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Design and discovery of a novel half-Heusler transparent hole conductor made of all-metallic heavy elements

Feng Yan^{1,*}, Xiuwen Zhang^{2,*}, Yonggang G. Yu², Liping Yu³, Arpun Nagaraja¹, Thomas O. Mason¹ & Alex Zunger²

Transparent conductors combine two generally contradictory physical properties, but there are numerous applications where both functionalities are crucial. Previous searches focused on doping wide-gap metal oxides. Focusing instead on the family of 18 valence electron ternary ABX compounds that consist of elements A, B and X in 1:1:1 stoichiometry, we search

Transparent conductors (TCs) needed in solar cell, light emitting diode and flat panel displays¹⁻⁵, represent the usually contraindicated functionalities of optical transparency (generally associated with electrical insulators) coexisting with electrical conductivity (generally associated with optically opaque metals)⁶. The search of TCs has generally focused on chemical groups characterized as light element wide gap oxides, such as Al-doped ZnO⁷, (for n-type) or CuAlO₂⁸, and K-doped SrCu₂O₂⁹ (for p-type) TCs. Rather than attempting discovery within such a preconceived chemical neighbourhood (either by high-throughput computation¹⁰ or via combinatorial synthesis), the discovery of TCs might be guided instead by a set of physics-based metrics that p-type TCs need to satisfy a priori^{9,11-14} then search not only light element oxides or nitrides but allow for a broader range of chemistries to be inspected. Such 'Design Principles' include a combination of (a) electronic structure features of the perfect crystal and, in parallel, (b) properties of the non-stoichiometric defected lattice. In category (a) we require a wide (≥ 2.5 eV) direct band gap for optical transparency (but the non-absorbing indirect band gap can be significantly smaller), whereas good mobility requires rather light ($< 0.5 m_0$) hole effective mass and a bulk hole wavefunction that avoids as much as possible the close neighbourhood of the ions so as to minimize scattering. In category (b) we require that the intrinsic defects are hole producers (acceptors such as cation vacancies), have low formation enthalpy (that is, be abundant) and have shallow acceptor levels (that is, be readily ionizable), whereas the intrinsic defects that are 'hole killers' (donors such as anion vacancies) must have high formation enthalpy. In considering such design principles it is not obvious a priori that only the traditionally sought light element oxides are eligible for satisfying these simultaneous conditions.

We choose to focus on the 18-electron ABX compounds that represent diverse chemical groups such as $A^n B^{10} X^{(8-n)}$ as well as $A^{(n+1)} B^9 X^{(8-n)}$ ($n = 1, 2, 3, 4$) with atoms spanning columns 1-5, 9-17 in the Periodic Table. This broad range of atoms (albeit within the group of ABX) encompasses a broad range of chemistries including light as well as heavy elements; anions as well as cations. The previously synthesized members from these groups manifest extraordinary functionalities such as thermoelectricity, superconductivity, piezoelectricity and topological insulation, but as yet no TCs. But not all atom combinations that, by the current understanding of solid-state chemistry, can plausibly lead to such ABX structures are in fact realized. For example, from a total of 483 possible 18 valence electron ABX compounds from the above noted chemical groups, only 83 are known¹⁵, whereas 400 are, in fact, 'missing compounds' that might constitute an attractive playing ground for new materials with new functionalities. We^{16,17} and others^{18,19} have developed theoretical, first principles techniques for examining the thermodynamic stability of missing compounds sorting out the 'missing and predicted unstable' from the 'missing and predicted stable'. Our first principles thermodynamics search includes the examination of (a) the lowest-energy crystalline form of the ABX phase, (b) its stability with respect to decomposition into

In contrast, we find that ABX with light X atoms (that is, O, S, Se, N, P, As, C, Si and Ge) tends to have non-cubic structure and thus are often metallic. This is so because for light X the A and B metals carry ionic charges and thus strongly

