Ultra-fast oxygen conduction in Sillén Oxychlorides

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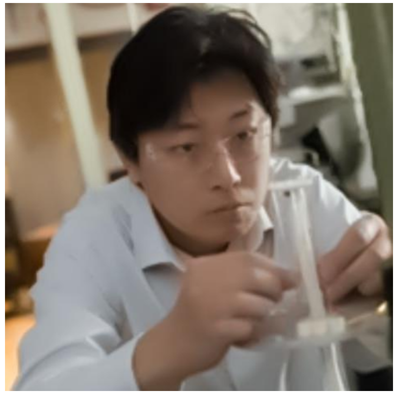

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Acknowledgement

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DOE BES Materials Chemistry

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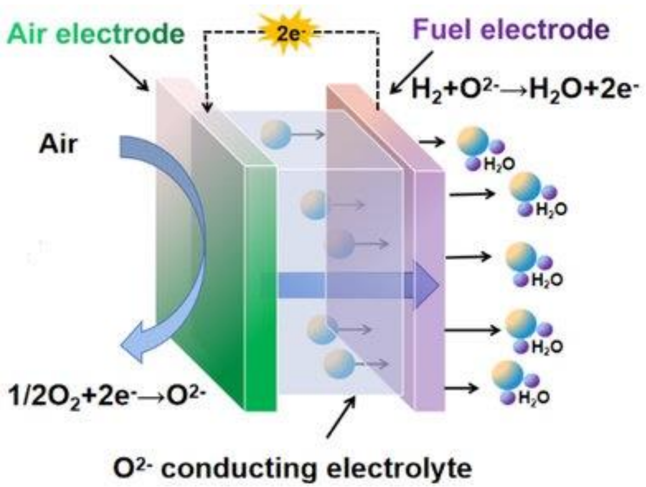
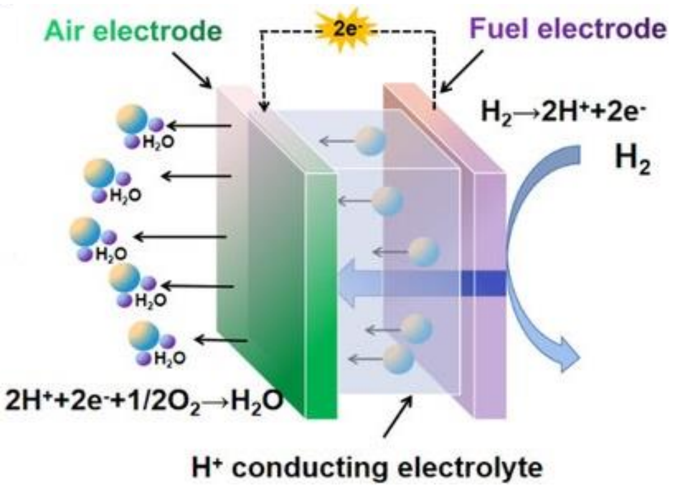
Background: Applications implemented with oxygen-active materials

