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The Holey Grail of Transparent Electronics

Aron Walsh[1,2,*] and Ji-Sang Park[3,*]

For decades, researchers have attempted to discover transparent conductors that transport holes. A robust p-type material would usher in a new era of technologies. Many reports have failed to live up to their hype; however, the screening by Williamson et al. has predicted $[Cu_2S_2][Ba_3Sc_2O_5]$ to support a conductivity exceeding 2,000 S cm^{-1}.

We are trained to think that metals are colored (e.g., Cu), while insulators are transparent (e.g., SiO_2). Transparent conductors break this conception by combining electrical conductivity and optical transparency in the same material.

Transparent Conductors Prefer Electrons

The highest-performance transparent conductors are n-type widegap semiconductors. Many of these are metal oxides, where oxygen sub-stoichoimetry or extrinsic dopants produce high excess electron concentrations. For example, Sn-doped In_2O_3 (ITO), Al-doped ZnO (AZO), and F-doped SnO_2 (FTO) can be deposited as thin films that are transparent to visible light (380–700 nm) and simultaneously have high electron concentrations ($>10^{20}$ cm^{-3}) with a low sheet resistance. A discussion of the underlying physics can be found in Edward et al.[1] One feature that these materials (ITO, AZO, FTO) have in common is that the conduction bands are formed of overlapping metal s orbitals. The crystal wavefunctions associated with these orbitals are diffuse, the overlap is isotropic and insensitive to disorder, and the low effective masses can support high electron mobility.

The Search for Hole Conductors

Converting electron-conducting metal oxides to hole conductors should be straightforward in principle. Simply dope them with acceptors. This could be performed on the oxygen site (e.g., N_O in ZnO) or the metal site (e.g., Li_{Zn} in ZnO). While there are many reports on p-type doping of wide bandgap metal oxides, the results and conclusions are often contradictory. On the experimental side, there have been issues with sample instability and reproducibility.[2] On the theoretical side, overly optimistic predictions have been based upon unrealistic Hamiltonians that did not account for self-interaction errors; e.g., the N_O acceptor level is deep in the bandgap of ZnO when a hybrid exchange-correlation functional is employed.[3] A simple thermodynamic analysis reveals the origin of observed metastable p-type conductivity: instead of forming holes, acceptor-doped materials will simply lose oxygen over time.[4] Efficient ionic compensation of acceptors suppresses p-type doping. This behavior is often discussed in the context of the doping limits of semiconductors.[5]

The group led by Hideo Hosono should be credited for articulating many transparent conductor design principles that we now take for granted.[6,7] They understood that in order to realize robust hole conduction in metal oxides, the upper valence band must be modified. This can be achieved by introducing metals with low-binding-energy valence orbitals; e.g., Sn(II) has a $5s^2$ configuration, and SnO is p-type, while Cu(I) has a $3d^{10}$ state and Cu_2O is p-type. Unfortunately, both materials absorb light in the visible range. Similar p-type behavior can be achieved in doped transition metal systems such as NiO and Cr_2O_3; however, the hole mobility is lower, and the resistivity is too high for many applications.

More Elements Is Better

Beyond the limits of binary semiconductors exists a large chemical playground as illustrated in Figure 1. There have been a number of success cases in identifying p-type transparent conductors, including delafossites (e.g., $CuAlO_2$) and spinels ($ZnCo_2O_4$). Hosono moved beyond metal oxides and reported the

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https://doi.org/10.1016/j.matt.2020.08.008

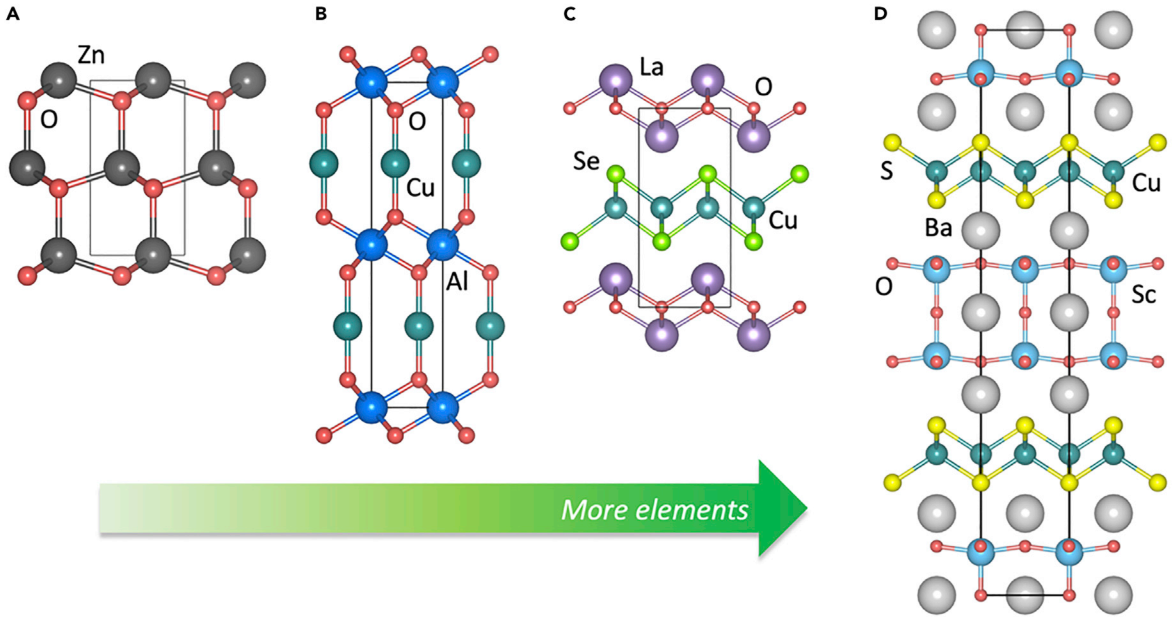

Figure 1. The Crystal Structures of Transparent Conductors with an Increasing Number of Elemental Components
(A) wurtzite ZnO, (B) delafossite $CuAlO_2$, (C) LaCuOS, and (D) $[Cu_2S_2][Ba_3Sc_2O_5]$.

