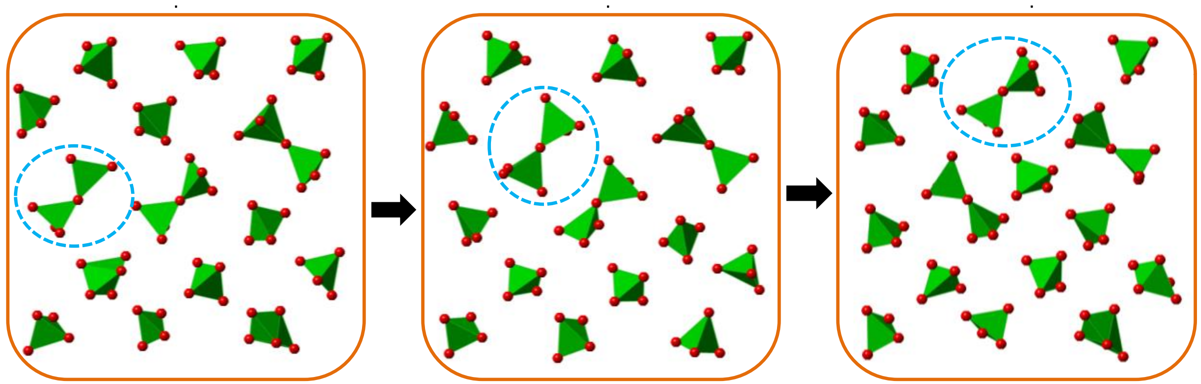
LE STUDIUM CONFERENCES ORLÉANS | 2023

Oxide Ion-Conducting Materials Containing Tetrahedral Moieties: Crystal Structures and Conduction Mechanisms



Alberto J. Fernández-Carrión[1]

[1]*Department of Inorganic Chemistry. University of Seville, 41012 Seville, Spain*

[1]*College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, P. R. China*

October 4th, 2023

Guadalquivir river

Royal Palace of Seville

Li river

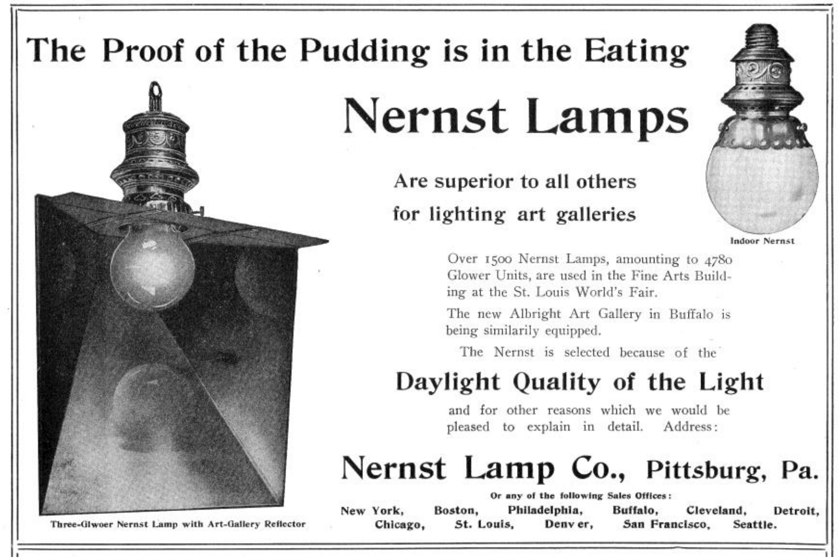
Moon & sun tower

Outline

1. **Introduction**
2. **Oxide ion migration in $La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$ melilite**
3. **Oxide ion migration in $Bi_{1-x}Sr_xVO_{4-0.5x}$ Scheelite**
4. **Oxide ion migration in $La_{1-x}Sr_{2+x}GaO_{4-0.5x}$ oxogallate**
5. **Conclusions**

