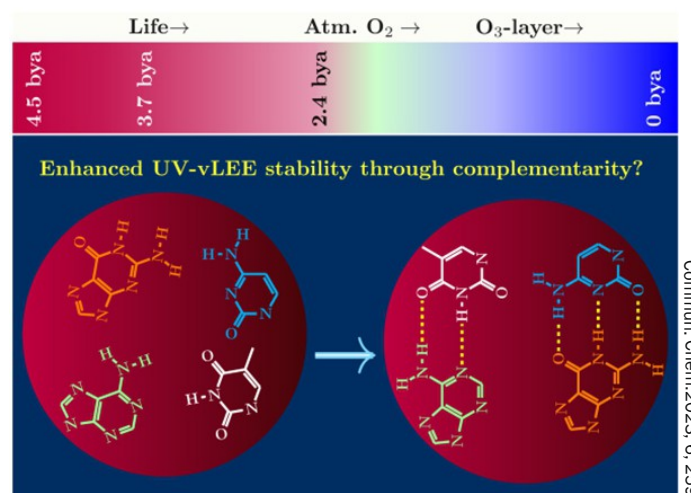


## Biomolecular Complementarity

# Prebiotic Origin of Biomolecular Complementarity



### Y. Sajeev

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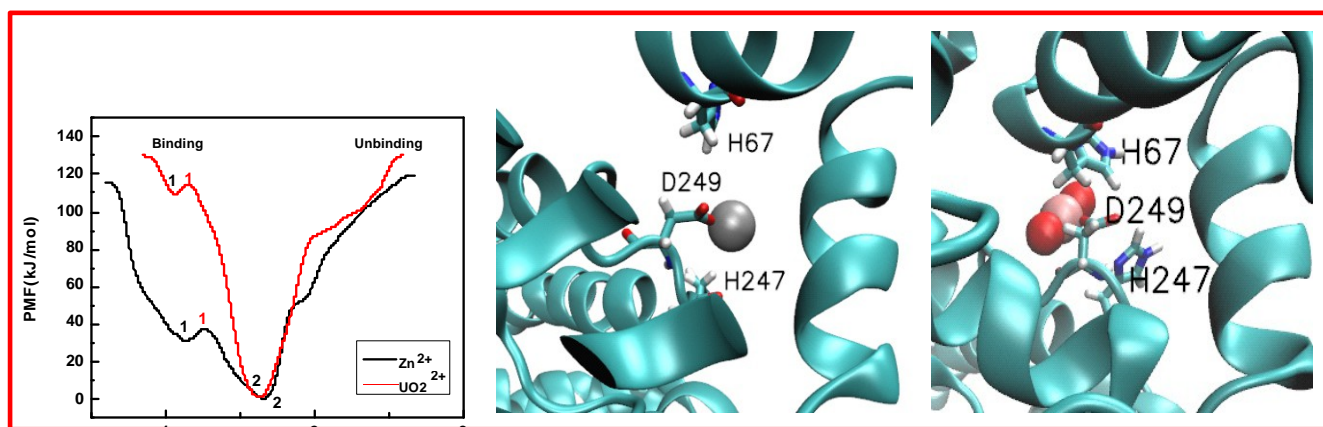
Our studies revealed that the inherent ability of complementary bases to survive adverse conditions of prebiotic medium rather than individual bases leads to their proliferation and consequently to the chemical evolution of their advanced molecular complements.

The long-held notion that complementarity based on intermolecular hydrogen bonding confers thermodynamic stability to DNA has recently been experimentally disproved. This experimental refutation made the origin of complementarity an enigma in the chemical origin of life. Our published article (*Commun. Chem.* 2023, 6, 259) presents a hypothesis that complementarity based on intermolecular hydrogen bonding originates from the broader molecular stability necessitated by the ambient physicochemical conditions of a prebiotic medium in which it chemically evolved. Due to the absence of a protective stratospheric ozone layer, a continuous flow of unattenuated shortwave UV photons reached the early Earth's surface and greatly intensified its prebiotic physico-chemical conditions.

