Computational discovery of fast oxygen conductors

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Acknowledgement

DOE BES Materials Chemistry

NSF

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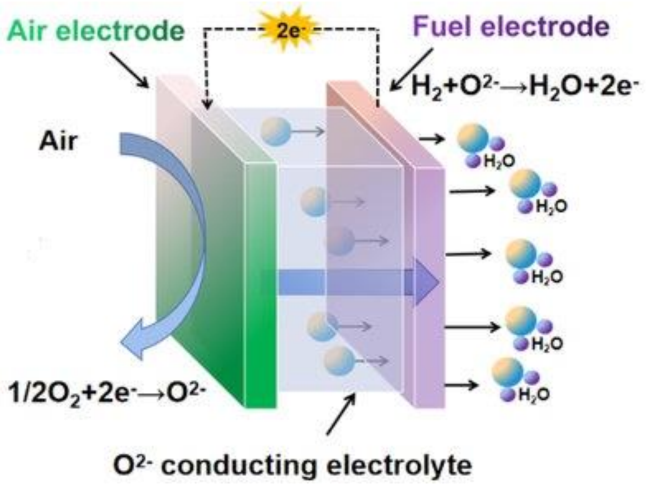
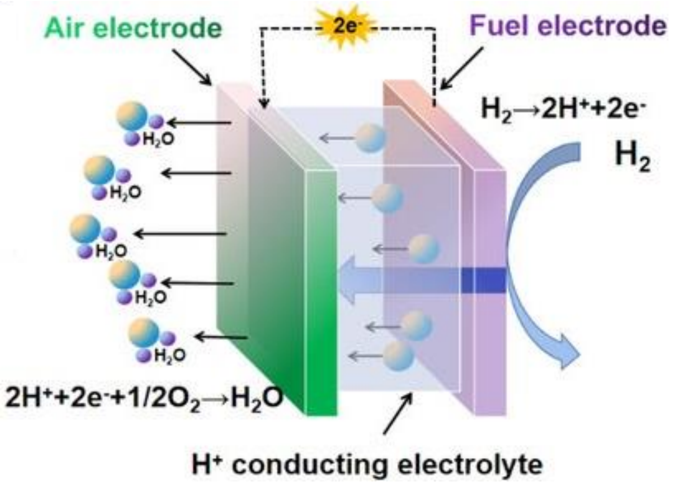
Background: Applications implemented with oxygen-active materials