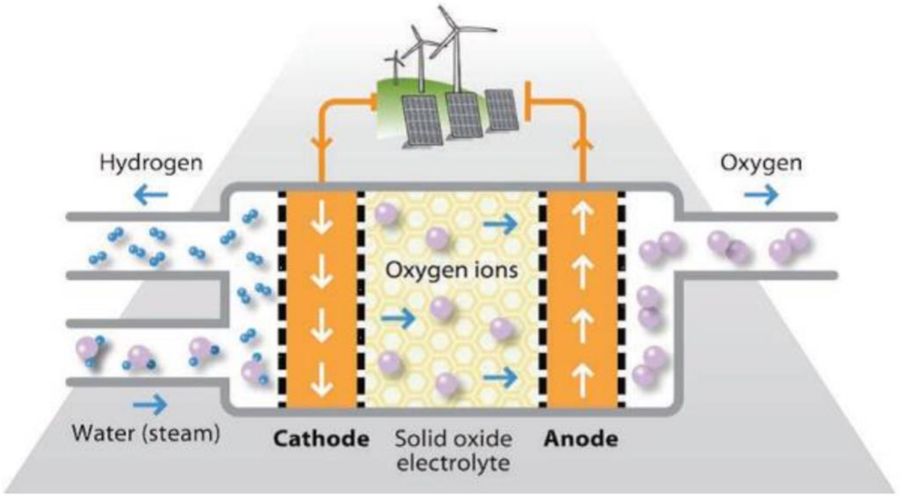
Solid Oxide Fuel Cell



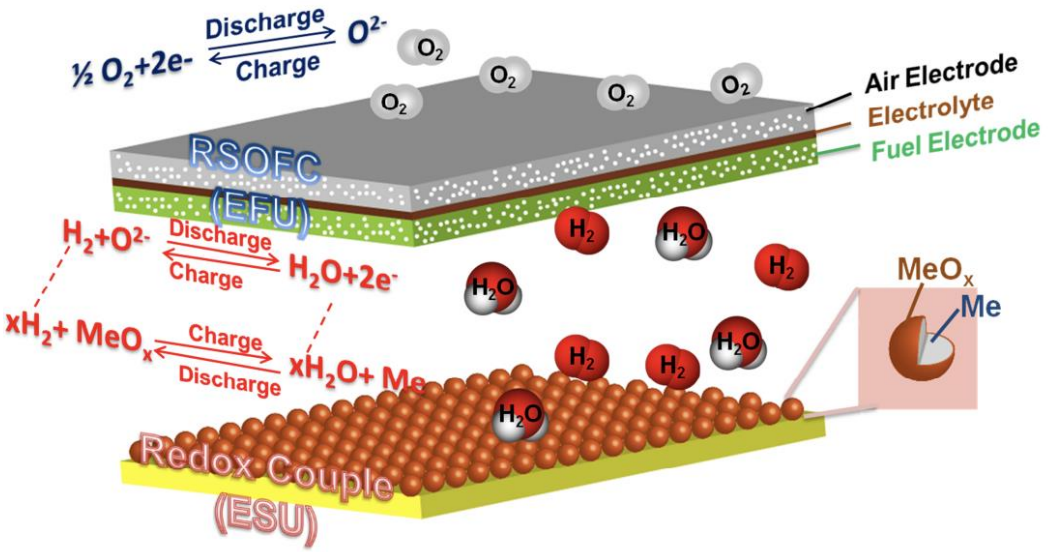
Proton-Exchange Membrane Fuel Cell



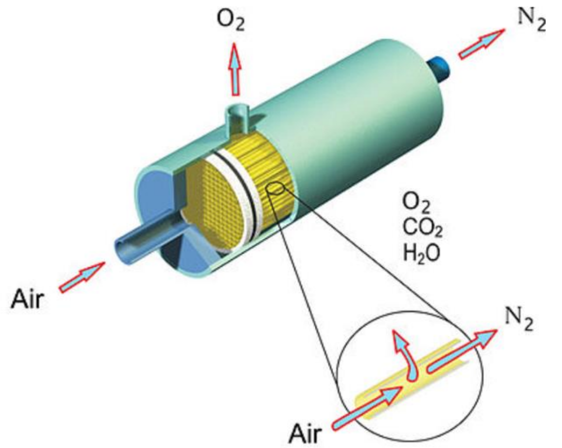
Solid Oxide Electrolysis Cell



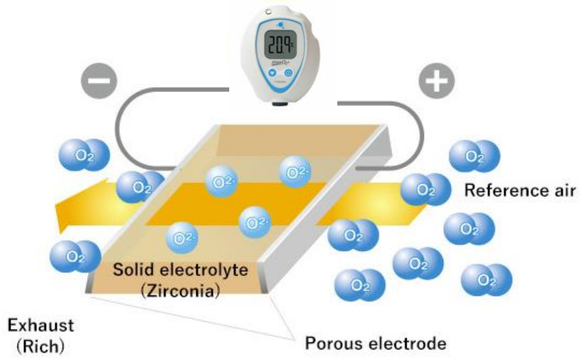
Solid Oxide Air Battery



Oxygen Separation Membrane



Oxygen Sensor

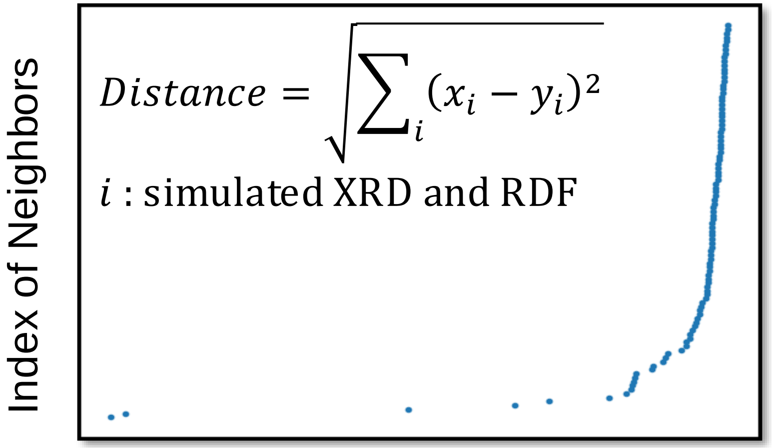


Energy Mater 2021;1:100002; *ECS Trans.* 2014; 58 67; *Int J Energy Res*. 2020; 44: 594– 611.
https://www.ngkntk.co.jp/english/product/sensors_plugs/zirconia_oxygen.html

Materials discovery based on structural features

Hypothesis: materials with similar structural features to known oxygen conductors are promising for high oxygen mobility.