A prebiotic chemical medium that constantly receives short-wave UV photons eventually becomes a breeding ground for very low-energy electrons (vLEEs). In other words, the prebiotic medium was intensified by two of the most efficient molecular deleterious agents, i.e., shortwave UV photons and vLEEs. We have reviewed the molecular stability inherent in nucleobases and in their chemically advanced structures against two of these most prominent prebiotic molecular deleterious agents. Our efforts revealed that the inherent ability of complementary bases to survive adverse conditions of prebiotic medium rather than individual bases leads to their proliferation and consequently to the chemical evolution of their advanced molecular complements.

## An All Atom Molecular Dynamics Study

# Binding of Human Serum Albumin with Uranyl Ion at Various pH



*J. Biomole. Struct.Dyna.* 2023, 41, 7318-7328.

**Vijayakruti Mishra, Arup K. Pathak, and Tusar Bandyopadhyay**

Scientific Officers, Chemistry Group

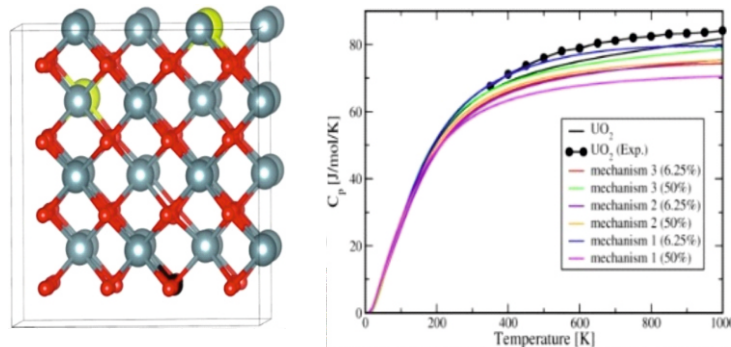
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

It is observed that the binding of metal ions with HSA is the result of the dynamical balance between metal-HSA and metal-water short range Coulomb interactions.

**A**ctinide, namely, uranium, poses a two-fold risk once it enters the human body. On the one hand, the major risk is due to their nuclear radiation, and on the other hand, it is a consequence of their heavy metal toxicity. Irrespective of the intake pathway, i.e., inhalation, ingestion, or cutaneous absorption, actinides are resorbed and transported by the bloodstream prior to deposition in target organs or tissues. The actinides exhibit long biological lifetimes of 20–50 years and are excreted at slower rates. They link with different biological ligands (proteins, amino acids, etc.) and mimic natural biological elements (iron, calcium, etc.). Uranium is routinely handled in various stages of the nuclear fuel cycle, and its association with human serum albumin (HSA) has been reported in the literature; however, their binding characteristics still remain obscure. Understanding binding characteristics is important for a better understanding of the mechanisms controlling their specific target deposition, the toxic effects, and the design of suitable decorporating agents. However, no efforts are given to understand the phenomenon at molecular level. For the first time, the enhanced sampling method, namely, well-tempered meta-dynamics, is employed to study the binding processes of uranyl and zinc ions with HSA at the molecular level (published in *J. Biomole. Struct.Dyna.* 2023, 41, 7318-7328). It is observed that the binding of metal ions with HSA is the result of the dynamical balance between metal-HSA and metal-water short range Coulomb interactions. It can be inferred that the uranyl ion cannot associate with the zinc bound HSA protein but can be captured by free HSA at all pH values, i.e., endosomal, alkaline, and physiological pH.

## Effect of Oxidation States

# Computational Study of Thermophysical Properties of Cerium doped $UO_2$



*J. Nucl. Mater.*2024, 588,154791.

**Tijo Vazhappilly and Arup K. Pathak**

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Our calculations were helpful in evaluating the fuel properties of  $UO_2$  with fission products in a complex environment where cations with multivalent oxidation states are present.