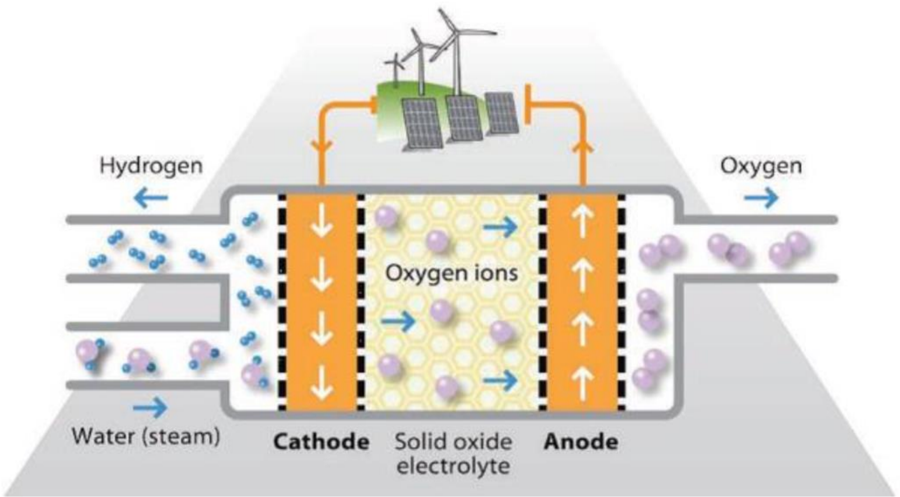
Solid Oxide Fuel Cell



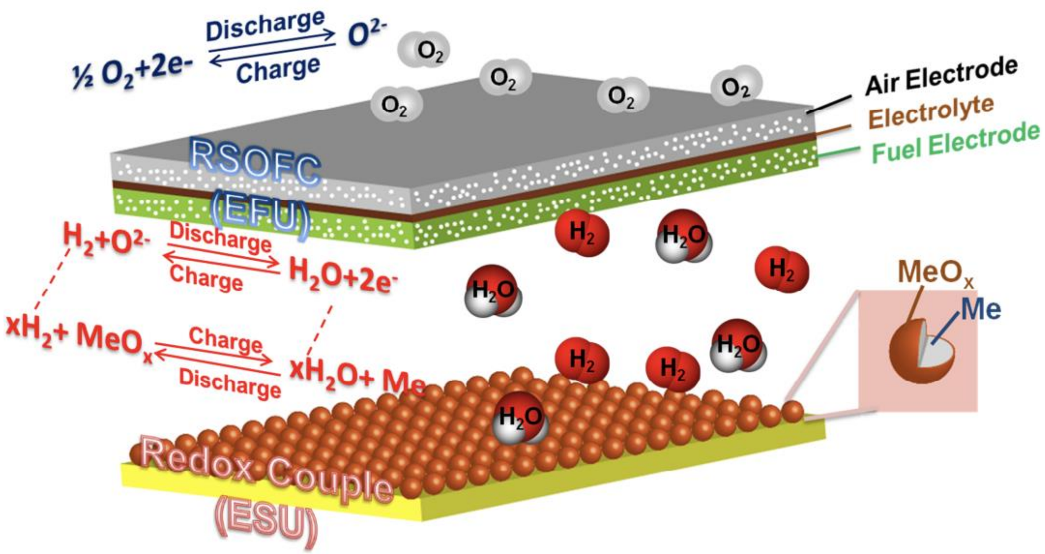
Proton-Exchange Membrane Fuel Cell



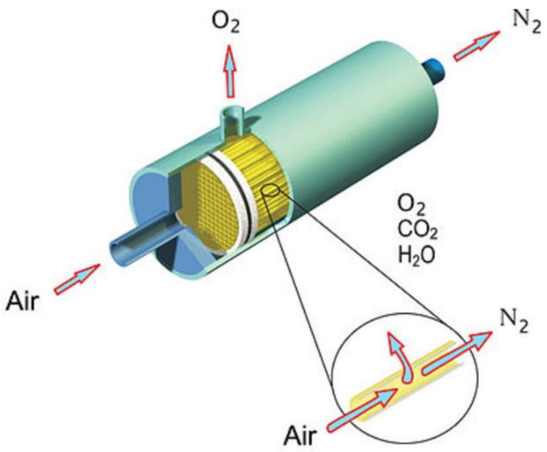
Solid Oxide Electrolysis Cell



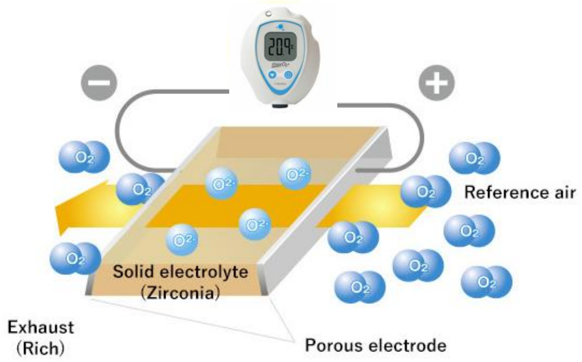
Solid Oxide Air Battery



Oxygen Separation Membrane



Oxygen Sensor

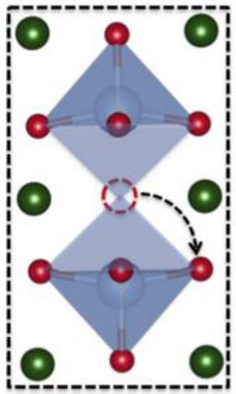


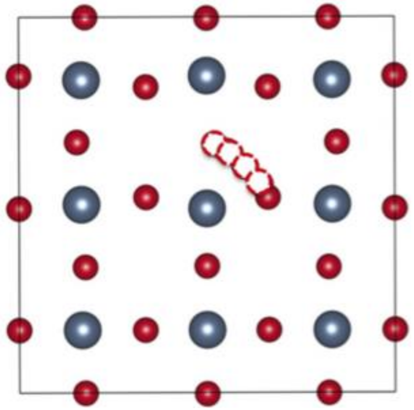
Energy Mater 2021;1:100002; *ECS Trans.* 2014; 58 67; *Int J Energy Res*. 2020; 44: 594– 611.
https://www.ngkntk.co.jp/english/product/sensors_plugs/zirconia_oxygen.html