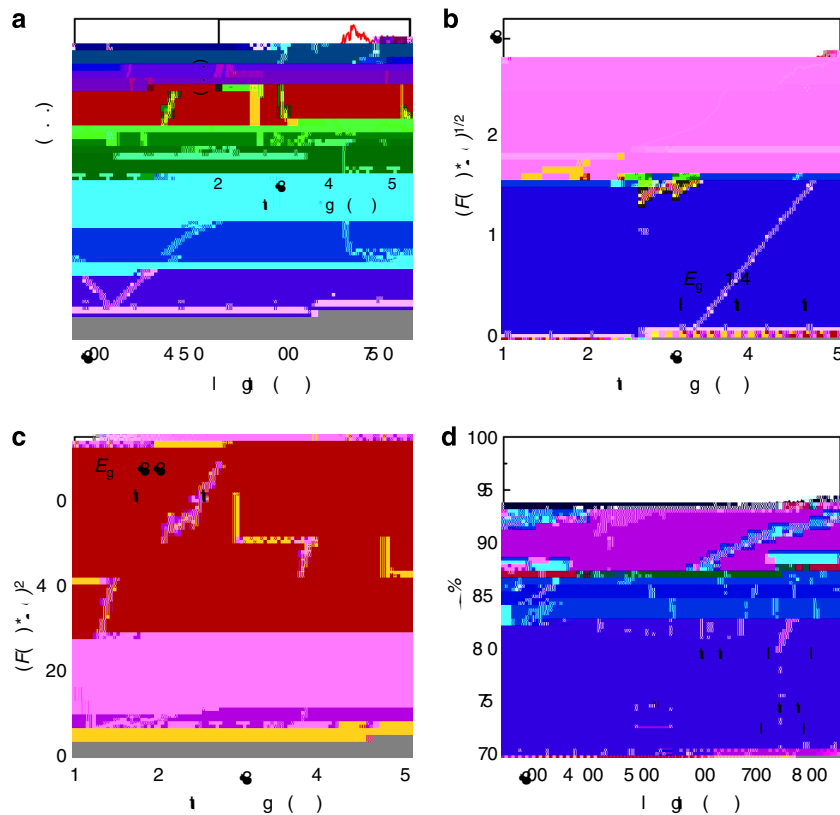


Figure 6 | Measured optical property of TaIrGe semiconductor. (a) Optical spectra. The absorption spectra are obtained from the ultraviolet/visible diffuse reflectance spectra converted by the Kubelka-Munk²⁶ (

(~ 350 to 700 nm). To confirm this optical band gap, we performed high-vacuum thin-film deposition using TaIrGe target in a pulsed laser deposition system and the obtained 30-nm-thick film is transparent in visible light. Figure 6d shows the optical transmittance spectrum of the TaIrGe film grown on transparent quartz substrate, which varies from 85 to 92% in the wavelength region of 350 to 700 nm. This demonstrates that the TaIrGe film is transparent in the visible region.

The electrical conductivity (σ) of the bulk specimen, measured using Van der Pauw method at room temperature is $\sim 0.35 \text{ S cm}^{-1}$. The Hall coefficient (R_{H1}), measured using a five-probe configuration, gave $+7.8 \times 10^3 \text{ cm}^3 \text{ C}^{-1}$, indicative of p-type conduction, which is in agreement with the results from the intrinsic defect calculation. (A Seebeck coefficient is found to be $+82 \text{ mV K}^{-1}$ at room temperature for the TaIrGe bulk, further confirming that the TaIrGe is a p-type semiconductor.) Combining the conductivity and Hall coefficient resulted in a hole concentration of $\sim 0.8 \times 10^{15} \text{ cm}^{-3}$ and a remarkably large Hall mobility of $\sim +2,730 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The achieved Hall mobility is much higher than that of known p-type transparent conducting oxides^{8,9} (for example, $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for CuAlO_2).

Discussion

We illustrate that a rather rare functionality of p-type transparent conductivity can be discovered by inverse design in a never before made compound. Whereas this functionality has been

traditionally searched in the general chemical neighbourhood of compounds containing light element oxides, we use a different search strategy that led to the identification of a good p-type TC in an all-metal heavy atom compound TaIrGe. A remarkable high hole mobility $2,730 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been found at room temperature. This study opens the way to search transparent conductors among non-oxide heavy-element materials and to designing high-mobility transparent electronic devices. Some of the important insights gained include:

Filling the gaps of ‘missing compounds’ in a group of materials allowed a confident formulation of interesting structure–property chemical rules enabling zooming effectively to the subgroup likely to contain p-type TCs. These include the rules that the 18-electron ABX with heavy X atoms tends to have a cubic half-Heusler structure and that insulation band gap are exclusively correlated with the cubic half-Heusler structure having two transition metals.

The X-on A antisite hole producer has low formation energy since both A and X sites are in a similar fourfold coordination (whereas B in eightfold) and the size of X (Ge) is smaller than A (Ta). In contrast to the favourable conditions for producing holes, the hole-compensating (electron producing) metal interstitials (Ir_i , Ta_i and Ge_i) that form by occupying the interstitial site in half-Heusler structure (Fig. 1b), require high formation energy due to the large atomic sizes (for Ir_i and Ta_i) or repulsion from iso-atom nearest neighbours (for Ta_i and Ge_i) and thus do not block the acceptors.

The previously studied p-type transparent conductors are prone to have low-hole mobilities^{8,9} (for example, $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for

CuAlO₂ and 0.46 cm²V⁻¹s⁻¹ for SrCu₂O₂), which limited their

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