1. Introduction: Discovery oxide ion conductors (1899)

W. Nernst


The Proof of the Pudding is in the Eating

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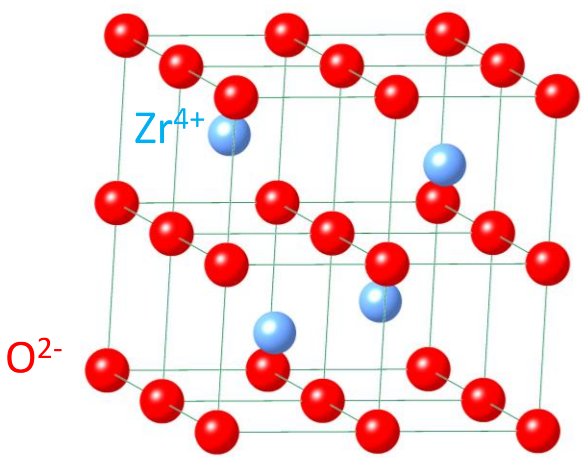
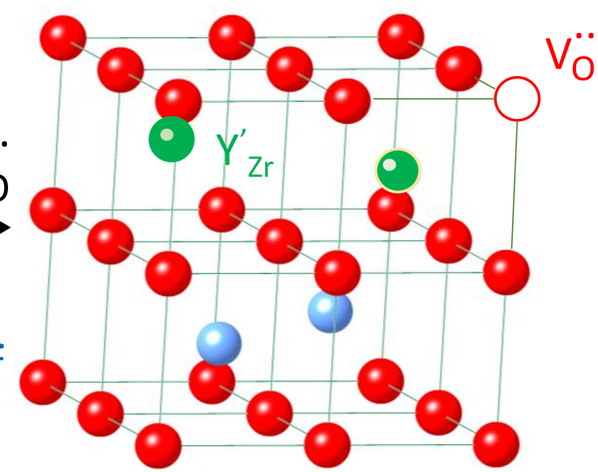


Fluorite structure

$$Y_2O_3 \rightarrow 2Y'_{Zr} + 3_O^X O + V_O^{\bullet\bullet}$$

Yttria-stabilized zirconia



1. Solid-state oxide ion conductors: Main technological applications

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GUILIN UNIVERSITY OF TECHNOLOGY

- ✓ **Electrolytes for solid oxide fuel cells (SOFCs)**
- ✓ Oxygen sensors and pumps
- ✓ Oxygen permeation membranes
- ✓ Catalysts for syngas production
- ✓ Cathodes for SOFCs

Development of oxide ionic conductors

- ✓ **σ_t ~10^{-2} S/cm at 500-600 °C**
- ✓ **Negligible electrical conductivity.**
- ✓ **Chemical stability ;10^{-20} bar < pO_2 < 1 bar**

Challenges

O^{2-} → large radius (~ 1.4 Å) and two negative charges!!!!!

1. Oxide ion conductors: Main structures

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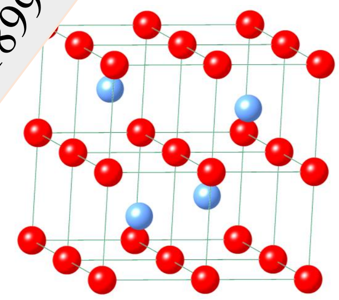
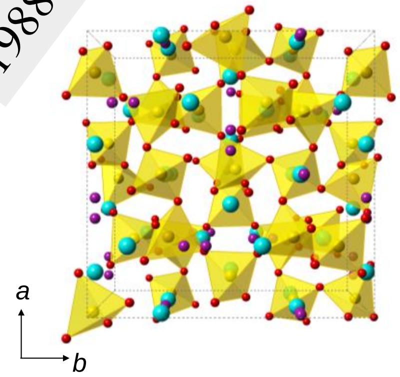
1899