Background: Known oxygen conduction materials

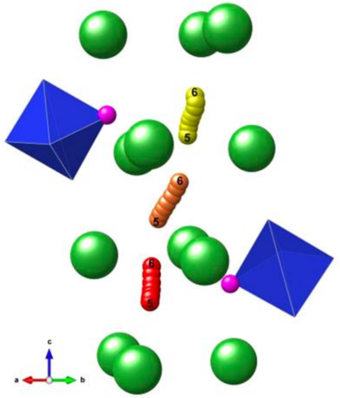
Vacancy diffusion mechanism

Perovskite $SrTiO_{3-\delta}$



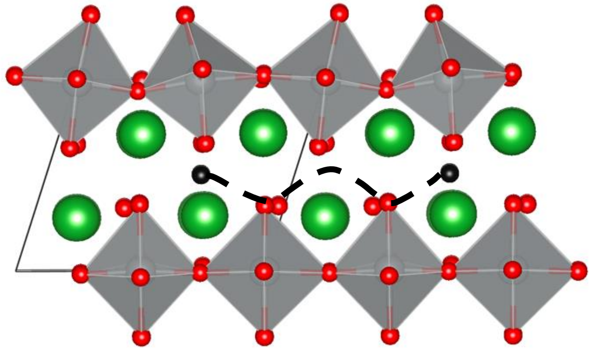


Interstitial diffusion mechanism

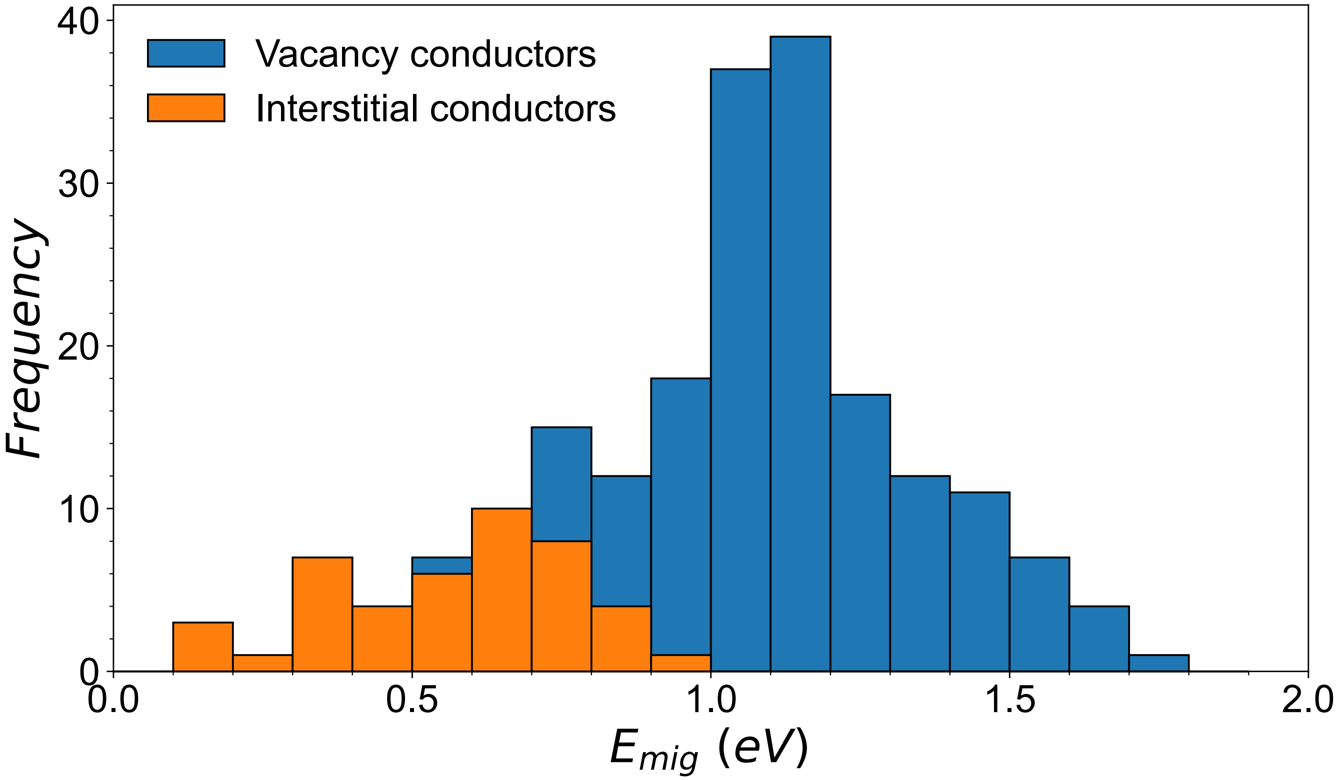


Apatite $La_{10}Si_6O_{27}$

Interstitialcy (kick-out) diffusion mechanism



Ruddlesden-Popper $La_2NiO_{4+\delta}$

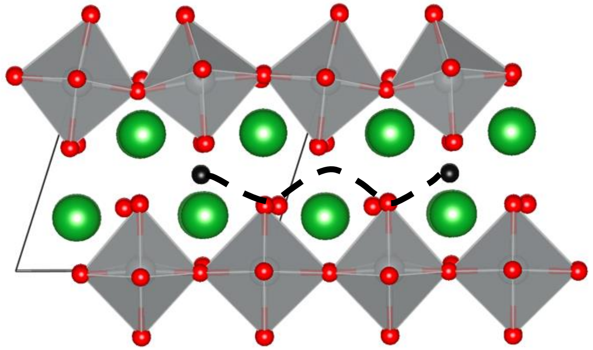


Interstitial oxygen (O_i) generally moves faster than vacancy oxygen (V_O)

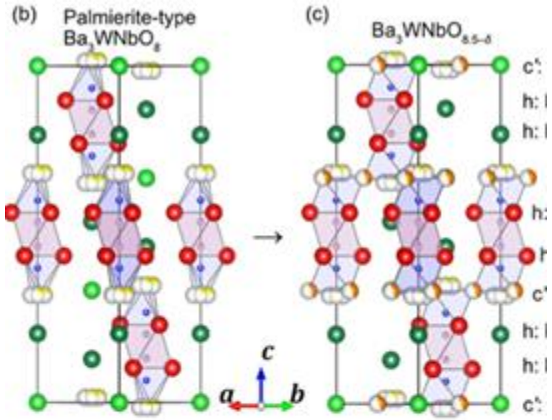
https://citrination.com/data_views/147/matrix_search?from=0

Background: Known interstitial oxygen conductors E_{mig} ~ 0.2-1eV

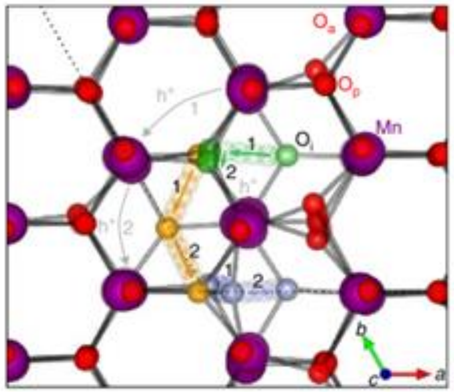
Ruddlesden–Popper ($La_2NiO_{4+\delta}$)



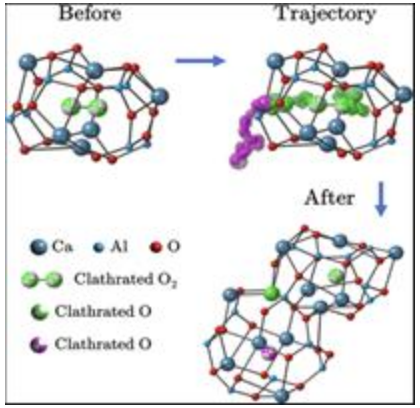
Hexagonal Perovskite (Ba_3WNbO_{9-x})



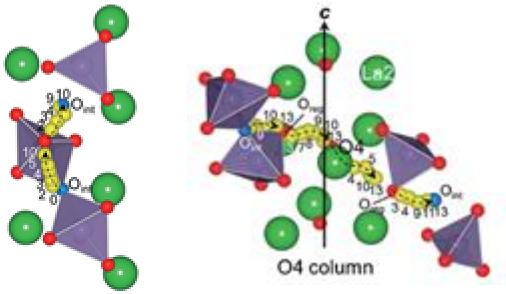
Hexagonal Manganites ($YMnO_3$)



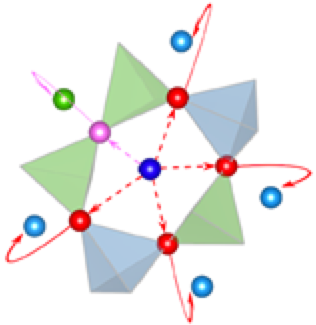
Mayenite-type cage compounds ($12CaO{\cdot}7Al_2O_3$)



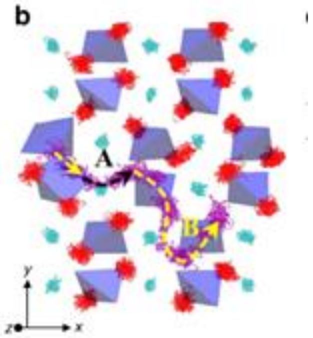
Apatite ($La_{10}Ge_6O_{27}$)



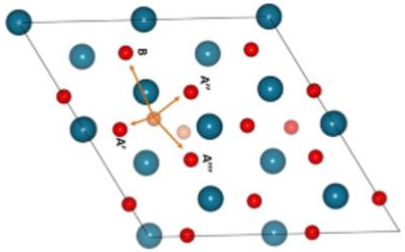
Melilite ($LaSrGa_3O_7$)



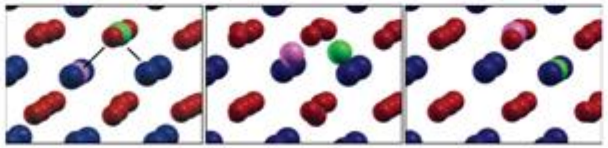
Scheelite ($CeNbO_{4+\delta}$)