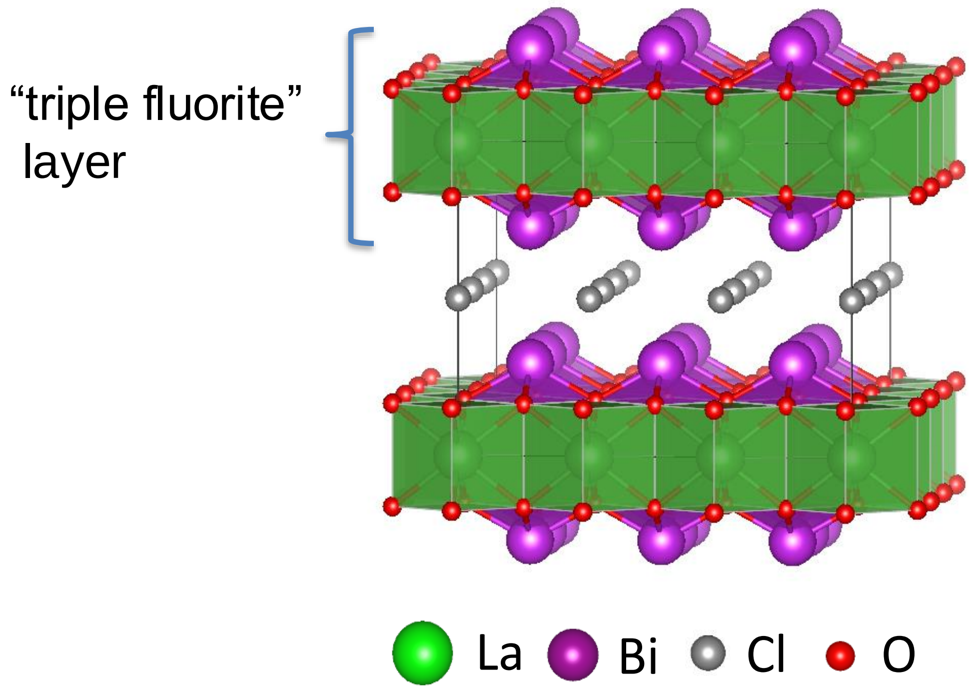
- 62,000 oxygen-containing compounds from the Materials Project were considered.
- Nearest neighbors were ranked based on their structural similarity to fluorite BiO_2, described by XRD of oxygen sublattice and RDF
- The Bi_2MO_4X = MBi_2O_4X (M= Rare-earth element, X= halogen) family was found as the nearest neighbors. Bi_2LaO_4Cl was selected as a prime candidate for further in-depth studies.

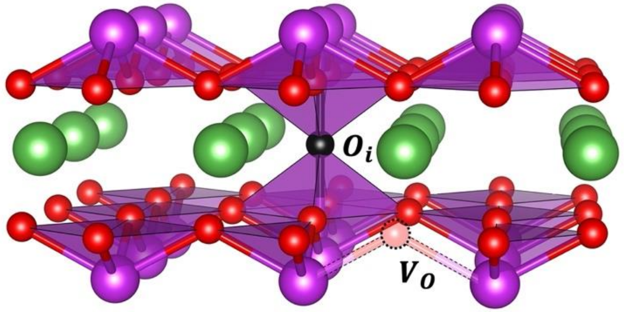


Nearest neighbors to fluorite BiO_2			
#	Materials ID	Formula	Distance
1	mp-546621	**Bi_2ErBrO_4**	18.67
2	mp-546350	**Bi_2TmBrO_4**	19.15
3	mp-549127	**Bi_2HoClO_4**	20.35
4	mp-549728	DyZnPO	21.85
5	mp-552738	**Bi_2TmIO_4**	22.69
6	mp-546625	**Bi_2HoBrO_4**	22.69
7	mp-3589	BPO_4	24.14
8	mp-1087483	ThCuPO	24.14
9	mp-6790	$Ba_2Y(CuO_2)_4$	24.17
10	mp-8789	Ca_4As_2O	24.25

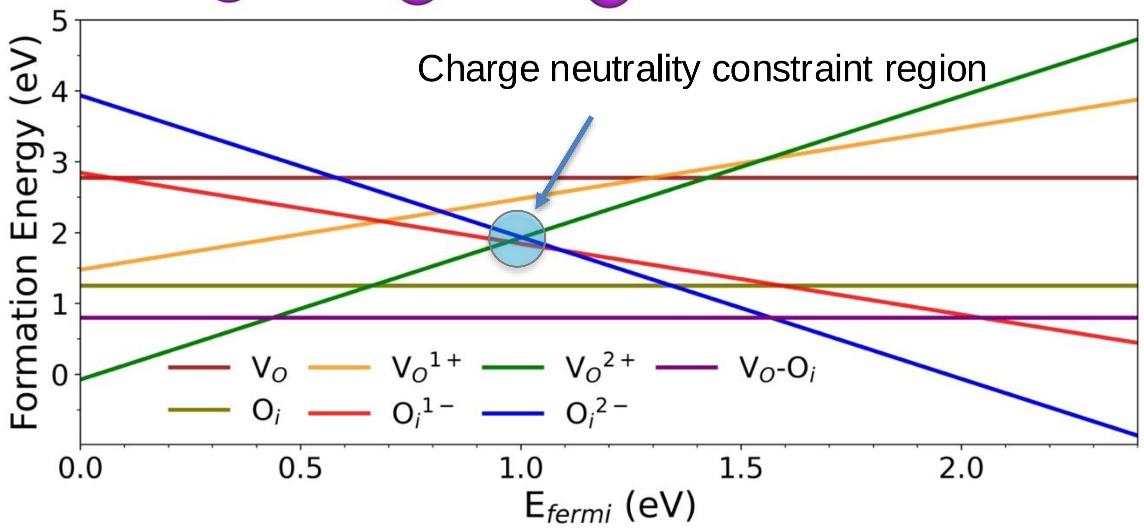
Structure and defect chemistry of LBC

- $LaBi_2O_4Cl$ (LBC) is a layered bismuth oxyhalide, adopts a “triple fluorite” layer $[Bi_2LaO_4]^+$, balanced by the Cl^- layer.
- LBC is a wide band gap insulator with $E_{gap} = 2.65\ eV$, consistent results achieved from exp., DFT-HSE, literatures.
- The Frenkel pair ($V_O - O_i$) is the most thermodynamically stable defects in a wide T (300K, 873K and 1073K) range under atmospheric $P(O_2)$.