Fluorite structure

σ ~ $4 \cdot 10^{-3}$ S/cm

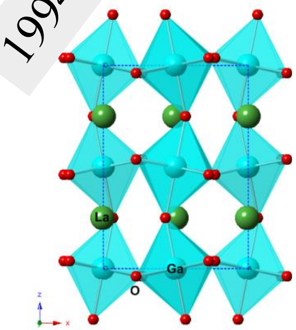
1988



Mayenite

σ ~ $3 \cdot 10^{-4}$ S/cm

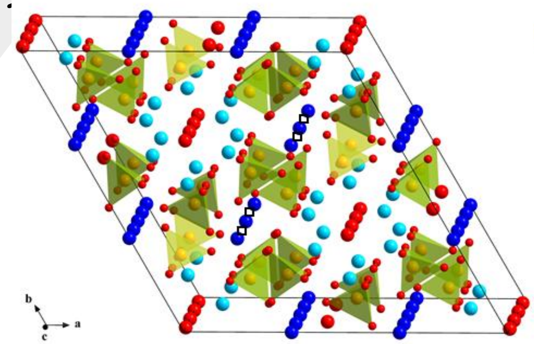
1994



Cubic -Perovskite
Mg, Sr-$LaGaO_3$

σ ~ $2 \cdot 10^{-2}$ S/cm

1995

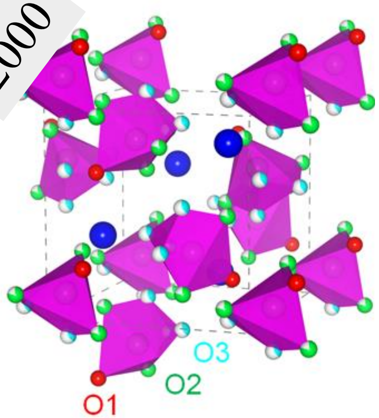


Apatite

σ ~ $1 \cdot 10^{-2}$ S/cm

* σ at 600 °C

2000

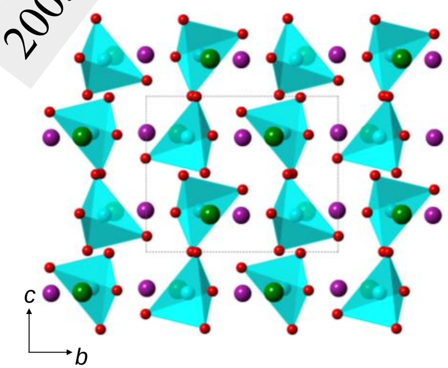


LAMOX

$La_2Mo_2O_9$

σ ~ $4 \cdot 10^{-3}$ S/cm

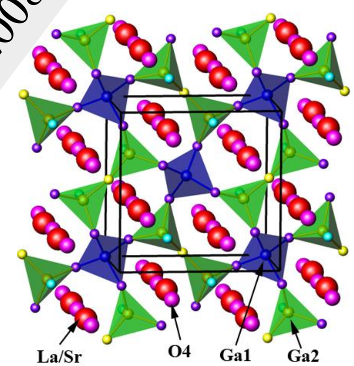
2003



$LaBaGaO_4$

σ ~ $4 \cdot 10^{-4}$ S/cm

2008

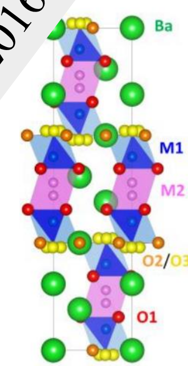


Non-stoichiometric melilite

$La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$

σ ~ $2 \cdot 10^{-2}$ S/cm

2016



Hexagonal perovskites

σ ~ $2 \cdot 10^{-3}$ S/cm

1. Oxide ion conductors: Metals coordinated by 4 oxygens

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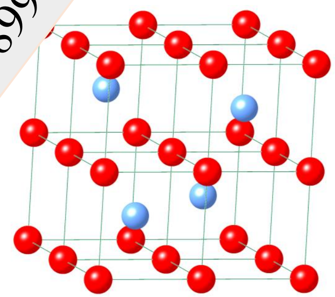
1899



Fluorite structure

σ ~ $4 \cdot 10^{-3}$ S/cm

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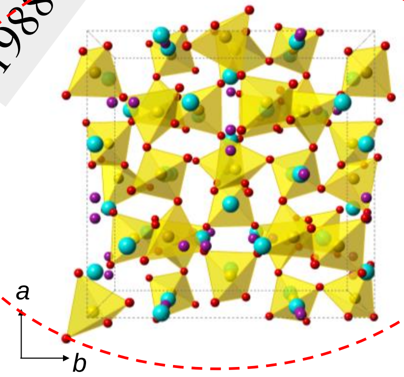
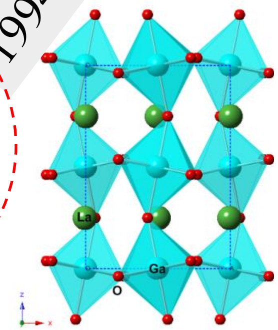


Mayenite

σ ~ $3 \cdot 10^{-4}$ S/cm

1994



Cubic -Perovskite

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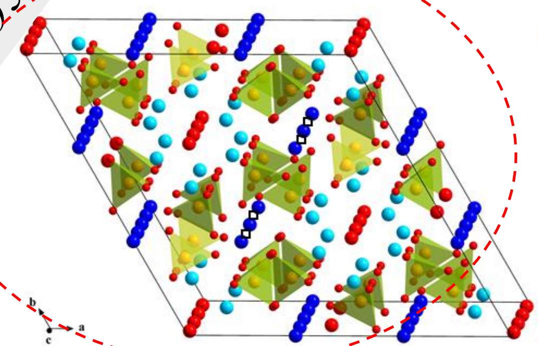
σ ~ $2 \cdot 10^{-2}$ S/cm