Cr_2O_3, Fe_2O_3

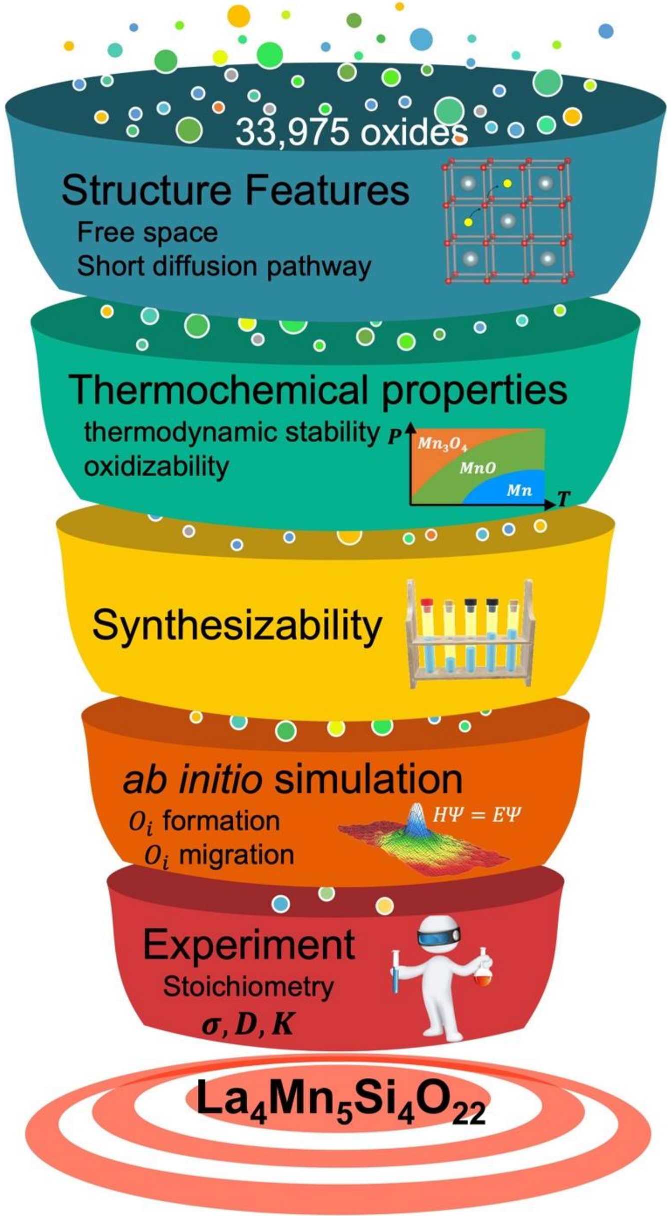


Fluorite (UO_{2+x})



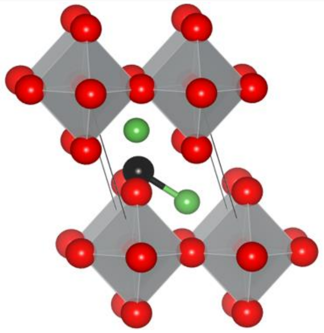
9 families reported!

High-throughput screening approach for new interstitial oxygen diffuser

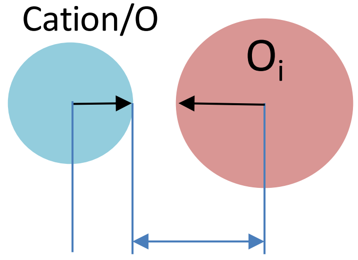


Free space: $d_{(O_i-O)} \geq 0.88Å$; $d_{(O_i-Cation)} \geq 1.0Å$

short pathway: $d_{(O_i-O_i)} \leq 3.0Å$



Ruddlesden-Popper



Phase stability: $E_{hull} < 100$ meV/atom (in air)
$E_{hull} < 200$ meV/atom (Vacuum)

