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Density functional theory study of 3R– and 2H–$CuAlO_2$ in tensile stress

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ABSTRACT

We report a direct computational result of a phase transformation from the 3R phase to the 2H phase in $CuAlO_2$ with the application of tensile stress using the first-principles density functional theory calculations. The calculations of enthalpy variation with tensile stress indicates the 3R-to-2H phase transformation is expected to occur around −26.0 GPa. As the applied tensile stress increases, the independent elastic constants of 3R– and 2H–$CuAlO_2$ show the presences of mechanical instability at −27.5 and −27.6 GPa, which are possibly related with the ideal tensile strength.

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1. Introduction

Transparent conducting oxides (TCOs) are important materials for remarkable applications such as transparent electrodes in flat panel displays, window layers in solar cells, room-temperature sensing of ozone, photovoltaics thin films, transparent diodes and transistors, dilute magnetic semiconductors, etc. [1–8] due to their some unusual physical properties: transparent similar to a glass but conductive almost like a metal [9]. The majority of TCOs are n-type conductors, e.g., ZnO, SnO_2 and In_2O_3 [10–12]. However, their use as oxide semiconductors is rather restricted and the absence of high-conductivity p-type TCOs induces the lack of TCO-based devices [2,7]. Luckily, the discovery of p-type conduction properties in $CuAlO_2$ thin films has attracted a great deal of attention and this transparent oxide exhibits p-type conductivity up to 1 $S\,cm^{-1}$ at room temperature [1].

As a known transparent oxide material, experimental measurements and calculations in $CuAlO_2$ have been widely reported. The discovered indirect and direct band gaps are 1.8 and 3.5 eV [2], 2.99 ± 0.01 and 3.53 ± 0.01 eV [13], 1.85 and 3.75 eV [14], 2.97 and 3.47 eV [15], 1.86 and 3.49 eV [16], 2.1 and 3.66 eV [17], respectively. As we know, $CuAlO_2$ crystallizes in a delafossite structure built of infinite one-octahedron-thick sheets of close-packed AlO_6 octahedra. These layers are linked together by Cu atoms, forming linear O–Cu–O units which are appropriate for Cu^+ cations. The successive stacking of layers of AlO_6 octahedra results in different polytypes, namely the most common polytypes 3R and 2H delafossite. In the trigonal 3R structure ($R\bar{3}m$, D^5_{3d}), there are three layers per unit cell and the fourth layer coincides with the first one. The hexagonal 2H structure ($P6_3/mmc$, D^4_{6h}) contains only two layers per unit cell. Theoretical calculations on $CuAlO_2$ both 3R and 2H phases have been developed, including the structural, elastic, electronic and optical properties as well as excitonic effects [8–10,18–23], defect properties and conductivity [24,25].

It can be seen that many papers emphasize particularly on the basic properties of $CuAlO_2$ at zero pressure. However, great interest in the high-pressure phases of this compound has been motivated [26–30] not only to clarify its phase diagram but also to learn about the evaluation of the delafossite-type AMO_2 oxides at high pressure. There is a reversible phase transition of 3R–$CuAlO_2$ at 34 ± 2 GPa by means of Raman scattering [26], but the density functional perturbation theory (DFPT)-LDA calculation shows the dynamical instability of 3R–$CuAlO_2$ at 45 GPa [28] due to the anharmonic effects when soft modes are presented. Recently the discovery [30] of phase transition pressure between 3R and 2H is 15.4 GPa, and the independent elastic constants of 3R– and 2H–$CuAlO_2$ show the presences of mechanical instability at 26.2 and 27.8 GPa, respectively. However, in addition to hydrostatic pressure, investigations of the structural, elastic and electronic properties of materials at finite strain are important to understand many fields such as phase transition, theoretical tensile strength, crack propagation, nanotechnology, and thin films. Therefore, we here focus on the responses of structural, elastic and electronic properties to tensile stress and predict phase transition and theoretical tensile strength in tensile stress using the plane-wave ultrasoft pseudopotential technique based on the first-principles density-functional theory.