The interaction of fission products with  $UO_2$  fuel, which is generated during the nuclear fission, can amend the fuel behaviour. Among different lanthanide (Ln) fission products produced, Cerium (Ce) shows considerable yield. In this work, the trivalent and tetravalent cerium (Ce) atom substitution in  $UO_2$  and their effect on thermophysical properties is investigated using density functional theory. Further, the effect of Ce doping concentrations in  $UO_2$  is assessed by varying the Ce atom concentrations in the lattice (6.25%, 12.5%, 25%, and 50%) for various charge balancing mechanisms. The lattice charge balance in the Ce doped  $UO_2$  structure is attained through different processes such as oxygen vacancy creation, accommodating excess oxygen in the lattice, and by altering the oxidation of state of U atoms. The volume of Ce doped  $UO_2$  lattices show higher or lower values compared to pure  $UO_2$  depending upon the oxidation state of Ce and U atoms. The mechanical properties tend to reduce for Ce substituted  $UO_2$  as compared to pure  $UO_2$ . The Ce dopant concentration and the electronic charge on Ce and U atoms effect the band structure of Ce doped  $UO_2$ . Thermal properties such as specific heat capacity are evaluated using quasi-harmonic approximation. Our results show good agreement with the reported experimental values (*published in J. Nucl. Mater.*2024, 588,154791). Especially, the effect of oxidation state of Ce on fuel properties of  $UO_2$ - $CeO_2$  matrix has never been investigated. Our calculations are helpful to evaluate the fuel properties of  $UO_2$  with fission products in a complex environment where cations with multivalent oxidation states are present.

## Quantifying the Role of Counter-Ions

# *Redox Potentials of Uranyl Ions in Macrocyclic Complexes*



ACS Omega, 2023, 8, 18041-18046.

### **Maresh Sundararajan**

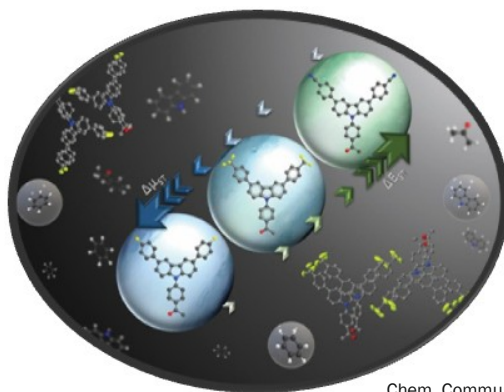
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The study showed that triflate anion can contribute more than 50% to the predicted redox potentials, suggesting that their vital role in the overall reduction processes cannot be neglected.

Several uranyl ions strapped with Schiff-base ligands in the presence of redox innocent metal ions are synthesized, and their reduction potentials are recently estimated. The change in Lewis acidity of the redox-innocent metal ions contributes to  $\sim 60$  mV/pKa unit quantified which is intriguing. Upon increasing the Lewis acidity of metal ions, the number of triflate molecules found near the metal ions also increases whose contributions toward the redox potentials remain poorly understood and not quantified until now. Most importantly, to ease the computational burden, triflate anions are often neglected in quantum chemical models due to their larger size and weak coordination to metal ions. Herein, we have quantified and dissected the individual contributions that arise alone from Lewis acid metal ions and from triflate anions with electronic structure calculations (published in *ACS Omega*, 2023, 8, 18041-18046). The triflate anion contributions are large, in particular, for divalent and trivalent anions that cannot be neglected. It was presumed to be innocent, but we here show that they can contribute more than 50% to the predicted redox potentials, suggesting that their vital role in the overall reduction processes cannot be neglected.

## Phosphorescence in Carbazole Derivatives

# Modulation of $\Delta E_{ST}$ and Room Temperature Phosphorescence in Carbazole Derivatives



Chem. Commun., 2024, 60, 1408.