Chemical reactivity: transition metal with low valence state

Synthesizability

intersection screening with ICSD database

DFT studies on 341 oxides: $E_{form}(O_{int}) < 0.3$ eV

AIMD simulation on 87 oxides: $E_{mig}(O_{int}) < 0.5$ eV

Synthesis, XRD, EPMA, ECR, 4-probe method

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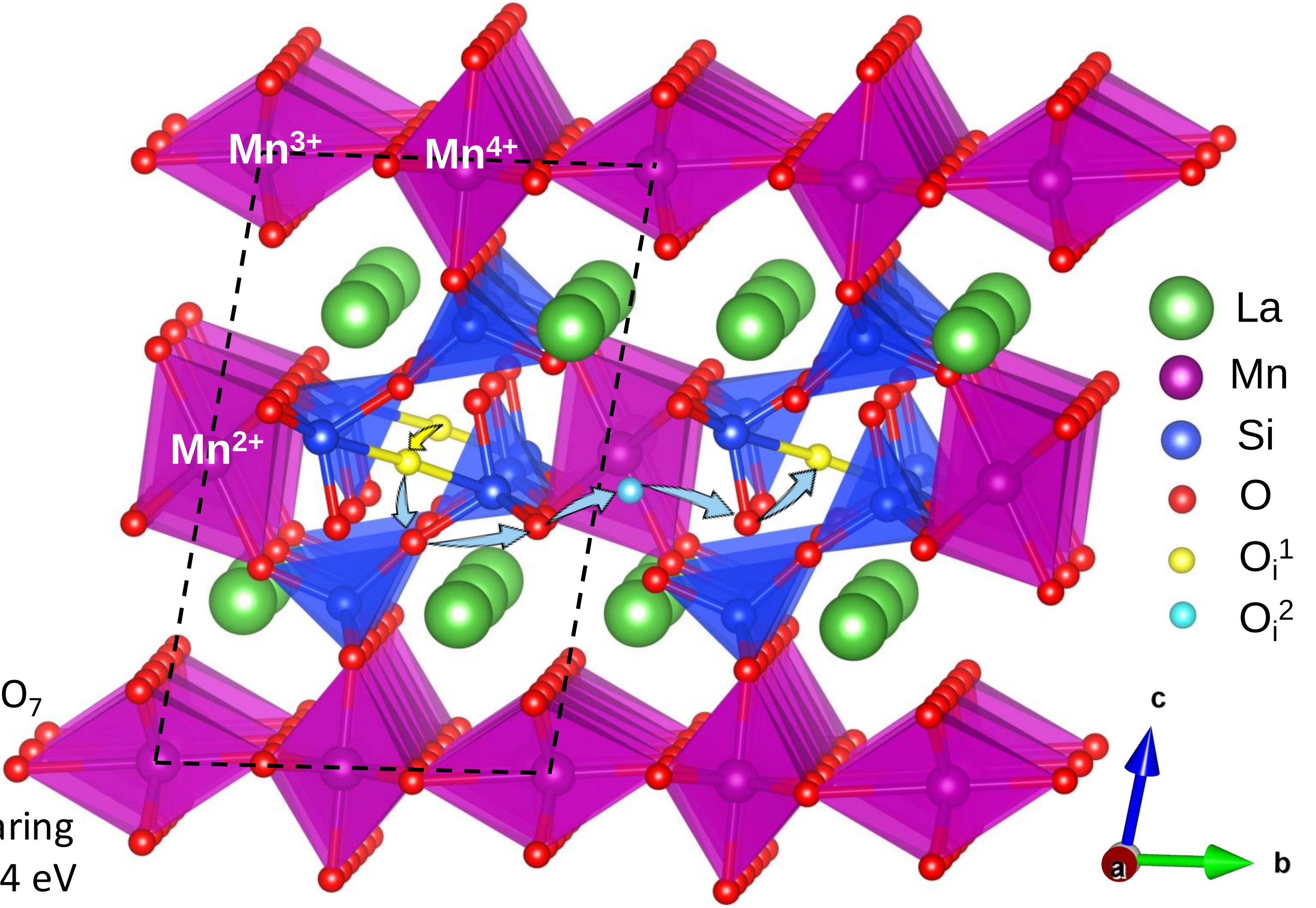
Structure of $La_4Mn_5Si_4O_{22}$

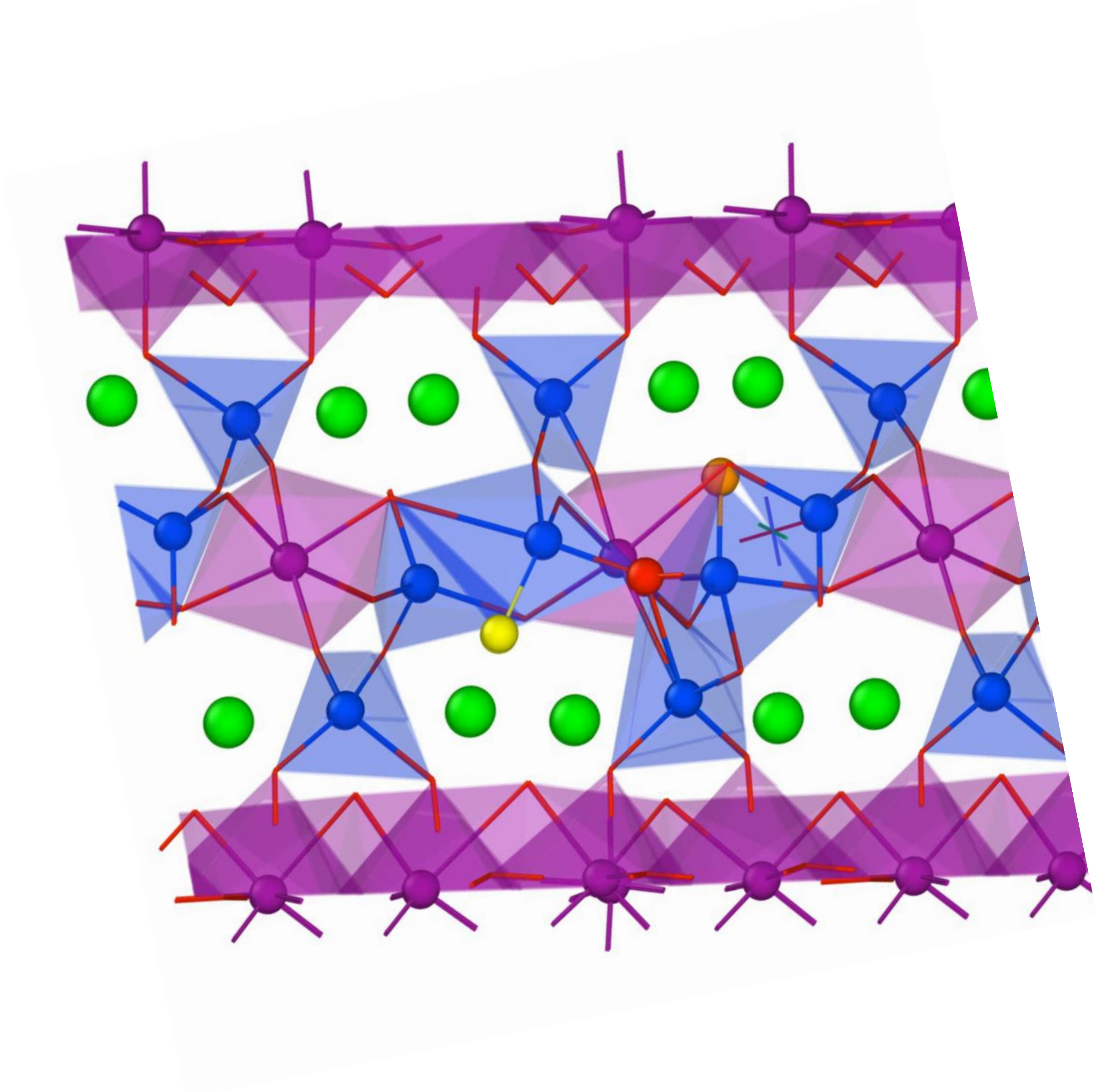
- Eclipsed sorosilicate Si_2O_7 groups connected with multivalent Mn polyhedral
- Free space in between unconnected Si_2O_7 chains.
- Redox-active Mn^{2+}
- Two stable oxygen interstitial sites under ambient