1995

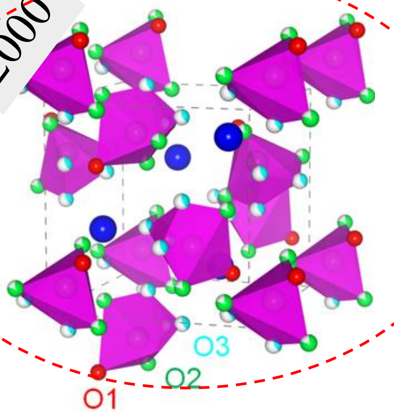


Apatite

σ ~ $6 \cdot 10^{-4}$ S/cm

* σ at 600 °C

2000

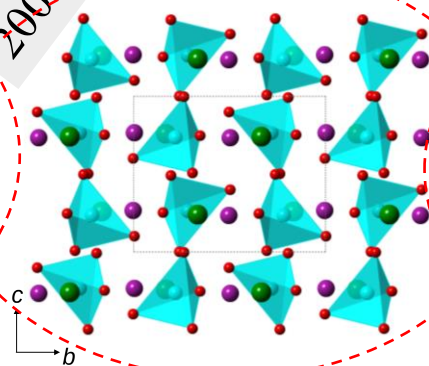


LAMOX

$La_2Mo_2O_9$

σ ~ $4 \cdot 10^{-3}$ S/cm

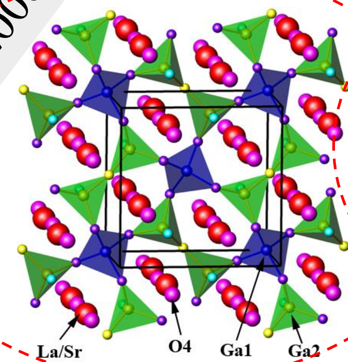
2003



$LaBaGaO_4$

σ ~ $4 \cdot 10^{-4}$ S/cm

2008

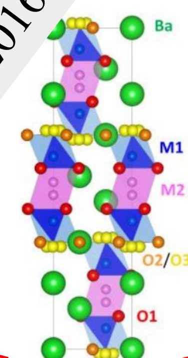


Non-stoichiometric melilite

$La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$

σ ~ $2 \cdot 10^{-2}$ S/cm

2016



Hexagonal perovskites

σ ~ $2 \cdot 10^{-3}$ S/cm

1. Main oxide ion conductors based on tetrahedral moieties

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No.	Structural prototype	Typical example	Defect (Polyhedra	(Year)
1	Mayenite	$Ca_{12}Al_{14}O_{33}$	Interstitial (caged extra O)	(1988)
2	Cubic perovskite	Mg, Sr-$LaGaO_3$	Vacancy (MO_4/$MO_{6-\delta}$)	(1990)
3	Apatite	$La_{9.33+x}Si_6O_{26+1.5x}$	Interstitial (MO_4Oint/MO_5)	(1995)
4	β-$SnWO_4$	$La_2Mo_2O_9$	Interstitial (MO_5/MO_6)	(2000)
5	Cuspidine	$La_4GaTiO_{9.5}$	Vacancy (MO_4/MO_5)	(2005)
6	$LaBaGaO_4$	$La_{0.8}Ba_{1.2}GaO_{3.9}$	Vacancy (M_2O_7)	(2007)
7	Melilite	$La_{1.54}Sr_{0.46}Ga_3O_{7.27}$	Interstitial (MO_5)	(2008)
8	Fluorite	$Bi_{1-x}V_xO_{1.5+x}$	Vacancy (MO_n)	(2012)
9	Scheelite	Sr-doped $BiVO_4$	Vacancy (M_2O_7)	(2014)
		$LaNb_{0.92}W_{0.08}O_{4.04}$	Interstitial (MO_5/MO_6)	(2018)
10	Hexagonal perovskite	$Ba_3MoNbO_{8.5}$	Vacancy (MO_4/$MO_{6-\delta}$)	(2016)
11	Molten substance	$Na_2W_2O_7$	/	(2018)
12	YBO_3	Zn-doped YBO_3	Vacancy (MO_3)	(2022)
13	$LaSr_2GaO_5$	Oxogallate	Vacancy (M_2O_7)	(2022)

