# Hybrid functional method screens the *p*-type defects in wide gap semiconductor $\alpha$-$LiAlTe_2$

Shuaiwei Fan,[1, 2,*] Jiayuan Wang,[1] Yuhang Deng,[1] Liu Yang[1]

[1] Department of Physics, China Three Gorges University, Yichang 443002, China

[2] Hubei Engineering Research Center of Weak Magnetic-field Detection, China Three Gorges University, Yichang 443002, China

## I. Design principles for *p*-type TCMs

The superior *p*-type TCMs must obey the following design principles,[1,2] and establish the precise target values for their transport and optical properties, *i*) acceptor defects (typically metal vacancies or metal anti-site defects) should have shallow levels and low formation energies, *ii*) donor defects (such as anionic vacancies or metal interstitials) should be difficult to form when the Fermi level ($E_F$) lies low in the band gap. Host materials with sufficiently high VBM, *i.e.*, low intrinsic work functions, such as tellurides and antimonides, are more likely to fulfill this condition,[1] *iii*) having a smaller hole-effective mass ($m_h^* < 1.0\ m_0$), which would result in higher hole mobility, *iv*) the compound should remain thermodynamically stable under conditions that support high hole density, *v*) the optical band gap should not less than 3.10 eV to ensure the transparency in visible light spectrum.

## II. Selection of the two crystal phases of $LiAlTe_2$

Previous studies have shown that $LiAlTe_2$ exists in two crystal phases: $\alpha$-$LiAlTe_2$ (space group: $I\bar{4}2d$, chalcopyrite structure) and $\beta$-$LiAlTe_2$ (space group: P3m1, trigonal crystal system),[3] and that the two phases can coexist at atmospheric pressure, with the $\alpha$-phase possessing lower formation enthalpy than the $\beta$-phase, suggesting that it is more thermodynamically stable.[4] Therefore, the next discussion focuses on the properties of the $\alpha$-$LiAlTe_2$.

## III. Schematic diagram of the supercell $\alpha$-$LiAlTe_2$

**Fig. S1** The 4 × 4 × 2 supercell (containing 512 atoms) of $\alpha$-LiAlTe$_2$, which crystallizes as the tetragonal structure with space group $I\bar{4}2d$ .

## IV. The calculation of the effective mass and relaxation time of $\alpha$-LiAlTe$_2$

The effective mass has been calculated in the previous work.[5] Based on the CBM and VBM, the carriers′ effective mass for the semiconductors can be computed using the following formula.

$$\frac{1}{m^*}=\frac{4\pi^2}{h^2}\frac{\partial^2 \mathrm{E}(k)}{\partial k^2}. \tag{1}$$

For the relaxation time calculation, it is necessary to calculate the electron-phonon coupling matrix elements with high density, thus, the calculation amount is very large. In a recently published paper, the relaxation time τ can be approximated by the following formula,[6]

$$\begin{aligned}\frac{1}{\tau_k}=&\frac{e^2\omega_{LO}\left(\frac{1}{\kappa_\infty}-\frac{1}{\kappa_0}\right)}{4\pi\varepsilon_0\hbar\sqrt{2E_k/m^*}}[N_\omega\sqrt{1+\frac{\hbar\omega_{LO}}{E_k}}+\left(N_\omega+1\right)\sqrt{1-\frac{\hbar\omega_{LO}}{E_k}}\\&-\frac{\hbar\omega_{LO}N_\omega}{E_k}\sinh^{-1}\left(\frac{\hbar\omega_{LO}}{E_k}\right)^{1/2}+\frac{\hbar\omega_{LO}\left(N_\omega+1\right)}{E_k}\sinh^{-1}\left(\frac{\hbar\omega_{LO}}{E_k}-1\right)^{1/2}]\end{aligned} \tag{2}$$

where $\hbar$ is the Planck constant, $\omega_{LO}$ is the optical longitudinal wave frequency at the Gamma point, $\kappa_0$ and $\kappa_\infty$ are the dielectric constants at high and zero frequencies, respectively, and $\varepsilon_0$ is the vacuum electrostatic constant. $N_\omega$ is the phonon occupancy given by the Bose-Einstein distribution function, and $E_k$ denotes the electron energy. The relaxation time $\tau$ is a function of the electron energy $E_k$, *i.e.*, $\tau_k$. The average time *«τ»* is obtained by averaging the $\tau$ of different electronic states,

$$\langle\langle\tau\rangle\rangle=\frac{\int dE_k D(E_k) f(E_k)\tau(E_k)E_k}{\int dE_k D(E_k) f(E_k)E_k} \qquad (3)$$

where $f$ is the Fermi-Dirac distribution function and $D$ is the density of states function. Both the dielectric constant and the phonon frequency can be obtained by VASP calculations, and the calculation of the density of states of the electronic structure, which we have discussed,[5] and thus the relaxation time $\tau$ can be obtained by calculations.

## V. Screening of ionization energies at different interstitial positions of compound $\alpha$-LiAlTe$_2$

In this work, site optimization is carried out to select intrinsic interstitial positions of compound $\alpha$-LiAlTe$_2$ by calculating the average coordinates of the other two elements besides the target element. Taking the Li atom as an example, the coordinates and mean values of the positions of the three Al atoms adjacent to the Li atom are calculated first (denoted position 1), then the coordinates and mean values of the three Te atoms adjacent to the Li atom are calculated (denoted position 2), and the coordinates and mean values of the positions of the Al and Te atoms adjacent to the Li atom are calculated (denoted position 3). On this basis, the generalized gradient approximation (GGA)[7] method is used to calculate the ionization energy of these positions, and the optimal intrinsic interstitial position is determined by screening the results for the smallest ionization energy.

**Table I. The ionization energies of the compounds $\alpha$-LiAlTe$_2$ at different interstitial positions are as follows, calculated by GGA method.**

| Positions / interstitial | Position 1 | Position 2 | Position 3 |
|---|---|---|---|
| $Li_{int}$ | 0.0911 eV | 0.0878 eV | 0.0955 eV |
| $Al_{int}$ | 0.3819 eV | 0.3870 eV | 0.8894 eV |
| $Te_{int}$ | 2.0854 eV | 2.0861 eV | 2.0943 eV |

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