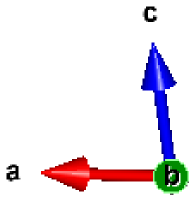


A dual diffusion mechanism

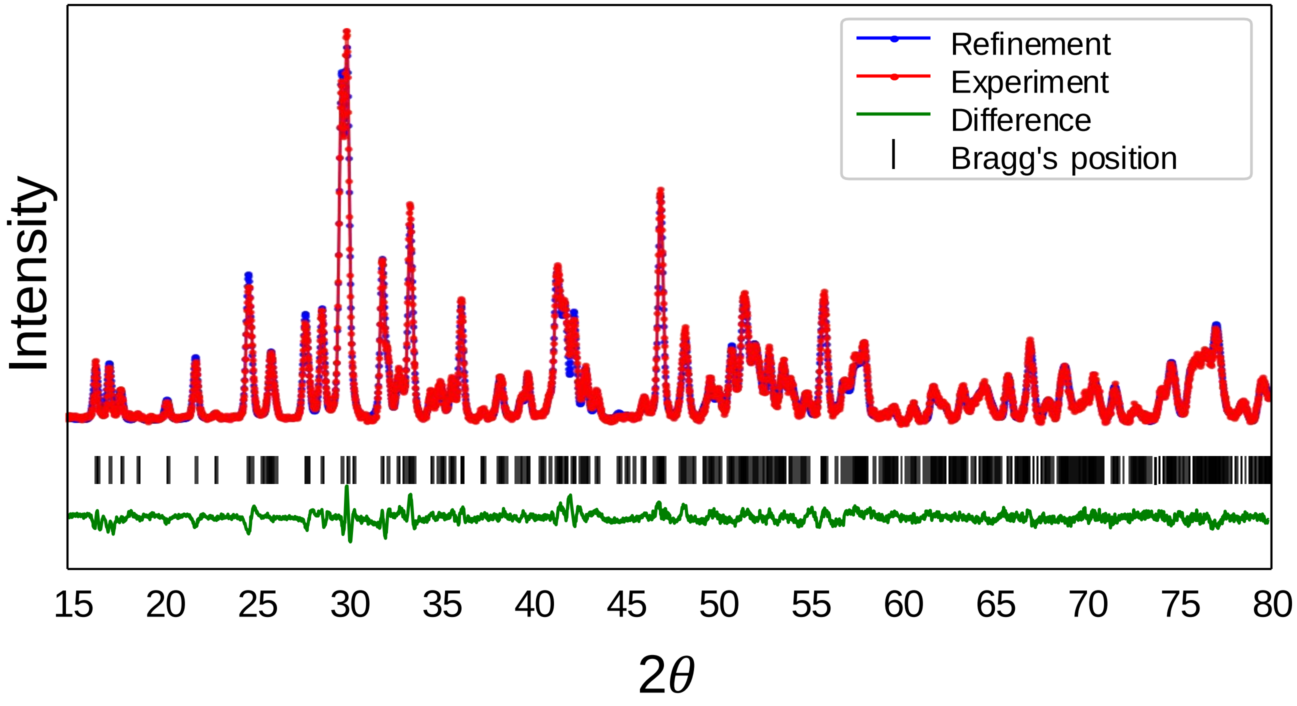
- Interstitial mechanism in between unconnected Si_2O_7 chains (yellow arrow) E_m=0.69 eV
- Interstitialcy mechanism enabled by the corner-sharing Si_2O_7-MnO_2-Si_2O_7 framework (cyan arrows) E_m=0.74 eV

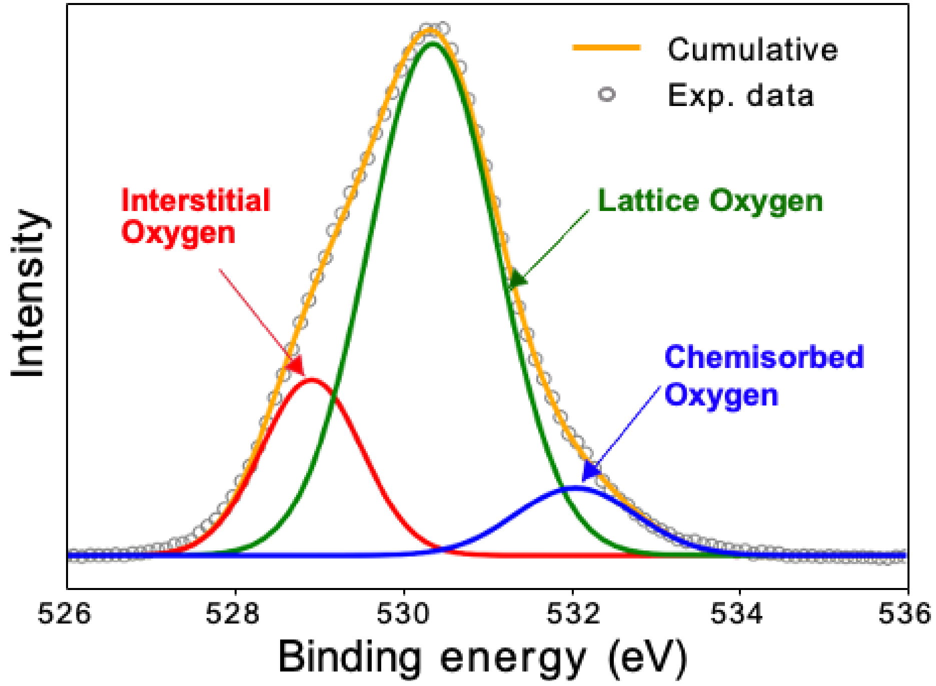
Ab initio studies of oxygen ion diffusion in $La_4Mn_5Si_4O_{22+\delta}$ (δ = 0.5)





Existence of interstitial oxygen in synthesized $La_4Mn_{4.69}Si_4O_{22+\delta}$ (δ = 0.42)