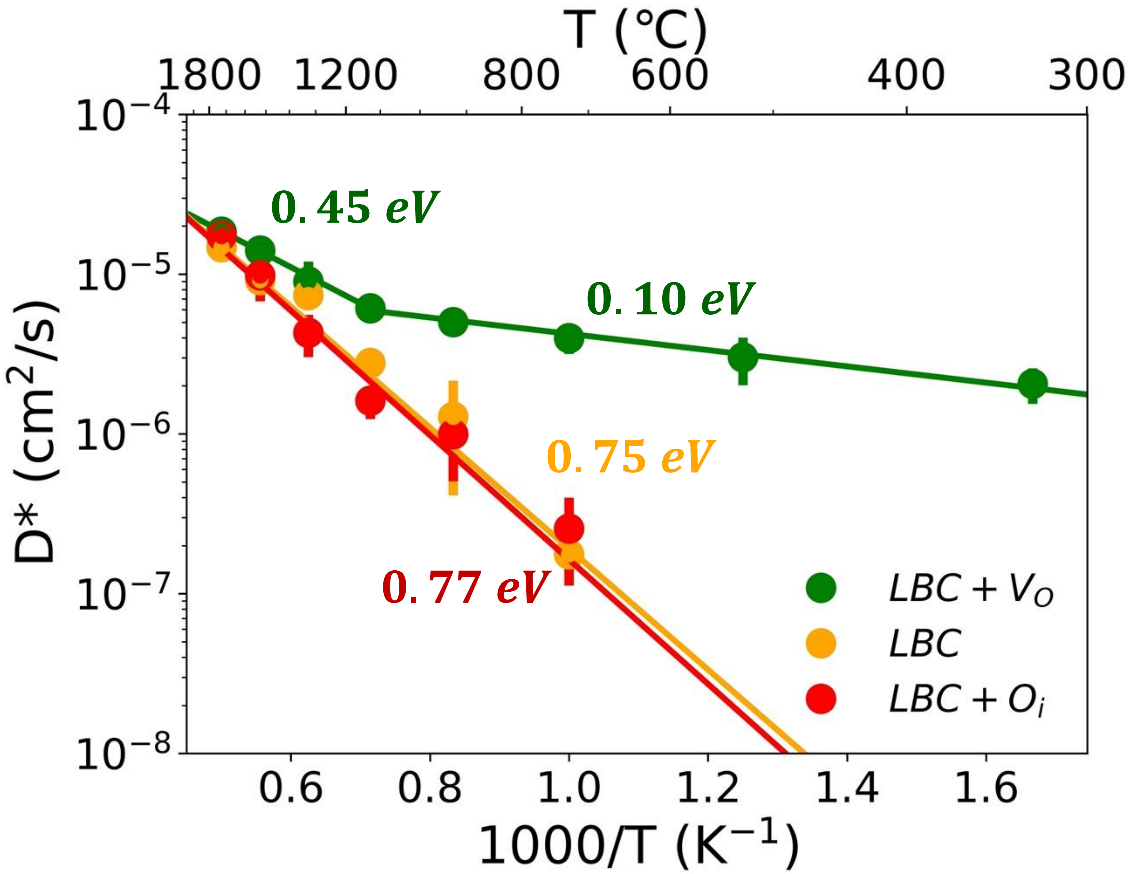
Frenkel pairs dominant in LBC

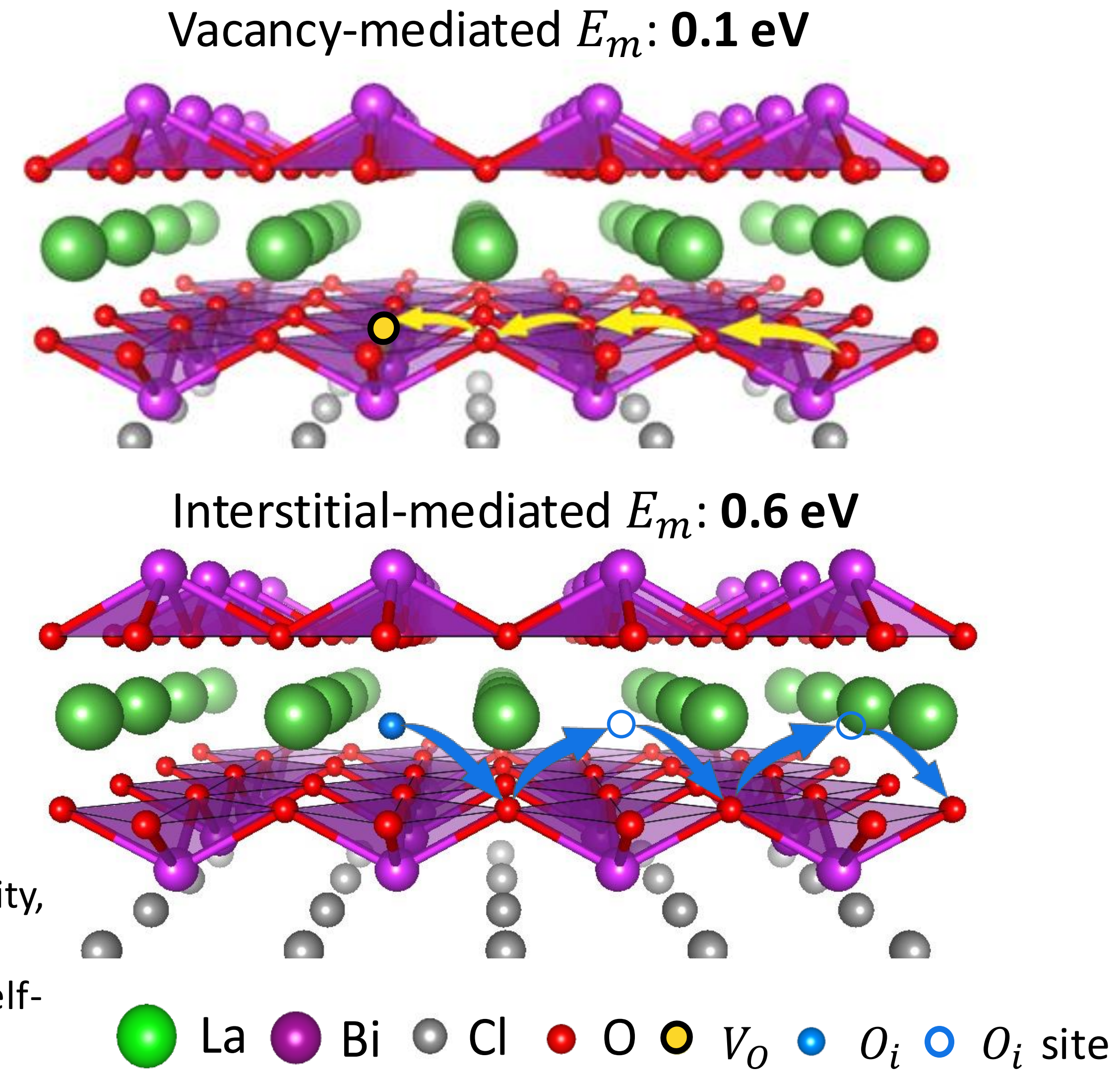


Formation energy of oxygen defects at room temperature, atmosphere

Ab initio studies on oxygen mobility in LBC with defects