**K. V. Barhate, A. P. Wadawale, \*K. R. S. Chandrakumar, and N. Agarwal**

\*Scientific Officer, Chemistry Group

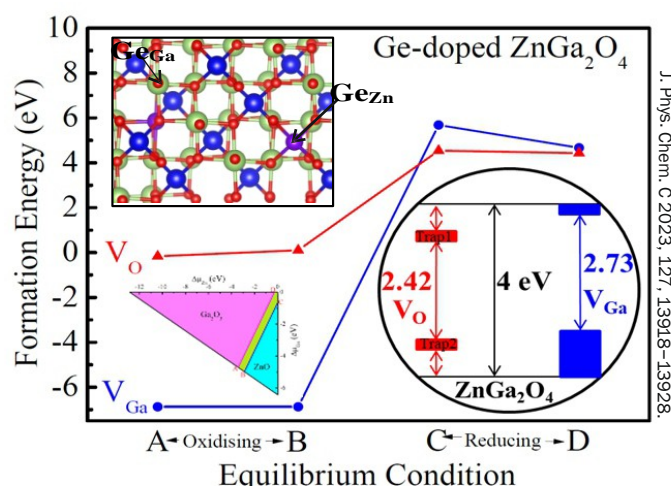
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

The results would be of interest in developing the metal free organic molecular systems having the property of room temperature phosphorescence.

For the first time in the literature, a correlation between the (i) difference in the dipole moment values of the singlet and triplet states  $\Delta\mu_{ST}$  and their respective energy gaps  $\Delta E_{ST}$  and (ii) HOMO-LUMO gap,  $\Delta E_{gap}$  with the  $\Delta E_{ST}$  values. In case of  $\Delta\mu_{ST}$ ,  $\Delta E_{ST}$  is found to be correlated inversely whereas there is a linear correlation with the  $\Delta E_{gap}$  values. These correlations have been observed with the molecular systems which exhibit room temperature phosphorescence. Materials with high ground-state polarity are capable of stabilizing the charge transfer excited states of emitters by having electrostatic interactions with its (emitter) excited-state dipole moment. This results in lowering of the singlet excited state (S1) of the emitter; therefore, the energy gap between S1 and the lowest triplet excited state (T1) is reduced. Similar to this, we believe that large  $\Delta\mu_{ST}$  will stabilize the charge transfer state to reduce the S1 level, which results in reduction of  $\Delta E_{ST}$ . These results would be of interest in developing the metal free organic molecular systems having the property of room temperature phosphorescence (*Chem. Commun.*, 2024, 60, 1408).

## Insight from DFT Study

# Intrinsic Charge Carrier-Trapping Defects in Ge-Doped $\text{ZnGa}_2\text{O}_4$

**Brindaban Modak**

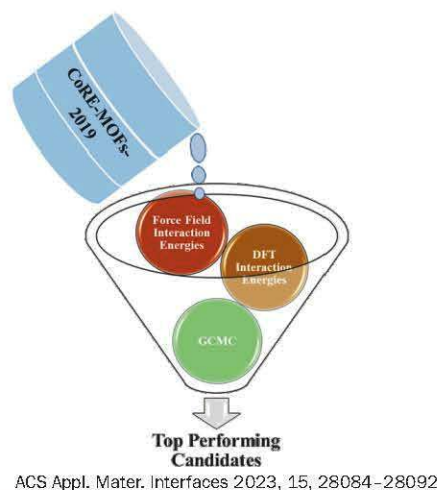
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The study showed that the presence of Ge favors formation of gallium vacancy, which can reduce the band gap significantly without the involvement of discrete mid gap trap states, resulting into enhanced optical output.

**W**ide band gap semiconductors with high dielectric constant and good thermal dissipation are very popular for wide range of optical and electronic devices. In the recent studies  $\text{ZnGa}_2\text{O}_4$  has been projected as an alternative to  $\text{Ga}_2\text{O}_3$ . The structural simplicity (face-centered-cubic spinel structure) results into isotropic electronic and optical properties for  $\text{ZnGa}_2\text{O}_4$ , in comparison to the large anisotropic properties for the  $\beta$ -monoclinic variety of  $\text{Ga}_2\text{O}_3$ . Recent experimental observation indicates that the doping with Ge into  $\text{ZnGa}_2\text{O}_4$  improves the optical properties. However, an unambiguous and ultimate explanation on microscopic origin of the experimentally observed optical property and the limiting factors has not been accomplished so far. This drives us to gain a detailed knowledge of the defect chemistry in Ge-doped  $\text{ZnGa}_2\text{O}_4$ . The present study explains the experimental observation of colour variation property of  $\text{ZnGa}_2\text{O}_4$  by oxidation-reduction process. The experimental observation of poor optical behaviour in the presence of oxygen vacancy and improvement due to doping with Ge have been explained. Present study showed that the presence of Ge favors formation of gallium vacancy, which can reduce the band gap significantly without the involvement of discrete mid gap trap states, resulting into enhanced optical output (*J. Phys. Chem. C* 2023, 127, 13918–13928). This unique strategy can be applied to large number of materials for the enhancement of their optical properties.