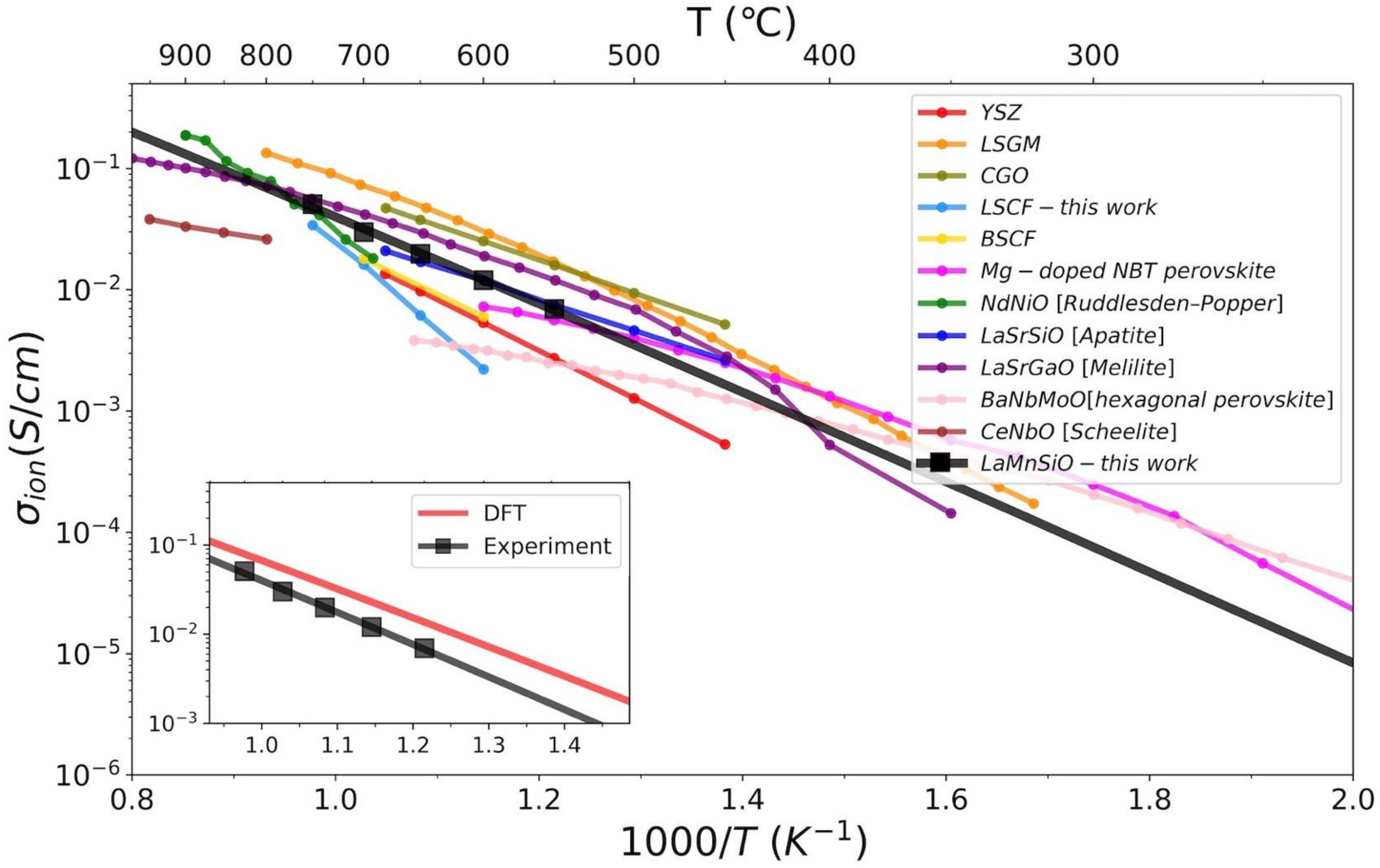


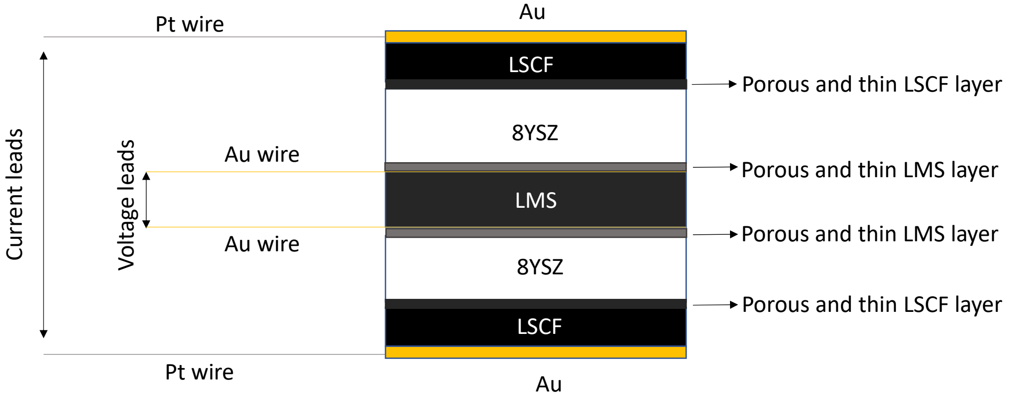


- Electron Probe Microscopy Analyzer (EPMA): $La_4Mn_{4.69}Si_4O_{22+0.42}$

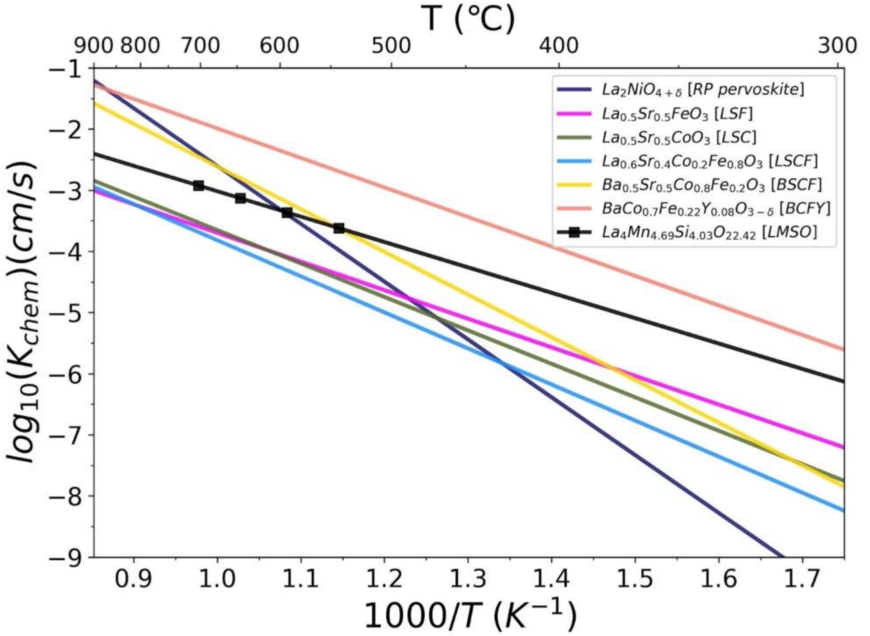
Experimental studied oxygen mobility in $La_4Mn_{4.69}Si_{4.03}O_{22.42}$