potential of the quaternary LaCuOS family with a record p-type conductivity of 910 S cm^{-1}.[8] However, a number of challenges remain, including the ability to control the optical (band gap) and conduction (mobility and carrier concentration) properties over a large range in addition to device considerations such as interface stability and work-function matching. This is where the work of Williamson et al.[9] comes in.

The new investigation reported in this issue of *Matter*[9] adds a further dimension with a search over the quinary compositional space $[Cu_2S_2][A_3M_2O_5]$, where A is a divalent and M is a trivalent metal. The layered modular structure type is shown in Figure 1d, which is reminiscent of the iron pnictide superconductors. Building on preliminary reports of p-type transport in $[Cu_2S_2][Sr_3Sc_2O_5]$, they have shown how the chemical and physical properties can be tuned within this family of modular compounds. They used first-principles calculations to examine 24 distinct compositions and predict the electronic and structure changes. Among them, the substitution of Sr with Ba increases the lattice parameter *a* the most, making the distance between Cu atoms longer. This change in the crystal structure reduces the electronic bandwidth, and therefore, the bandgap becomes larger. This direction of materials design to improve transparency also has a benefit on the electrical conductivity, as the overall effective masses are reduced, with an upper limit of 2058 S cm^{-1}. The behavior highlights the importance of strain engineering in modular layered compounds, which is an exciting route to realize new properties and performance beyond the limits of conventional densely packed structures.

Throw down the Crystal Gauntlet

From their compositional search, Williamson et al.[9] identified $[Cu_2S_2][Ba_3Sc_2O_5]$ as the optimal p-type transparent conductor in this family of layered compounds. This study shows the importance of going beyond data-driven studies of known materials and databases.[10] They further succeeded in powder synthesis of $[Cu_2S_2][Ba_3Sc_2O_5]$ samples to confirm its predicted structure and stability. However, the authors leave a clear open challenge to the community. The synthesis of thin films or single crystals is necessary for a direct probe of the electrical properties, which will require other research groups to accept the quest. While $[Cu_2S_2][Ba_3Sc_2O_5]$ may not promise everlasting life, if validated, it further confirms the power of modern computational chemistry to accelerate the design of materials with target properties while also providing a valuable new transparent hole conductor.

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Liquid Crystal Polymeric Skins "Sweat" to Provide Real-Time Drug Delivery

Yang Xu,[1] Yuxing Yao,[2] and Xiaoguang Wang[1,3]

To mimic the sweating functionality of human skin, Liu and coworkers have developed a liquid crystal (LC) polymeric network-based artificial skin with programmable liquid secretion and excretion driven by radio frequency (RF) electrical fields.

Can artificial skin be as smart as its natural counterpart? This is not only a fundamental question, but also an ultimate goal for scientists working on soft matter and organic electronics. A team led by Liu from China and the Netherlands has provided the basis of a general methodology for the preparation of a porous liquid crystal (LC) polymeric network that can program liquid secretion using radio frequency (RF) electrical fields.

As the outermost layer of living organisms, skins exhibit various functions to interface biology with their environments, which has been the inspiration for scientists to develop human-like, functional materials. For instance, tactile sensing embedded in human skin serves as one of five main senses for human body to perceive the physical world, which is realized by patterned action potential through sensory receptors in the skins and interpreted by the brain. This behavior has stimulated the development of artificial electronic skin with tactile responsiveness.[1] Capacitive and resistive mechanisms have been mainly employed to sense static force/strain through the changing electric signal as a function of the distance between two electrodes (capacitive) or between a structured conductor and an electrode (resistive). Recent progress has observed the integration of these two mechanisms to produce a compliance sensor capable of measuring both the pressure and strain.[2] Further implementation of piezoelectric or triboelectric sensors enables the dynamic force transduction in artificial electronic skin through the voltage reading induced by the changing electric dipole of piezoelectric components in response to applied forces.[3] These pioneering works have shown promise in applications including prosthetic skins, biomedical devices, and robotics.

Beyond sensing modality, human skins provide additional features to regulate biological behaviors. As an example, sweat secretion enables effective heat management for body temperatures. Other biological systems also utilize the liquid immobilized on their outer surfaces for additional functions, e.g., the pitcher plant *Nepenthes Alata* takes advantage of a lubricant layer to regulate its inner surface slipperiness to trap prey. Inspired by such a hierarchical natural structure, researchers have developed liquid-infused surfaces by combining a porous solid matrix and a lubricating liquid (generally termed as slippery lubricant-infused porous surface[s], SLIPS) to mimic the biological skin structures and functions introduced by the liquid layer.[4] Potential uses in loss-free object transportation, ultralow friction, and anti-adhesion of ice and biological creatures have been presented with such liquid-infused materials. However, these works have mainly focused on providing the fundamental physical understanding of a static liquid-infused system; there are only few examples demonstrating skin-like dynamic liquid secretion.[5] Additionally, electric field-responsive liquid secretion is rarely achieved, which may provide significant advantages to interface with the electronic-based tactile sensing platform to build a functional surface more similar to human skins.

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https://doi.org/10.1016/j.matt.2020.08.014