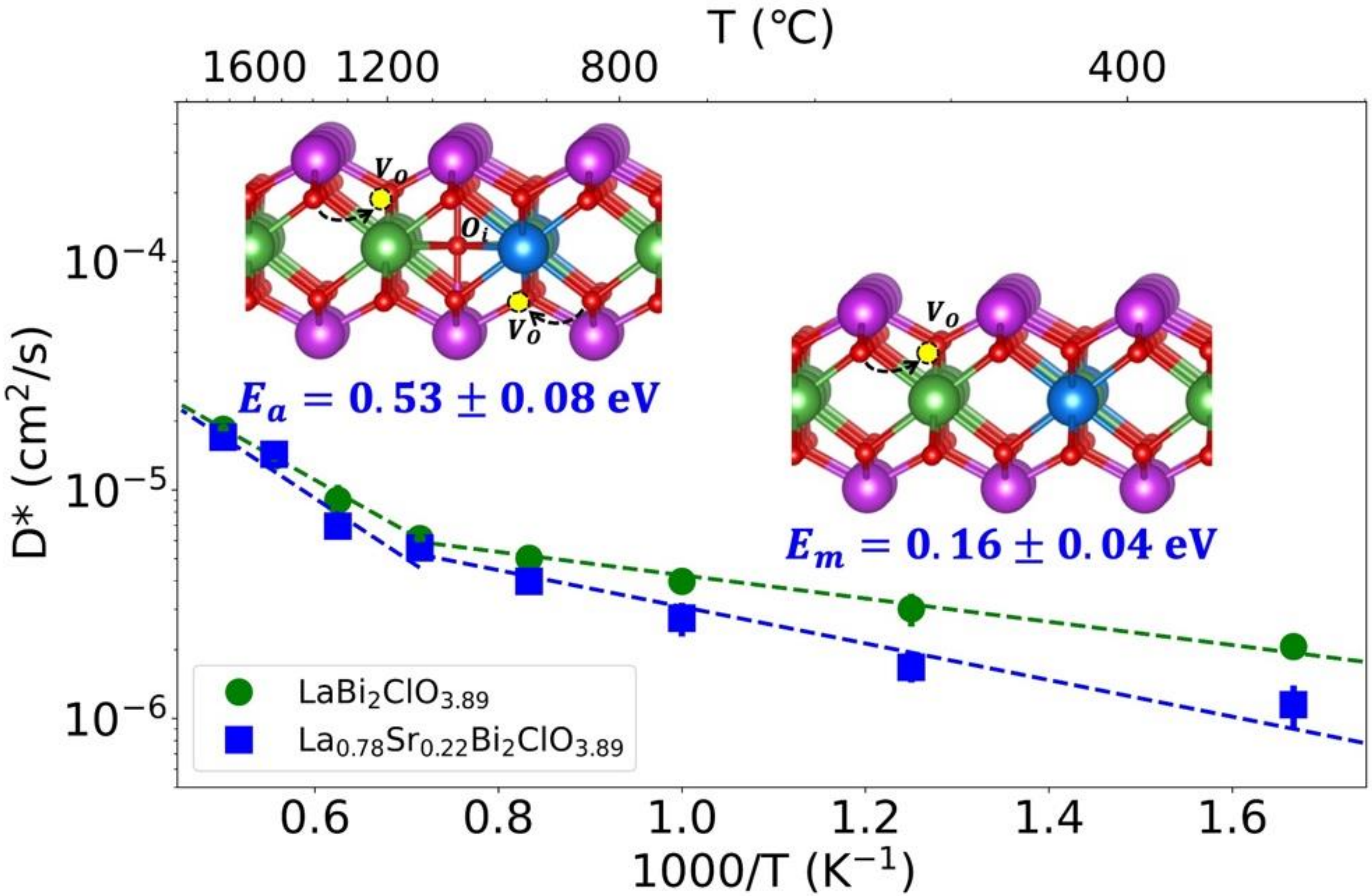
Ab initio studies indicate that vacancy diffusion in the "triple-fluorite" layer features an ultra-low migration barrier of **~ 0.1 eV !**