## Porous Materials for Carbon Capture

# *Computational High-throughput Studies to explore porous materials for carbon capture*



**\*S. Kancharlapalli and R.Q. Snurr**

\*Scientific Officer, Chemistry Group

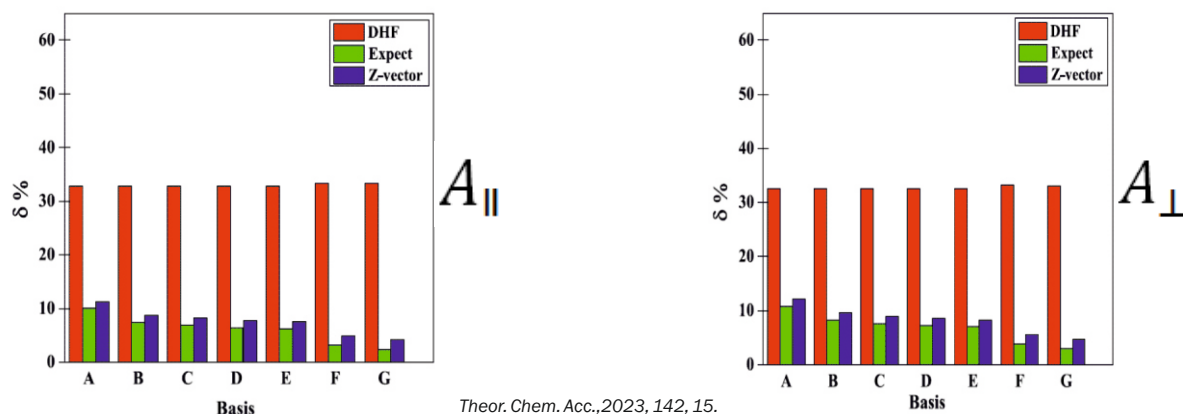
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

Our study identified MOFs that show selective CO<sub>2</sub> adsorption under wet flue gas conditions with significant CO<sub>2</sub> uptake capacity and CO<sub>2</sub>/N<sub>2</sub> selectivity.

Computational high-throughput screening (HTS) has the potential to identify top-performing materials for a particular application, like gas storage and separation applications, from large database of materials. For such large scale studies, fast and efficient computational tools are in high demand. For screening metal-organic frameworks (MOFs) for CO<sub>2</sub> capture from wet flue gas, a random forest machine learning model that can predict the partial atomic charges in MOFs was developed and deployed as python library that has been extensively used. Model was trained and tested on a collection of about 320000 atomic charges calculated through density-derived electrostatic and chemical (DDEC) on a subset of the Computation-Ready Experimental Metal-Organic Framework (CoRE MOF-2019) database. Using the trained model and other state-of-the-art computational techniques, a systematic computational HTS of the all-solvent-removed version of the CoRE-MOF-2019 was carried out for selective adsorption of CO<sub>2</sub> from a wet flue gas mixture. Our screening study identified MOFs that show selective CO<sub>2</sub> adsorption under wet flue gas conditions with significant CO<sub>2</sub> uptake capacity and CO<sub>2</sub>/N<sub>2</sub> selectivity (*JACS Appl. Mater. Interfaces* 2023, 15, 28084–28092). We also analyzed the nature of pore confinements responsible for the observed CO<sub>2</sub> selectivity.