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Outline

1. Introduction

2. Oxide ion migration in $La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$

3. Oxide ion migration in $Bi_{1-x}Sr_xVO_{4-0.5x}$

4. Oxide ion migration in $La_{1-x}Sr_{2+x}GaO_{4-0.5x}$ oxogallate

5. Conclusions

2. Melilite. $LaSrGa_3O_7$

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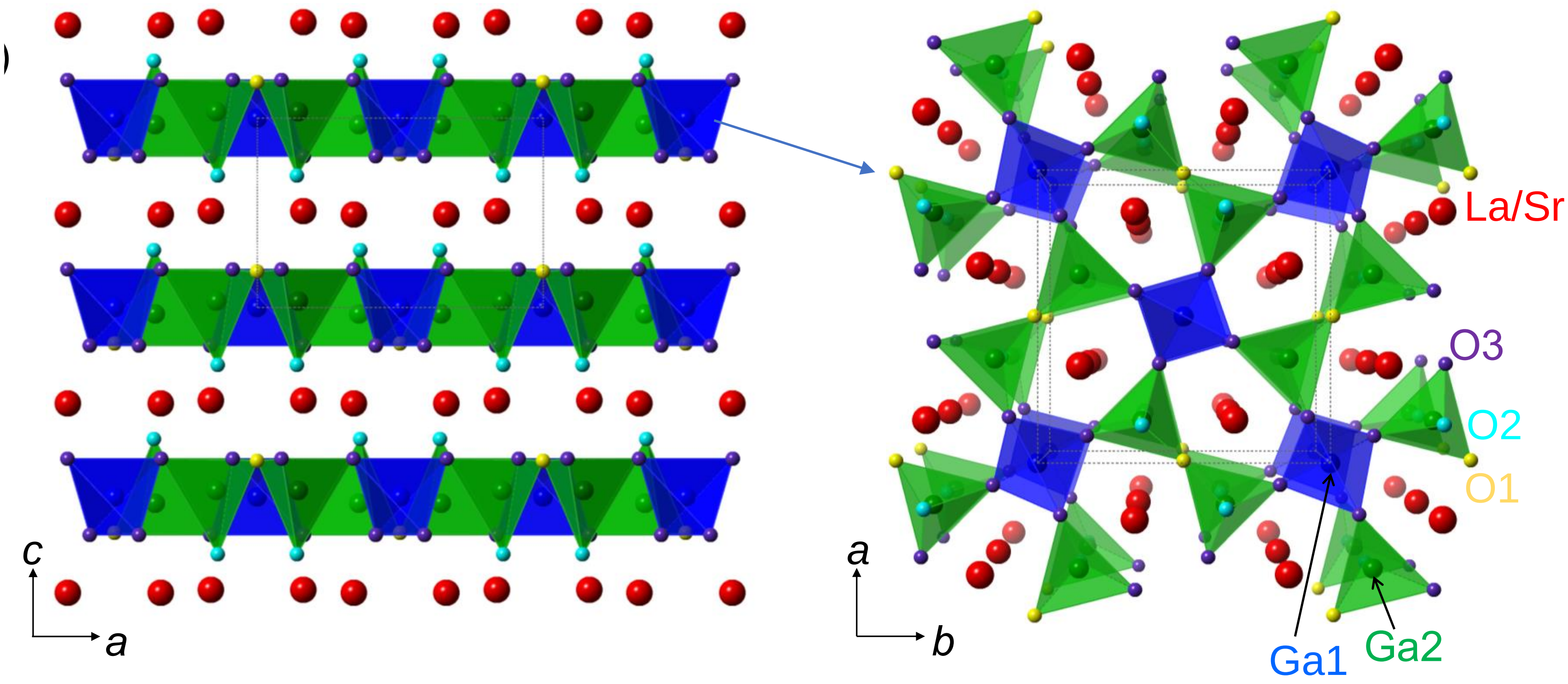
Insulator!