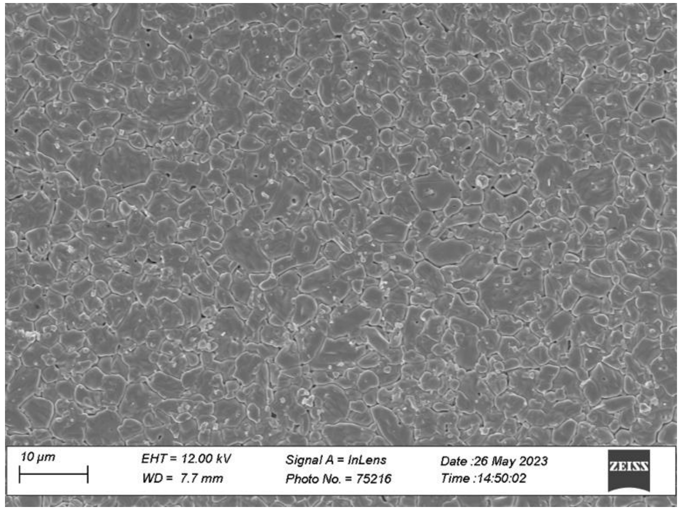
- With oxygen vacancy V_O, LBC exhibits ultra-high oxygen self-diffusivity, and ultra-low migration barrier
- With or without oxygen interstitial O_i, LBC exhibits similar oxygen self-diffusivities, and moderate migration barriers

Similar oxygen diffusivity and diffusion barriers observed in Sr-doped LBC

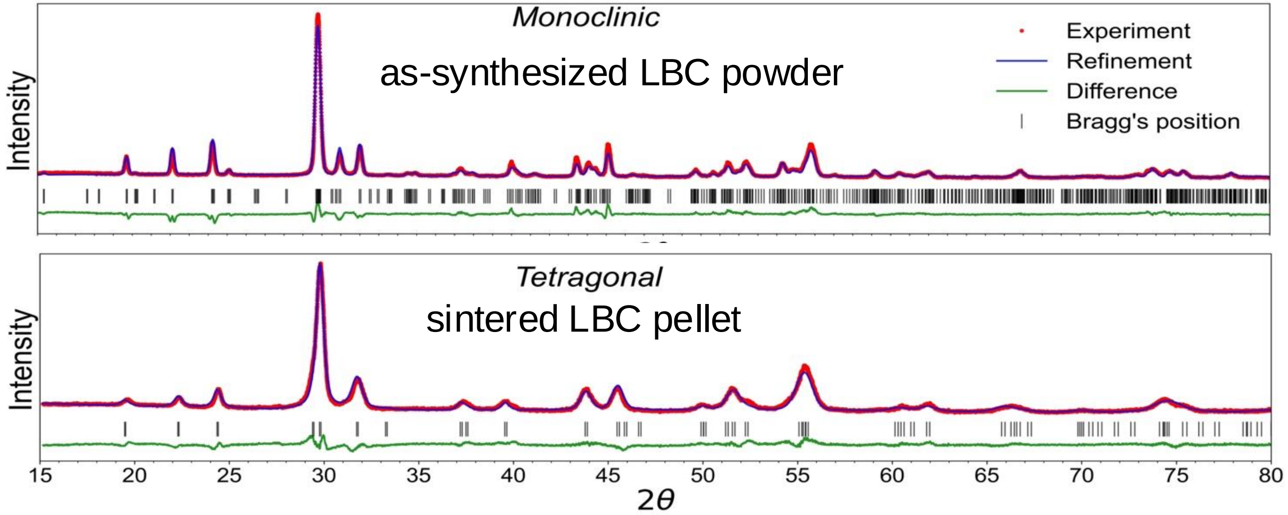


Experimental studies for LBC and Sr-doped LBC

SEM of sintered LBC with grain size of 2.9 µm



XRD studies have revealed that LBC undergoes a phase transition from monoclinic to tetragonal after sintering.



