. In Fig. 2, the total energy of both structures is shown as a function of unit cell volume. The energy and volume of zircon-type structure are taken as reference values. It is well known that the structural phase transition would occur at a pressure when the Gibbs free energies of the two structures are equal. The Gibbs free energy, $G=E_0+PV-TS$, becomes equal to the enthalpy, $H=E_0+PV$ at $T=0$ K considered here. So the common tangent line to the curves in Fig. 2 determined the phase transition pressure. The calculated phase transition (zircon → scheelite) pressure is about 5.8 GPa, which is in well agreement with the experimental value ∼6 GPa [6].

3.2. Electronic properties

The total and partial density of states of zircon-type and scheelite-type $CaCrO_4$ are shown in Figs. 3 and 4, respectively. The Fermi level is located at $E=0$. It is obvious that $CaCrO_4$ is an insulated material. From the contribution of the partial density of states of the two phases, it is clear that O states dominate the character of the valence bands. The bottom of the

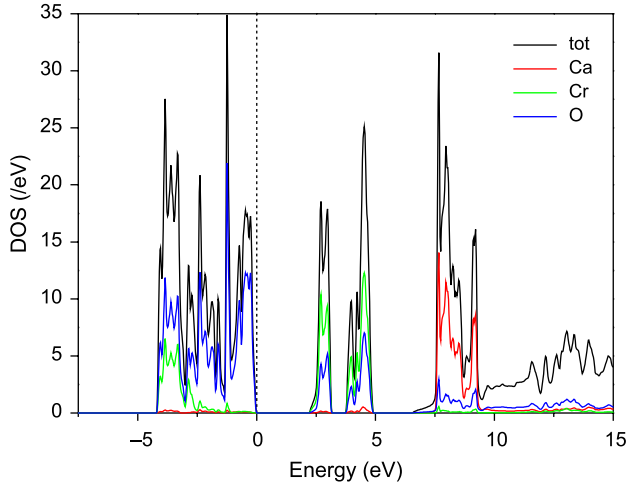

Fig. 3. Total and partial density of states of $CaCrO_4$ in zircon-type structure (space group *I*41/*amd*, NO. 141).

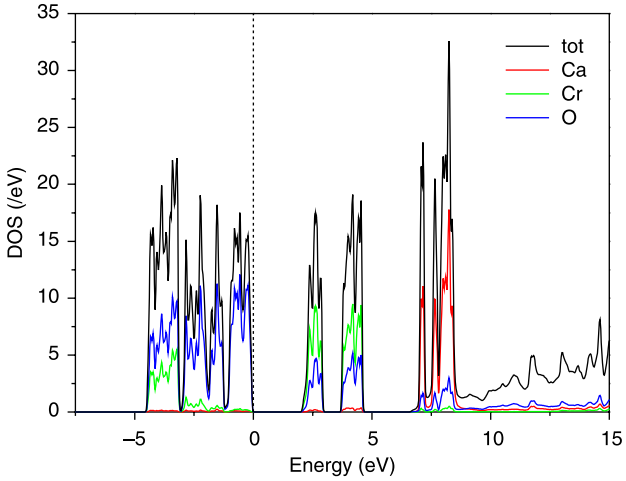

Fig. 4. Total and partial density of states of $CaCrO_4$ in scheelite-type structure (space group *I*41/*a*, NO. 88).

conduction bands is dominated by Cr states and some contribution comes from O states. The additional conduction-band contribution mainly comes from Ca states, which is located at approximately 4.3 and 4.7 eV above the bottom of the conduction band for zircon phase and scheelite phase, respectively.

The band structures of both phases are plotted along five high symmetry directions in the Brillouin zone, shown in Figs. 5 and 6, respectively. In zircon-type structure there is a direct band gap with a maximum of valence band and the minimum of conduction band at the Γ point. In scheelite-type structure the minimum of conduction band is located at the Γ point but the maximum of valence band is in the Σ direction. It exhibits an indirect band gap feature. The band gap is found to be 2.16 eV for zircon phase and 1.98 eV for scheelite phase.

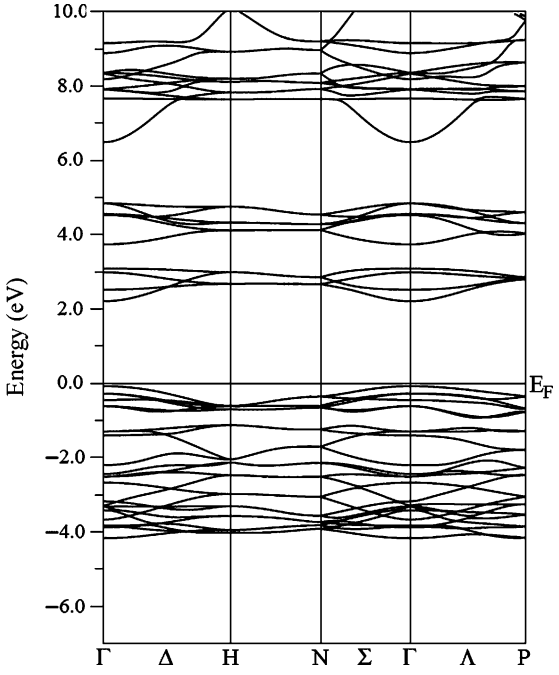

Fig. 5. Band structure of zircon-type $CaCrO_4$ (space group *I*41/*amd*, NO. 141).

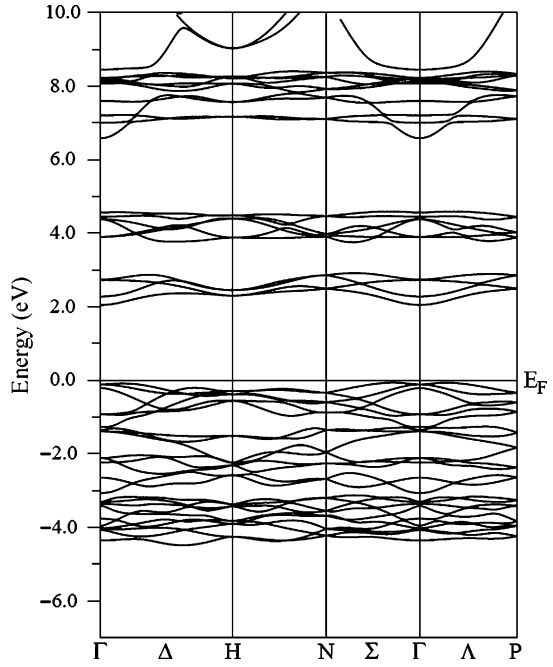

Fig. 6. Band structure of scheelite-type $CaCrO_4$ (space group *I*41/*a*, NO. 88).

The excitation energy decreased due to enhanced e–e interaction caused by the shortened neighboring atomic distance in the high-pressure phase.

4. Conclusions

We have investigated the structural properties and electronic properties of zircon-type and scheelite-type $CaCrO_4$ using first-principles method. The calculated lattice parameters and the atomic positions of the zircon-type $CaCrO_4$ are agreement with the experiment. The theoretical calculations of scheelite-type $CaCrO_4$ are performed for the first time. The calculated phase transition pressure from zircon-type structure to scheelite-type structure is about 5.8 GPa. The calculated bulk modulus is 81 GPa for zircon phase and 94 GPa for scheelite phase. From the density of states and band structures, zircon phase of $CaCrO_4$ is a direct-band-gap insulator and scheelite phase is an indirect-band-gap insulator but with a reduced excitation energy. The calculated band gap is 2.16 and 1.98 eV for zircon phase and scheelite phase, respectively.

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