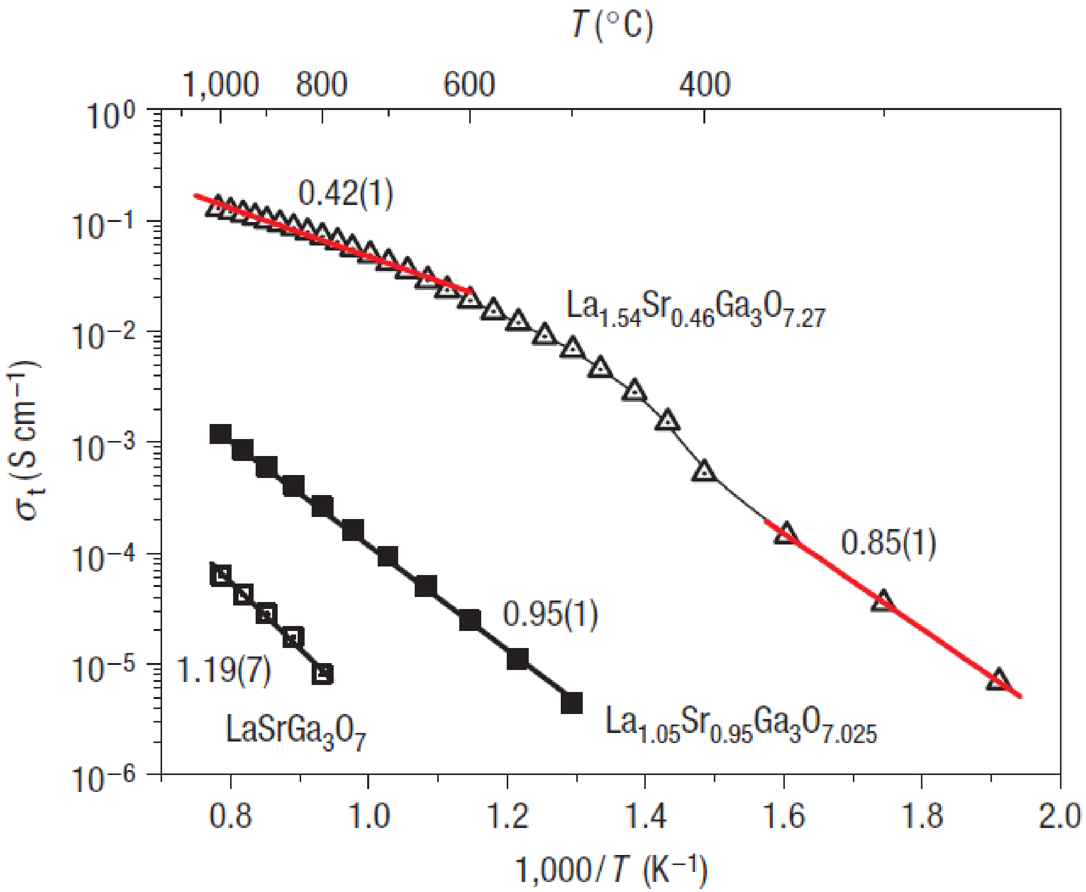
S. G. $P42_1m$

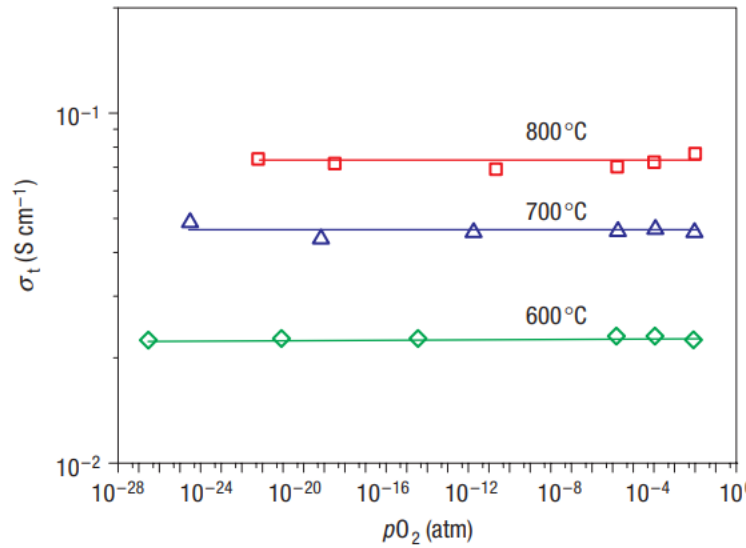
2. Non-stoichiometric melilite compounds

$La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$: $La_2O_3 + 2Sr_{Sr}^{\times} \rightarrow 2La_{Sr}^{\cdot} + O_i'' + SrO$

High mobility of oxygen interstitials: $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$, $\sigma \sim 10^{-2}$ S/cm at 600°C

Dr. X. Kuang





$t_{O^{2-}} \sim$ **0.95 (600-1000 °C)**

X. Kuang. Nat. Mater., 2008, 7, 498.

2. Non-stoichiometric melilite compounds. Introduction of interstitial oxygens

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$La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$: $La_2O_3 + 2Sr_{Sr}^{\times} \rightarrow 2La_{Sr}^{\cdot} + O_i'' + SrO$

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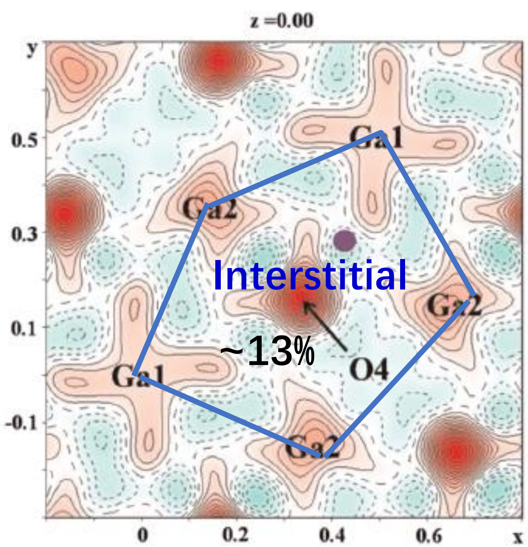