Stoichiometry of LBC and Sr-doped LBC analyzed by Field Emission Electron Probe Microanalyzer (FE-EPMA) analysis, indicating small slight La and oxygen deficiencies, and excess Cl in LBC

	La	Sr	Bi	O	Cl	Suggested formula
Ideal LBC	1	-	2	4	1	$LaBi_2O_4Cl$
synthesized LBC	0.97 ± 0.03	-	2.00 ± 0.04	3.91 ± 0.06	1.05 ± 0.02	$La_{0.97}Bi_2O_{3.93}Cl_{1.05}$
Ideal Sr-doped LBC	0.95	0.05	2	3.975	1	
synthesized Sr-doped LBC	0.89 ± 0.02	0.01 ± 0.00	2.00 ± 0.04	3.89 ± 0.07	1.02 ± 0.02	$La_{0.89}Sr_{0.01}Bi_2O_{3.84}Cl_{1.02}$

The stochiometric values are shown as 1σ ranges from the sample mean.

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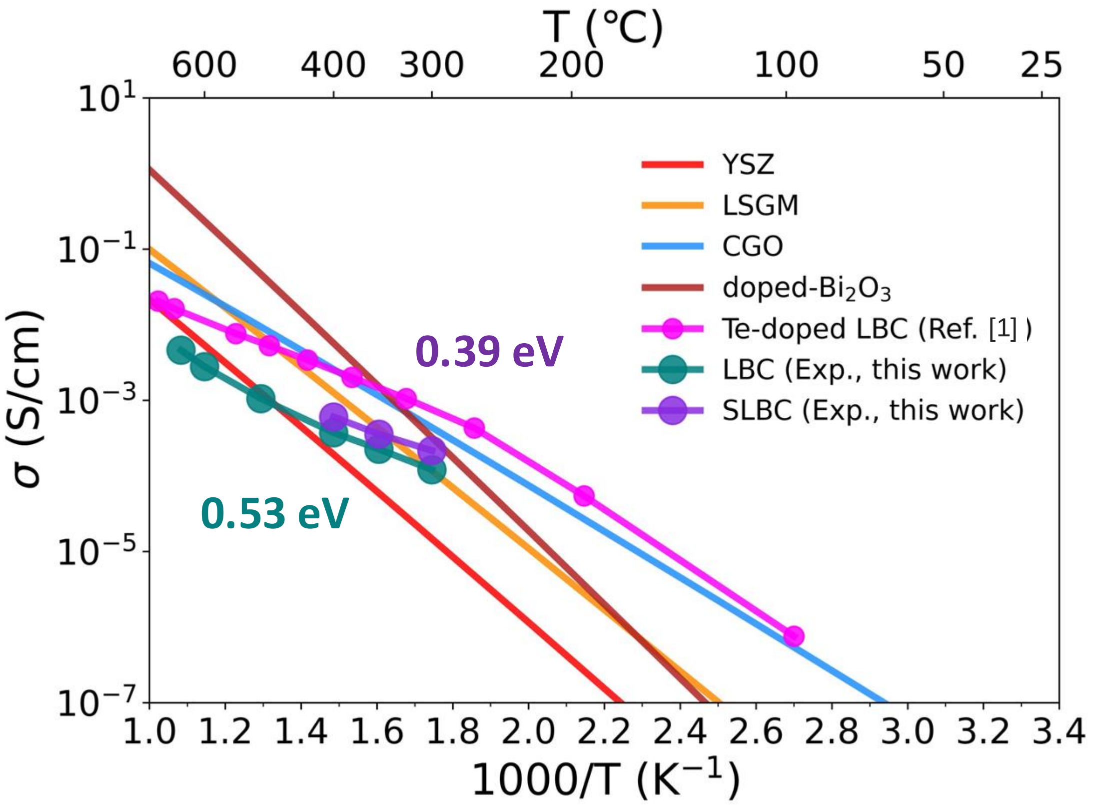
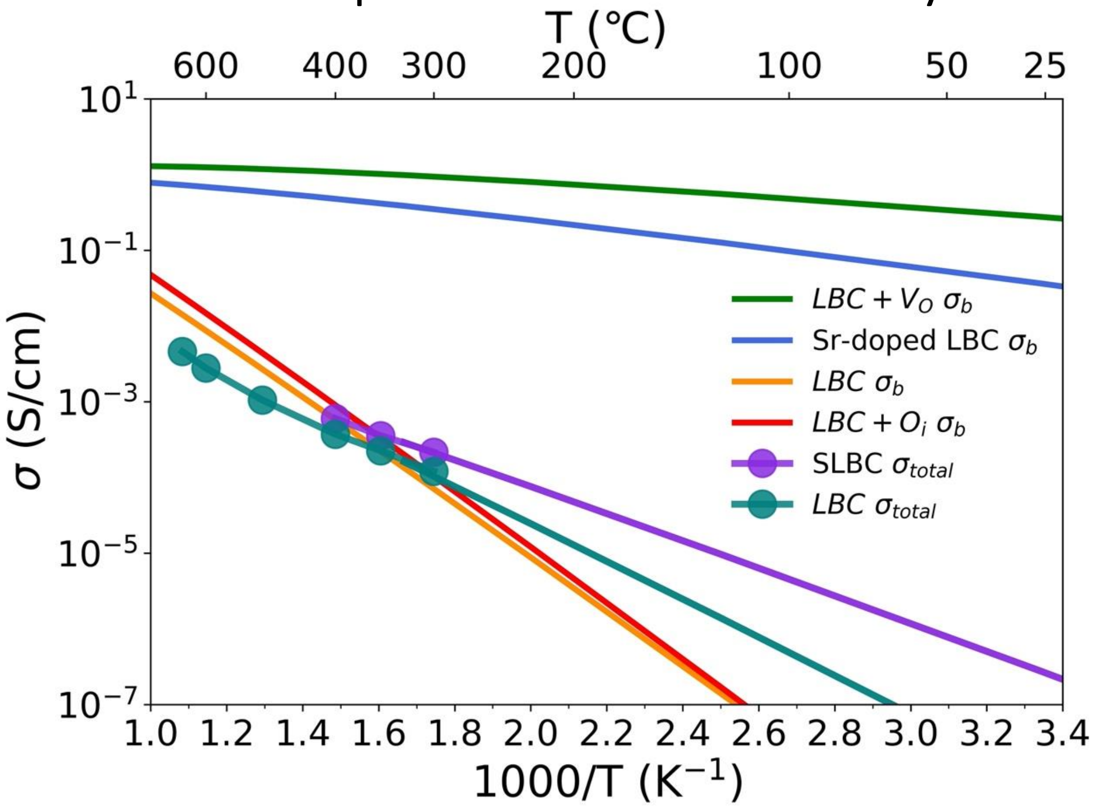
Comparison on experimental total conductivity