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Table 1
Calculated lattice parameters a and c (in Å), internal parameter u of 3R– and 2H–$CuAlO_2$ with different tensile stress.

		0	−10	−20	−25	−27.5	−30
a	3R	2.8813	2.9674	3.0978	3.2097	3.3048	3.8137
	2H	2.8809	2.9671	3.0976	3.2082	3.3073	3.6308
c	3R	17.1006	17.3204	17.6553	17.9521	18.2027	20.1323
	2H	11.4023	11.5455	11.7668	11.9634	12.1399	12.8973
u	3R	0.1101	0.1108	0.1116	0.1121	0.1126	0.1112
	2H	0.0847	0.0838	0.0826	0.0816	0.0811	0.0833

2. Computational methodology

We employed the plane-wave ultrasoft pseudopotential using the generalized gradient approximation (GGA) with the Perdew–Wang 1991 (PW91) functional [31] as implemented in the CASTEP code [32]. The ionic cores are represented by ultrasoft pseudopotentials for Cu, Al and O atoms. The Cu $3d^{10}$, $4s^1$ electrons, Al $3s^2$, $3p^1$ electrons and O $2s^2$, $2p^4$ electrons are explicitly treated as valence electrons. The plane-wave cutoff energy is 380 eV and the set of parameters assures the total energy convergence of 5.0×10^{-6} eV/atom, the maximum force of 0.01 eV/Å, the maximum stress of 0.02 GPa, and the maximum displacement of 5.0×10^{-4} Å.

3. Results and discussion

Through the total energy calculations, we obtain the equilibrium lattice parameters a and c of 3R– and 2H–$CuAlO_2$ at zero pressure. The lattice parameters a and c are about 2.8813 and 17.1006 Å for 3R–$CuAlO_2$, 2.8809 and 11.4023 Å for 2H–$CuAlO_2$, respectively, which are consistent with the experimental data of 3R–$CuAlO_2$ [15,21,22] and 2H–$CuAlO_2$ [21,33] and other theoretical results of 3R-$CuAlO_2$ [9,18,21,28] and 2H-$CuAlO_2$ [18,21]. We can see that the selection of the plane-wave ultrasoft pseudopotential is reasonable. Moreover, the calculated lattice parameters a and c (in Å), internal parameter u of 3R– and 2H–$CuAlO_2$ with different tensile stress have been shown in Table 1.

In order to determine the thermodynamic character of phase transition, we investigate the variation of volume as a function of tensile stress. We show the normalized volume V_n ($V_n = V/V_0$, V_0 is our calculated equilibrium volume at zero pressure) dependence of the resulting tensile stress of 3R– and 2H–$CuAlO_2$ in Fig. 1. When the tensile stress increases from −27.5 GPa to −30 GPa, the volumes of 3R– and 2H–$CuAlO_2$ suddenly increase a lot, which are relative to phase transition or tensile strength. Enthalpy H is an important and valuable parameter to study the phase stability and transition pressure, which takes the form of $H = E + PV$. We show the H curves of 3R– and 2H–$CuAlO_2$ versus tensile stress in Fig. 1 and the crossing at −26.0 GPa of two H curves indicates a phase transition from 3R to 2H.

Elastic constants provide a link between the mechanical and dynamical behaviors of crystals. Our calculated elastic constants of 3R–$CuAlO_2$ at zero pressure and zero K are $c_{11} = 277.7$, $c_{12} = 68.9$, $c_{13} = 82.7$, $c_{14} = 0$, $c_{33} = 533.7$ and $c_{44} = 41.0$ GPa [23] and the results of 2H–$CuAlO_2$ are $c_{11} = 282.3$, $c_{12} = 73.1$, $c_{13} = 81.4$, $c_{33} = 534.2$ and $c_{44} = 43.5$ GPa [30]. In Fig. 2, we present the tensile stress dependence of the elastic constants of (a) 3R and (b) 2H at zero temperature and different tensile stress. It is found that c_{11}, c_{13} and c_{33} decrease monotonically with the applied tensile stress up to −27.5 GPa, but c_{12} and c_{44} have some differences shown in Fig. 2. Additionally, $c_{33} > c_{11}$ implicates that the atomic bonds along the {001} planes between nearest neighbors are stronger than those along the {100} planes. However, the applied tensile stress weaken this difference. Along with increasing tensile stress up to −30 GPa, there are tremendous breaks. The magnitudes of