## Low-energy Precision Tests

# Relativistic Coupled-cluster Study of SrF for Low-energy Precision Tests of Fundamental Physics



*Theor. Chem. Acc.*, 2023, 142, 15.

K. Talukdar, H. Buragohain, \*M. K. Nayak, N. Vaval and S. Pal

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The study showed that the SrF molecule could be useful for high-precision molecular experiments to explore physics beyond the Standard Model of elementary particles.

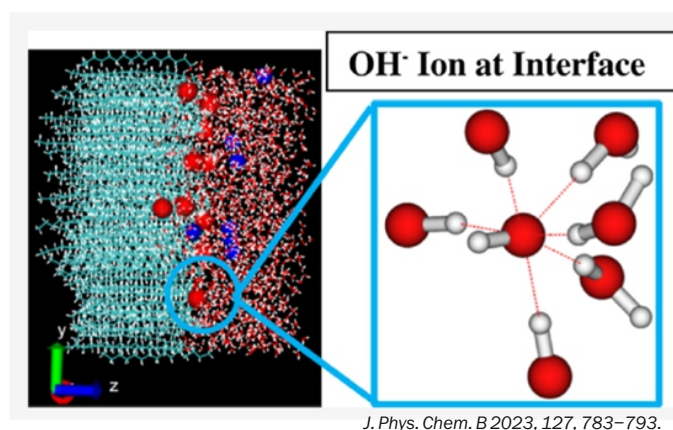
**A** Laser-coolable molecule, SrF, can be an interesting system for spectroscopic tests of fundamental physics. We present an electronic structure study of this molecule within the four-component relativistic coupled-cluster singles and doubles (RCCSD) framework and employ the RCCSD-based methods to compute its molecular-frame dipole moment and core properties such as hyperfine structure coupling constant and molecular P, T-odd electronic structure parameters that are of great importance for the high-precision tests of fundamental physics.

The impact of basis set size, Hamiltonian and nuclear model on the property calculation of SrF is also investigated. The computed results are in good agreement with the available experimental values. The present study shows that the SrF molecule could be useful for high-precision molecular experiments to explore physics beyond the Standard Model of elementary particles (*Theor. Chem. Acc.*, 2023, 142, 15).



## Propensity of Excess Hydroxide Ions

# *On the Propensity of Excess Hydroxide Ions at the Alcohol Monolayer–Water Interface*



**D. Bandyopadhyay, K. Bhanja and N. Choudhury**

Scientific Officers, Chemistry and Chemical Engineering Groups  
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

The study showed that the two self-ions of water are entirely different in terms of their ability to act as H-bond acceptors or donors. These results are to be experimentally verified by VSFG or 2D-IR spectroscopy.

**A**ir–water and oil–water interfaces are ubiquitous in many natural and technological processes. Understanding the distributions of different ions at such interfaces relative to bulk is of fundamental as well as technological importance. A large number of investigations have been devoted to understand structure and orientation of water and the distributions of different ions at the air–water interface through vibrational sum frequency generation spectroscopy (VSFG) and molecular dynamics (MD) simulations. However, interfaces between long-chain organic molecules and water are also of utmost importance because of their ubiquitous presence in several systems, such as various electrochemical systems, biological membranes, atmospheric aerosols and fuel cells. Knowledge on the alcohol–water interface is also essential to understand the formation of sea spray aerosol, which has significant influence in cloud formations and climate change. In the present work, using extensive molecular dynamics simulations and advanced techniques, the distributions of self-ions ( $H^+$  and  $OH^-$ ) of water at the cetyl ( $C_{16}$ ) alcohol – water interface have been studied. Present study demonstrates that hydroxyl ions accumulate at the interface, but hydronium ions are distributed homogeneously throughout the bulk and the interface (*J. Phys. Chem. B* 2023, 127, 783–793). It is also observed from the present study that these two self-ions of water are entirely different in terms of their ability to act as H-bond acceptors or donors. These results are to be experimentally verified by VSFG or 2D-IR spectroscopy.

