Crystallochemical approach to high-throughput screening of potential ionic electrides

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At present, about 200 structures of inorganic electrides are known, most of which were theoretically predicted but have not experimentally confirmed yet. This number amounts to only 0.1% of more than 200,000 crystalline compounds deposited in the Inorganic Crystal Structure database (ICSD). However, the real number of electrides can be much larger; the problem is that the electride properties are difficult for detecting both theoretically and experimentally. A number of criteria that indicate a crystal structure to be electride were proposed, but none of them is universal and sufficient. In particular, Dale and Johnson [1] highlighted eight important electride properties applicable for inorganic electrides. Most of these criteria are calculated by quantum-mechanics methods; hence, they are hard-to-obtain data that significantly depend on the initial calculation parameters. Thus the search for other criteria, which can be estimated by less resource-consuming methods, remains an actual task.

The excess electron can be considered as an anion or a pseudo atom in crystal structure. This means that we can apply crystallochemical methods, which are designed for the description of atoms, to the characterization of the interstitial electrons. We use for this purpose Voronoi polyhedra, which have exhibited their effectiveness for the representation of atoms in crystals of any chemical nature. An important geometrical property of atomic Voronoi polyhedron is that its vertices coincide with the points, which are most distant from the surrounding atoms, i.e. mimic the centers of structural cages. Like the $Cs_7O{\cdot}5e^-$ structure shown in the Figure 1, most of electrides have a positive charge imbalance, since they contain an excess number of metal atoms compared to the formally charge-balanced composition (Cs_2O for $Cs_7O{\cdot}5e^-$). Similar to the elementary substances, many metal-to-metal contacts exist in electrides. For this reason, we use atomic radii to determine the boundaries of the region not occupied by atoms and estimate the size of the localized electron domain with the modified Voronoi polyhedron (Figure 1).

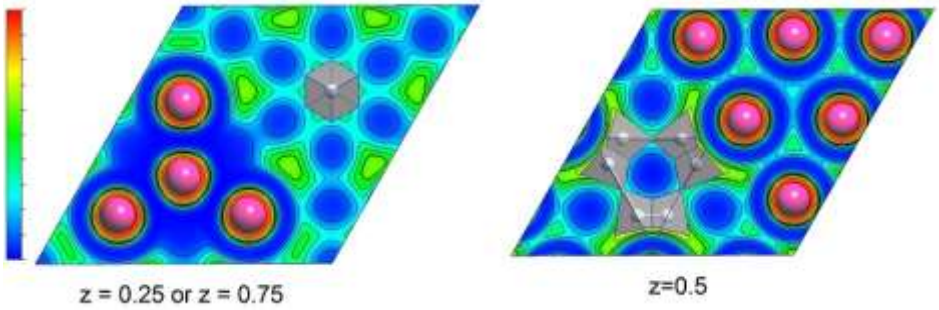

Figure 1. The electron localization function for the structure in sections at z=0.25 (or 0.75) and 0.5, on which the modified Voronoi polyhedra are superimposed, which are calculated using atomic radii.

References

1. Dale S.G. and Johnson E.R. *J. Phys. Chem. A* **2018**, 122, 49, 9371.