MAX-Phase Partial Optical Properties

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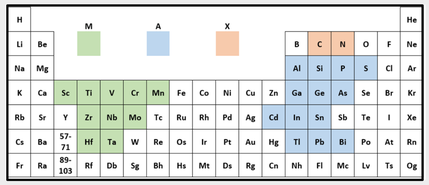
Abstract / Background

The optical and electrical properties of MAX-phase materials have been thoroughly studied in the past. We present here a new technique to determine and study the partial contributions to the optical properties. Following the same methodology as the decomposition of the density of states to the partial density of states, we have decomposed the optical properties into the partial optical properties. Using this technique, the differences of elemental and layer resolved optical properties are displayed for both the 211 and 312 phase of TiSiC and TiAlC MAX-phase materials.

Introduction



MAX-phase materials are layered ternary transition-metal carbides and nitrides.

Formula: $M_{(n+1)}AX_n$ [1-5]

Properties[6-8]:

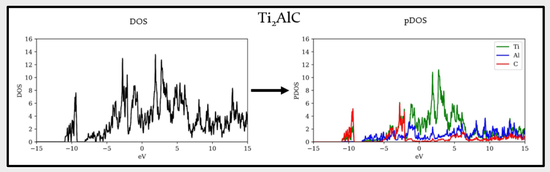
- Conduct heat and electricity like metals
- Elastically stiff, strong and heat-tolerant like ceramics
- Resistant to oxidation, corrosion, and thermal shock
- Lightweight and easily machinable due to low hardness

Applications[6-8]:

- Surface coatings to protect against corrosion
- High-temperature coatings and structural materials
- Heating elements
- Biocompatible materials

Previous Research[6-20]:

- Band Structure
- Bonding Properties
- Density of states (DOS) and Partial Density of States pDOS

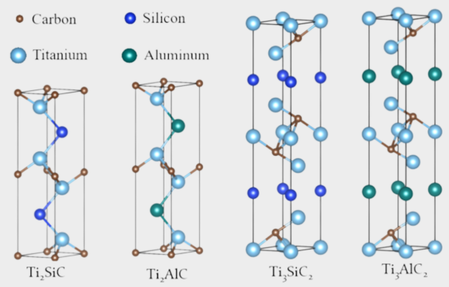


- Optical Properties (Optical Conductivity & Complex Dielectric Function)

Current Research:

- Development of the Partial Optical Properties (POPTC) calculation following the same methodology as the pDOS

Systems



Methods

Possible Decompositions	
1. Element	Ex: C, O, Ti …
2. Element Species	Ex: Ti1, Ti2, … Differing environments
3. Element Species + Type	Ex: XANES/ELNES calculations (Not currently connected)
4. Orbital (n, l)	Ex: 2s, 2p, 3d …
5. Orbital (n, l, m)	Ex: $2p_x$, $2p_y$, $2p_z$
6. All Atom	Ex: Each atom is its' own group
Directional	x-direction, y-direction, z-direction
Spin	Spin-up or Spin-down

Decomposition through orbital identification within the OLCAO basis set.

Solid State Wavefunction[+]:

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{i,\alpha} C_{i\alpha}^{n}(\vec{k}) b_{i\alpha}(\vec{k},\vec{r})$$

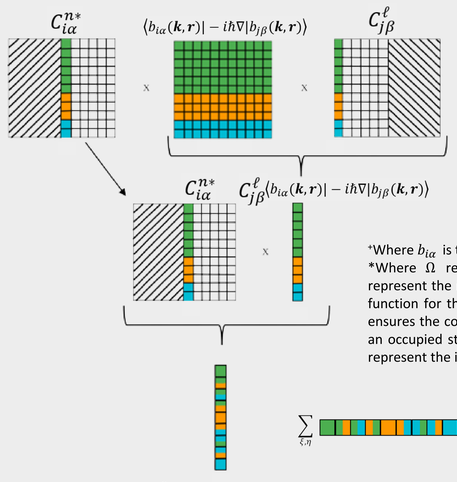
Original Calculation for the optical conductivity[21]*:

$$\sigma_1(\hbar\omega) = \frac{2\pi e\hbar^2}{3m^2\omega\Omega}\sum_{n,\ell} |\langle\psi_n(\boldsymbol{k},\boldsymbol{r})| - i\hbar\nabla|\psi_\ell(\boldsymbol{k},\boldsymbol{r})\rangle|^2 f_\ell[1-f_n]\delta(E_n - E_\ell - \hbar\omega)$$

New (POPTC) Calculation for the optical conductivity of one POPTC Pair*:

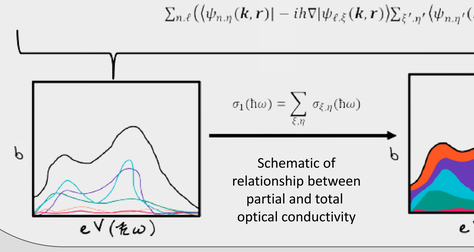
$$\sigma_{\xi,\eta}(\hbar\omega) = \frac{2\pi e\hbar^2}{3m^2\omega\Omega}\int_{BZ} dk^3\, f_\ell[1-f_n]\delta(E_n - E_\ell - \hbar\omega)\times$$
$$\sum_{n,\ell}\left(\underbrace{\langle\psi_{n,\eta}(\boldsymbol{k},\boldsymbol{r})|-i\hbar\nabla|\psi_{\ell,\xi}(\boldsymbol{k},\boldsymbol{r})\rangle}\sum_{\xi',\eta'}\langle\psi_{n,\eta'}(\boldsymbol{k},\boldsymbol{r})|-i\hbar\nabla|\psi_{\ell,\xi'}(\boldsymbol{k},\boldsymbol{r})\rangle\right)$$

$$\langle\psi_n(\boldsymbol{k},\boldsymbol{r})| - i\hbar\nabla|\psi_\ell(\boldsymbol{k},\boldsymbol{r})\rangle = C_{i\alpha}^{n*}C_{j\beta}^{\ell}\langle b_{i\alpha}(\boldsymbol{k},\boldsymbol{r})| - i\hbar\nabla|b_{j\beta}(\boldsymbol{k},\boldsymbol{r})\rangle$$



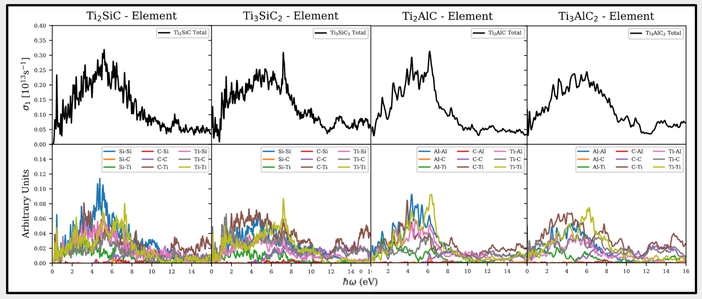
*Where $b_{i\alpha}$ is the Bloch sum for orbital i and atom α.
*Where Ω represents the unit cell volume, ℓ and n represent the initial and final states, f_ℓ is the Fermi-Dirac function for the occupied band state and the δ function ensures the conservation of energy in the transition from an occupied state, ℓ, to an unoccupied state, n. ξ and η represent the initial state and final state pOptc groups.

$$\sigma_{\xi,\eta}(\hbar\omega) = \frac{2\pi eh^2}{3m^2\omega\Omega}\int_{BZ} dk^3 f_\ell[1-f_n]\delta(E_n - E_\ell - \hbar\omega)\times$$
$$\sum_{n,\ell}\left(\langle\psi_{n,\eta}(\boldsymbol{k},\boldsymbol{r})| - i\hbar\nabla|\psi_{\ell,\xi}(\boldsymbol{k},\boldsymbol{r})\rangle\right)\sum_{\xi',\eta'}\langle\psi_{n,\eta'}(\boldsymbol{k},\boldsymbol{r})| - i\hbar\nabla|\psi_{\ell,\xi'}(\boldsymbol{k},\boldsymbol{r})\rangle\Big)$$



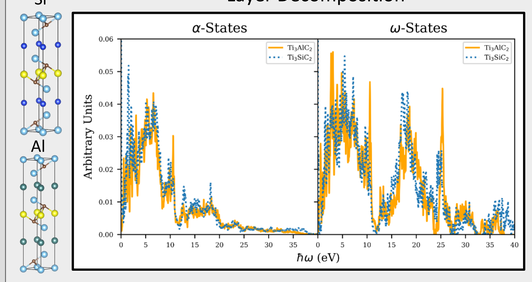
Results

Element Decomposition



- Differences between the MAX-phases tend to be modest because the atomic and electronic structures of the four models are quite similar.
- Ti_2SiC and Ti_2AlC – Silicon to Silicon/Aluminum to Aluminum, Titanium to Titanium, and Carbon to Titanium pairs produce the greatest influence on the total optical conductivity.
- Ti_3SiC_2 and Ti_3AlC_2 – Carbon to Titanium and Titanium to Titanium pairings produce the greatest influence on the total optical conductivity.

Layer Decomposition



α-State – initial state of the selected atom to a final state of any other atom within the system

ω-State – an initial state of any atom within the system to the final state of the selected atom

- Ti_3SiC_2 contains more α-States in the 0-10 eV range.
- Ti_3AlC_2 contains more ω-States in the 0-10 eV range.

Future Work

- Comparisons of MAX-phases and their MXene derivatives
- Different types of layered materials
- X-ray absorption near edge structure (XANES) spectroscopy
- Electron energy loss near edge structure (ELNES) spectroscopy
- Larger systems with distinct sub-components
  - e.g., a macromolecule with functionally different regions

Acknowledgements

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