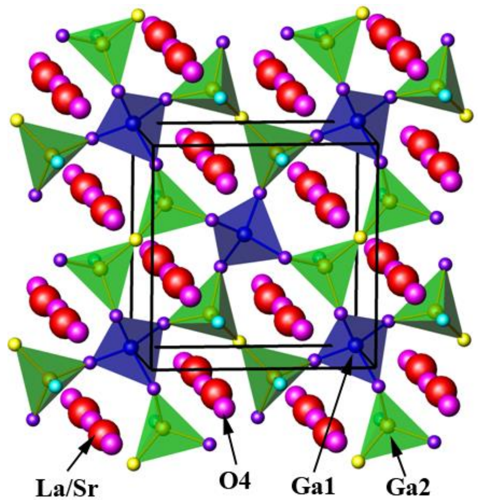

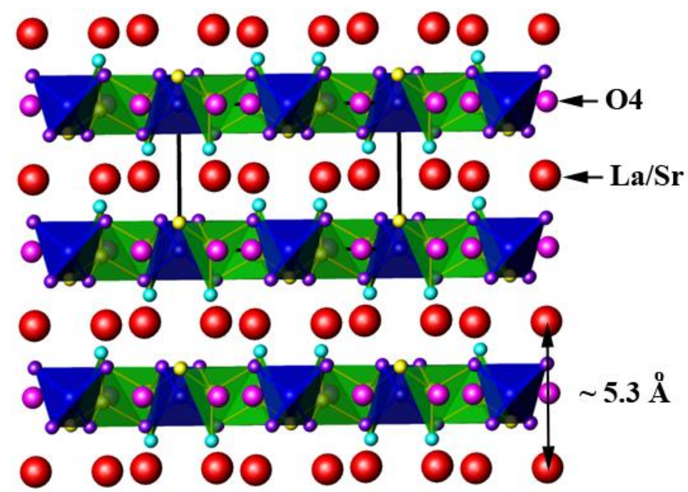

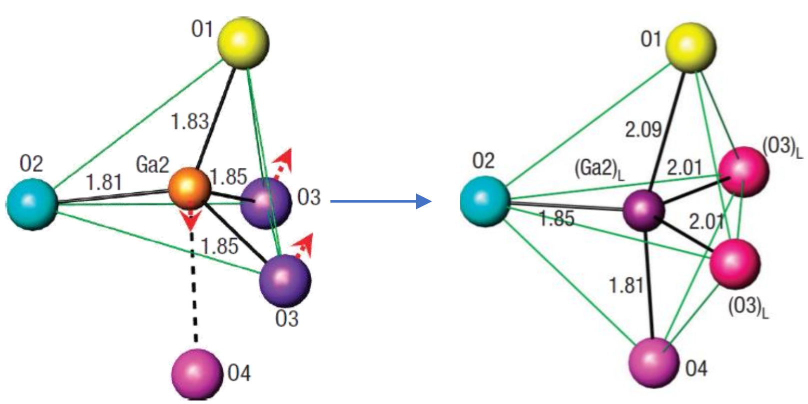

- ✓ Difference Fourier map and average structure from neutron powder diffraction data
- ✓ Interstitial oxygen: within pentagonal ring, between La/Sr cations, lies within Ga plane