LBC and SLBC show comparable or higher total conductivity than YSZ and LSGM below 400 °C, with lower activation energies.

Comparison across experimental total conductivity and *ab initio*-predicted bulk conductivity

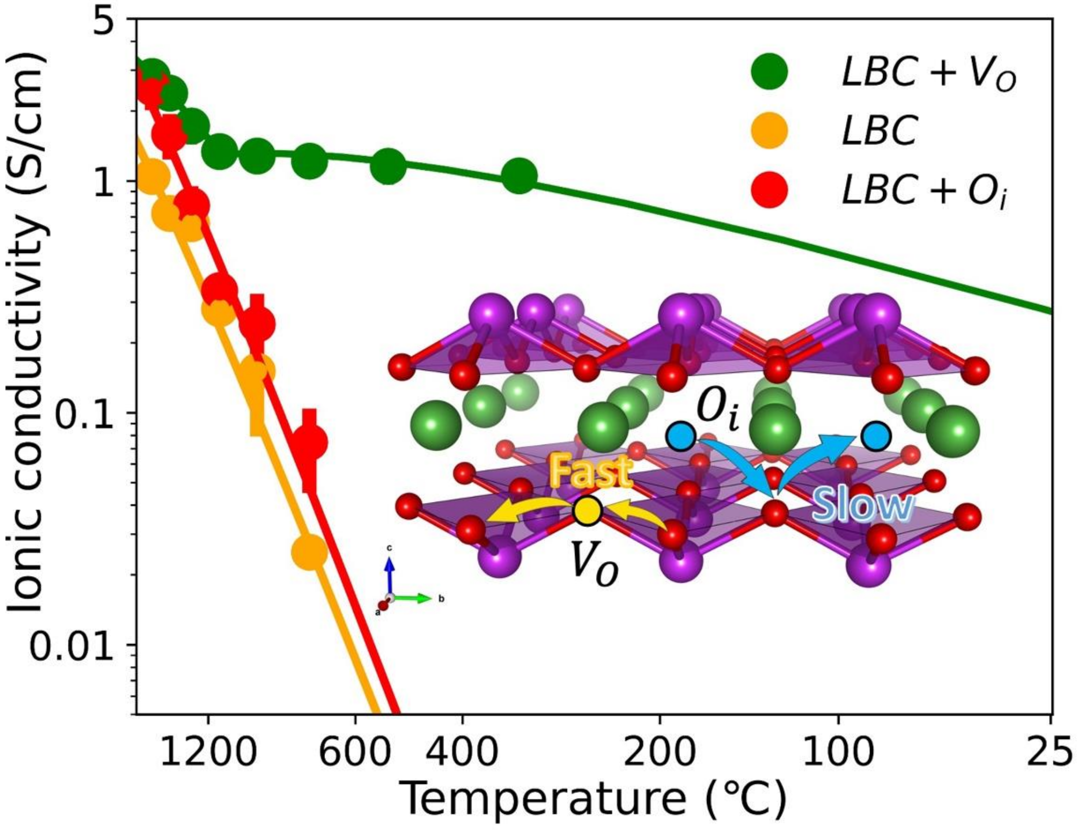


The predicted ultra-high conductivity in LBC+V_O is not observed in our samples, which might be attributed to:

i. The grain boundary effect
ii. The lack of sufficient oxygen vacancies.

[1] H. Yaguchi, *et al. Adv. Funct. Mater.* **2023**, *33*, 2214082.

- $LaBi_2O_4Cl$ (LBC) is identified as an ultra-fast oxygen conductor with ultra-low barrier of 0.1 eV, enabling ultra-high conductivity of 0.3 S/cm at 25 °C.
- LBC and Sr-doped LBC show superior conductivity and lower activation energy, although the predicted ultra-high conductivity is not fully realized yet.
- Experimental effort on aliovalent doping to create vacancies and microstructure refinement for LBC-based materials is needed to unlock its full potential of ultra-fast oxygen conduction approaching room temperature.



Scan to read the paper

Acknowledgement

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Many students involved in the Informatics Skunkworks

Computational Materials Group

Thank you!