## Futuristic Battery Materials

# Exploring Solid-State Battery Materials using Neutron Spectroscopy and *ab-initio* Simulations

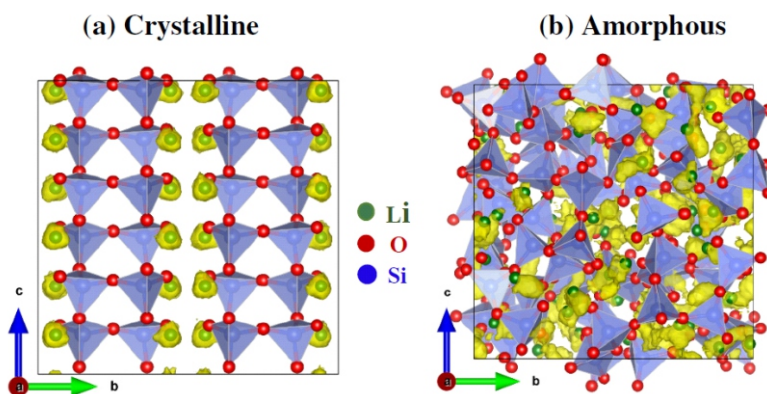


Fig.: The structure of (a) *crystalline-Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>* and (b) *amorphous-Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>* used in simulations. The Li probability iso-surface plot (yellow dots) from AIMD simulations at 1000K. The disjoint iso-surface plots in *crystalline-Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>* shows absence of Li<sup>+</sup> diffusion, while connected iso-surface plots in amorphous phase reveal Li<sup>+</sup> diffusion.

**Dr. R. Mittal and Dr. M. K. Gupta**

Scientific Officers, Solid State Physics Division, Physics Group  
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

Our studies showed that manipulating the ionic stoichiometry of these materials and prompting the formation of the amorphous phase can significantly improve the diffusion process, improving the material's potential performance in a battery.

**R**enewable energy produced by solar and wind technologies is intermittent, so there is a need for economical storage devices that have long life cycles. Electrochemical batteries are a promising solution for renewable energy storage. The scientists are studying a range of battery materials and their properties, including conventional lithium-ion batteries and the next-generation battery materials. Solid-state batteries have higher energy density compared to traditional Li-ion batteries and have the potential to offer great advantages as batteries in electric vehicles.

Understanding the diffusion process of Li or Na ions in these electrolytes is important, as the faster movement of these ions increases the battery's storage capacity. For a battery material, high ionic diffusion is favourable for the charge/discharge process. We have proposed a few strategies (*J. Mater. Chem. A11, 1712, 2023; J. Mater. Chem. A 11, 23940, 2023*) to enhance the Li/Na-ion conductivity and tune the operating temperature in solid-state electrolytes, such as doping, amorphization, reducing dimensionality, etc. Quasi-elastic neutron spectroscopy is a spectroscopic technique that is a great tool for investigating these diffusion processes, as the motions of particles can be explored at the atomic scale. *Ab-initio* molecular dynamics simulations alongside the experiments were extremely helpful in enabling to interpret the data.

In the solid electrolyte material  $\text{Li}_2\text{Si}_2\text{O}_5$ , we have shown (*J. Mater. Chem. A11, 1712, 2023*) that the dynamics of silicon polyhedral units play an important part in the lithium diffusion process. It has been shown that amorphous phase of  $\text{Li}_2\text{Si}_2\text{O}_5$  facilitates the fast motion of lithium. We have identified that the specific topology of Na zig-zag chains in  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S, Se}$ ) provides (*J. Mater. Chem. A 11, 23940, 2023*) the low-barrier energy pathways for Na-ion diffusion. We bring out the role of specific zig-zag Na chains topology in the framework structure and its dynamics, leading to Na diffusion.

Our studies showed that manipulating the ionic stoichiometry of these materials and prompting the formation of the amorphous phase can significantly improve the diffusion process and also material's potential performance in a battery. This is an important consideration which needs to be taken into account in designing future solid-state battery materials.