

Computationally Driven Electride Discovery

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Any Solid State Chemist or Materials Scientist will tell you that one of the foundations in our understanding of chemical bonding in solids is that of electroneutrality, i.e. the formal charges of all constituent atoms in a material should sum to zero.¹ Electrides, however, do not adhere to the standard rules of valency.² In an electride, all of the electrons do not occupy atomic orbitals associated with elements as would be expected based on conventional bonding behaviour, but rather some electrons occupy interstitial voids in a crystal structure and acts as an anion. These unusual electronic characteristics impart unique chemical properties to these systems, including low work function and metallic or near-metallic conductivity.

Thirty years ago, electrides were seen as chemical curiosities; organic electrides were synthesizable although they suffered from severe air and moisture sensitivity and low thermal stability.³ The advent of inorganic electrides,⁴ and more importantly air stable, room temperature inorganic electrides have helped them to transition from being mere curiosities to being of real technological relevance.⁵ Inorganic electrides have now found success in light emitting diodes, as superconductors, as catalysts for N₂ and CO₂ splitting, as cathodes for electrochemical reactions, and in the generation of exotic ions.⁶ This emergence of technologically important electrides has stimulated an explosion of research effort into discovering novel electrides, with computational screening leading the charge.

Choudhary and co-workers⁷ have used the high-throughput calculated data in the Materials Project data base⁸ to screen in excess of 69,000 known solids to find new electrides. Based on a survey of known electrides, they noticed that three main features appear to be ever present: (a) the presence of interstitial electrons, (b) the systems display mostly ionic bonding and (c) the electrons associated with the interstitials appear near the Fermi level of the system. From these observations, Choudhary and co-workers devised a multistep computational screening strategy, starting with the computation of the electron localization function (ELF) of a material, which allows the analysis of electron localization in solids and molecules. Any systems with a degree of electron localization at an interstitial void were therefore allowed through to the next screening step. Next the authors plotted the partial charge density within a range of ± 0.05 eV from the Fermi level, deciding that the material was a potential electride if the maximum of the charge density resided at the same interstitial void that displayed the electron localization from the previous screening step. Next the authors took inspiration from the Bader charge partitioning approach and placed a pseudo atom on the exact site of the ELF maximum in the voids. From this, they calculate the density of states and volume of the interstitial site, and they expect that for a perfect electride, the “anionic electron” should occupy the entire volume of the interstitial voids, and should dominate the density of states around the Fermi energy.

This screening process predicted 167 potential electrides, 114 of which had never been considered before. Although the study found 48 distinct structure types which could host electride behaviour, eight structure types were found to possess families (more than 5) of electrides. It is instructive to note that a previous high throughput study also screened the Materials Project database for electrides and proposed 69 potential electrides.⁹ The main differences in both approaches was that the earlier study used the calculated band structure in the screening process, and not all systems in the database have band structures calculated yet. This lack of data is a likely reason for the lower number of prospective electrides found. In addition, although the initial screening paper proposed 69 electrides, only 36 of these are proposed in the work of Choudhary, illustrating the differences in the screening procedures, and the exact reason for this discrepancy remains unexplained. It remains to be seen if these “missing” systems will be confirmed to be electrides.

We have now entered an era where theory and simulation are at the forefront of materials discovery, effectively directing and informing synthesis and characterisation. Choudhary and co-workers have provided the materials community with a large number of potential electrides, throwing down the gauntlet to the experimental community to test these predictions and to probe their potential technological applications. Encouragingly, the recent computational prediction of the electride nature of Sr_3CrN_3 has very recently been experimentally validated,¹⁰ increasing our confidence in the value of these screening studies. Thus the future looks bright for the field of inorganic electrides.

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