Oxygen ionic conductivity measurement using YSZ-blocked DC 4-probe method

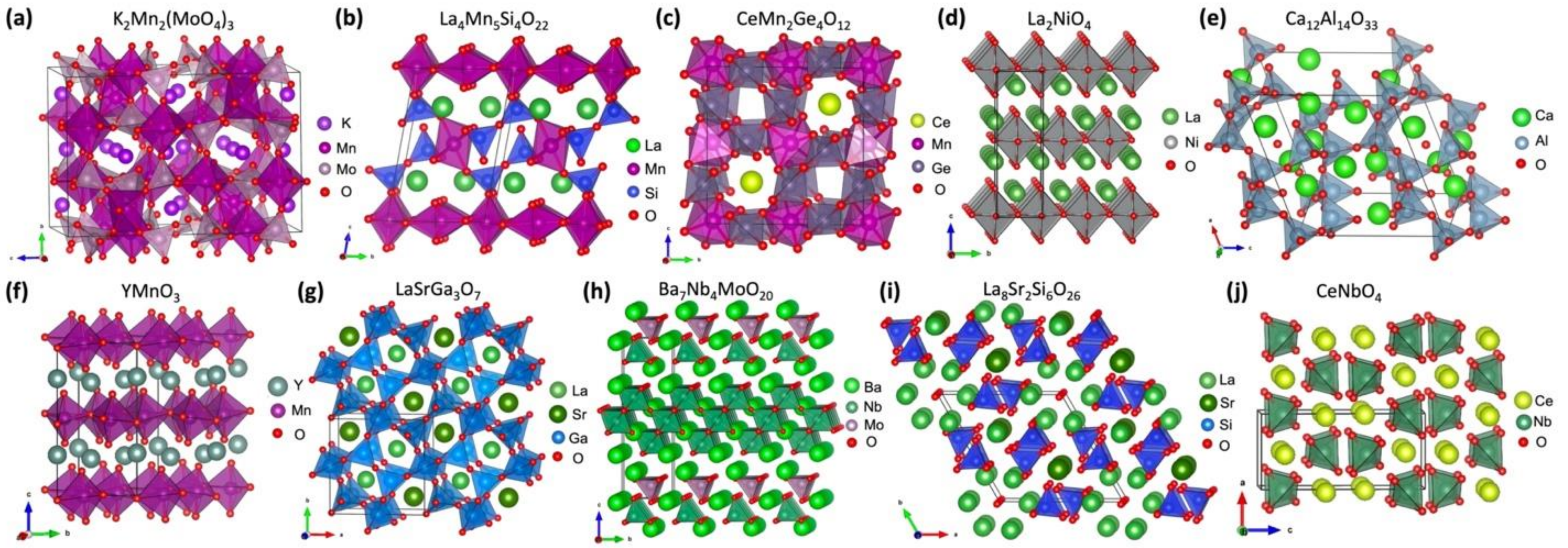




Oxygen surface exchange coefficient ECR (Electrical conductivity relaxation)



Universal features of high-performing interstitial oxygen conductors



- The availability of electrons for oxygen reduction
- Structural flexibility enabling sufficient accessible volume
    i. corner-sharing polyhedral networks
    ii. isolated polyhedra

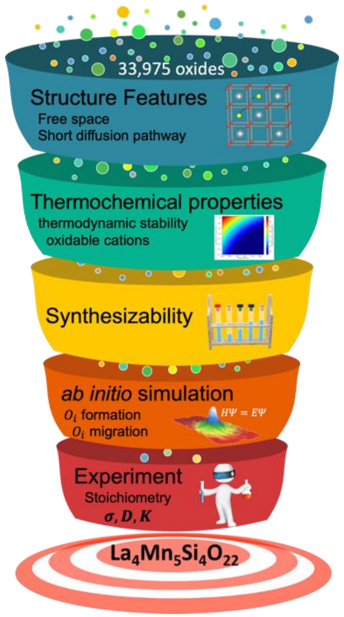
Summary

- A new family of interstitial oxygen diffuser $La_4Mn_5Si_4O_{22+\delta}$ is discovered by a pre-designed high-throughput screening approach along with experimental validation

- $La_4Mn_5Si_4O_{22+\delta}$ shows fast oxygen ionic conductivity, and excellent surface oxygen exchange rate

- Availability of electrons and structural flexibility with accessible volume are the universal features identified among high-performing interstitial oxygen conductors

- **Huge space to explore for new promising oxygen-active materials!!!**



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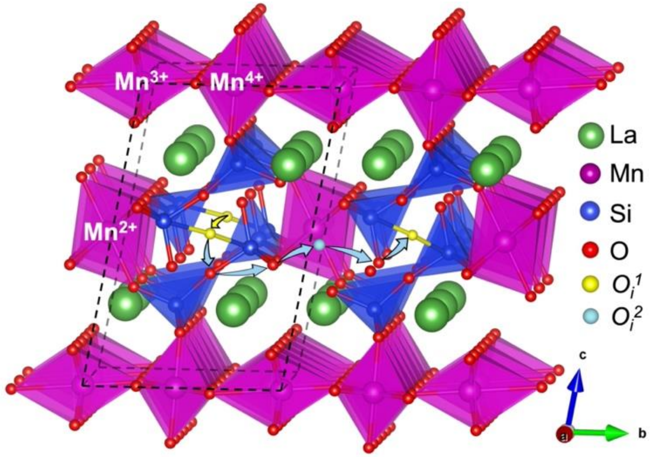

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Undergraduate Students

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Computational Materials Group

Thank you!