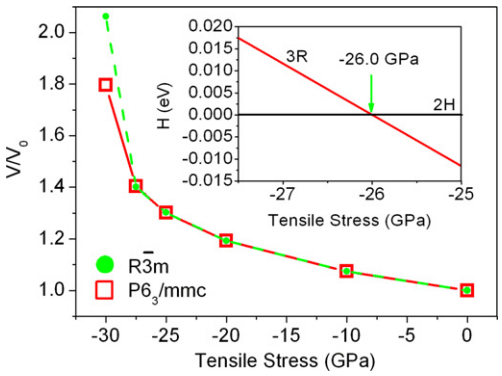

Fig. 1. The normalized volume V_n as a function of the tensile stress of 3R– and 2H–$CuAlO_2$, together with enthalpy (H) versus tensile stress.

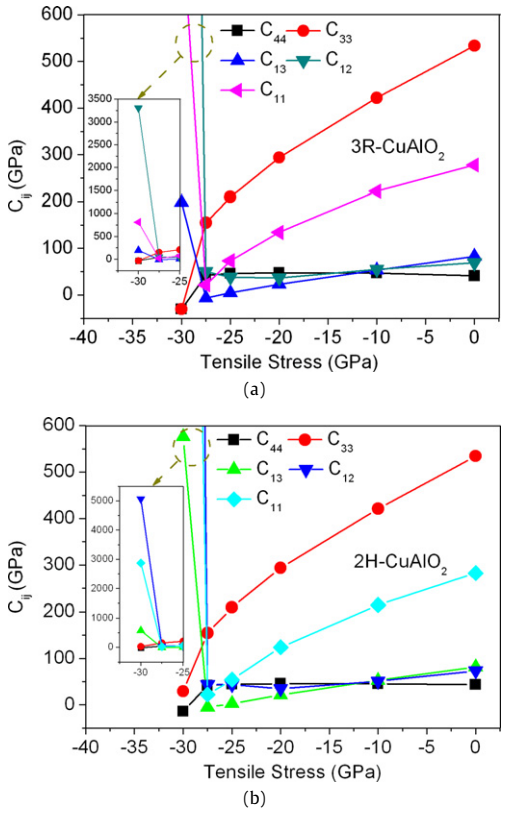

Fig. 2. Elastic constants versus tensile stress of (a) 3R and (b) 2H.

c_{11} and c_{12} as well as c_{13} are unimaginable, which may be linked to ideal tensile strength from −27.5 to −30 GPa.

Employing the mechanical stability criteria, we can study the mechanical stability of 3R– and 2H–$CuAlO_2$. According to Sin'ko's and Smirnov's conditions of mechanical stability [34], the mechanical stability occurs under the following conditions:

$$\tilde{c}_{44} > 0, \qquad \tilde{c}_{11} > |\tilde{c}_{12}|, \qquad \tilde{c}_{33}(\tilde{c}_{11} + \tilde{c}_{12}) > 2\tilde{c}_{13}^2 \tag{1}$$

where $\tilde{c}_{\alpha\alpha} = c_{\alpha\alpha} - P$ ($\alpha = 1, 3, 4$), $\tilde{c}_{12} = c_{12} + P$, $\tilde{c}_{13} = c_{13} + P$. We plot the mechanical stability of (a) 3R and (b) 2H versus tensile stress in Fig. 3. When the one of the above conditions is no longer fulfilled, it indicates that this compound is not mechanical stable. In Fig. 3, we can see that the critical tensile stress is ≈ −27.5 GPa and ≈ −27.6 GPa, which are possibly related with the ideal tensile strength.

The calculated indirect and direct gaps of 3R and 2H at zero pressure are 1.80 eV (F–Γ) and 2.86 eV (Γ–Γ), 1.82 eV (H–Γ) and 2.66 eV (Γ–Γ), respectively, which are consistent with the prior

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