X. Kuang. Nat. Mater., 2008, 7, 498.

2. Non-stoichiometric melilite compounds. Oxide interstitial migration mechanism. 2D migration pathway

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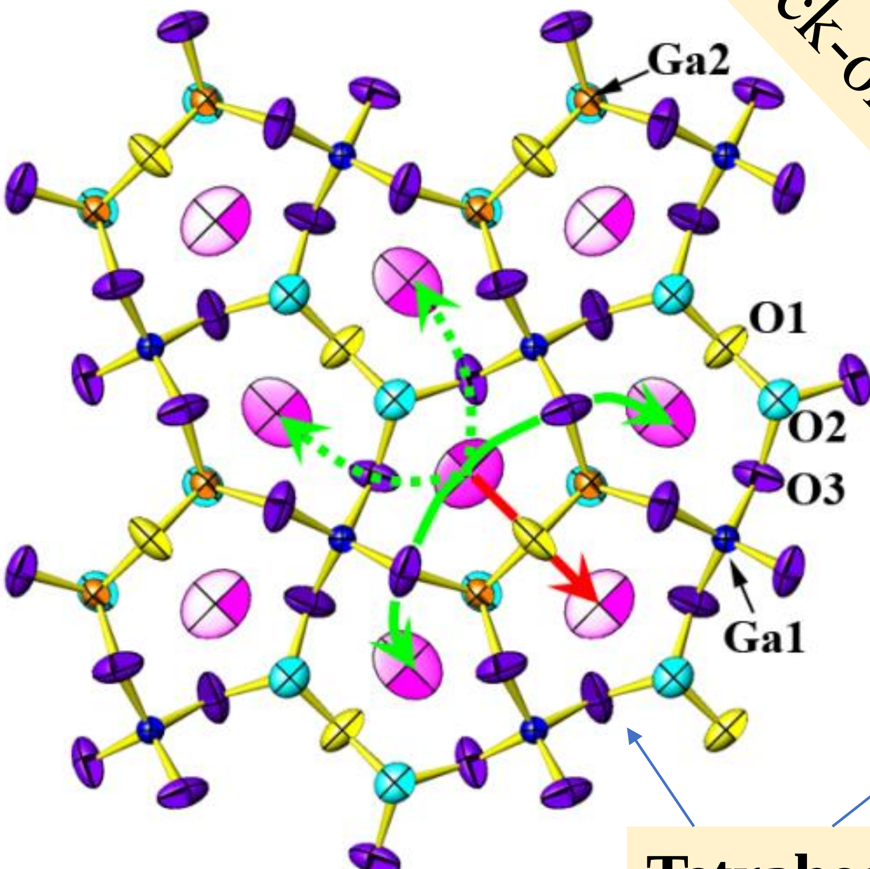
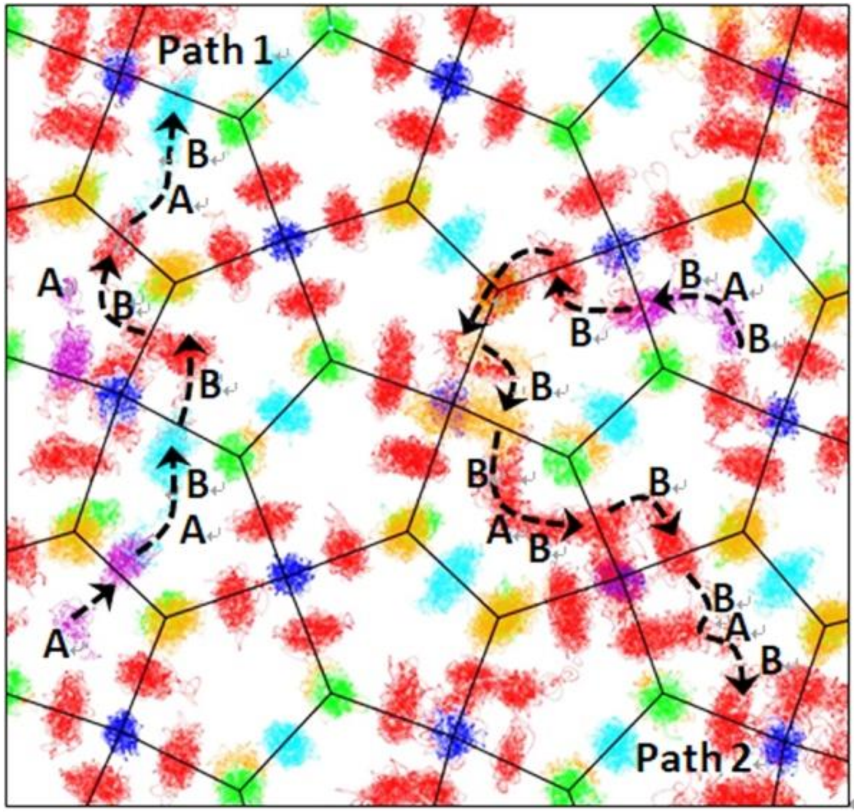
From VT ND data

knock-on

From MD simulation





Tetrahedral layer

Nat. Mater., 2008, 7, 498.

ACS Appl. Energy Mater. 2019, *2*, 2878.

2. Transparent melilite. Aerodynamic levitation synthesis method for $RESrGa_3O_7$

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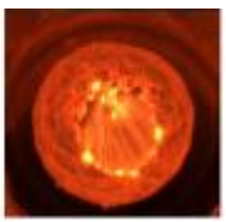
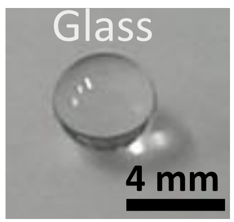
Aerodynamic Levitation + CO_2 lasers heating

- Up to ≥ 3000 °C
- Contactless
- High quenching rate ≈ 300 °C/s→ metastability!



Vitrification

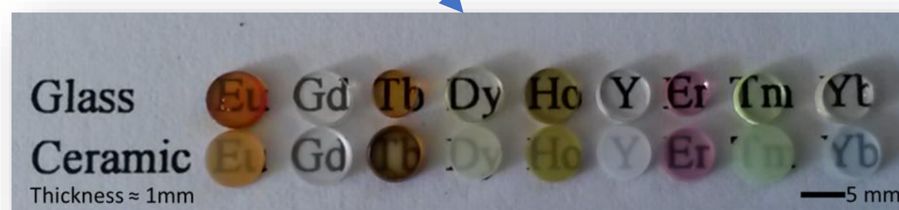
1st



Crystallization

2nd

Careful Annealing treatment



- Single heat treatment
- Full crystallization

Dr. M. Boyer Dr. M. Allix

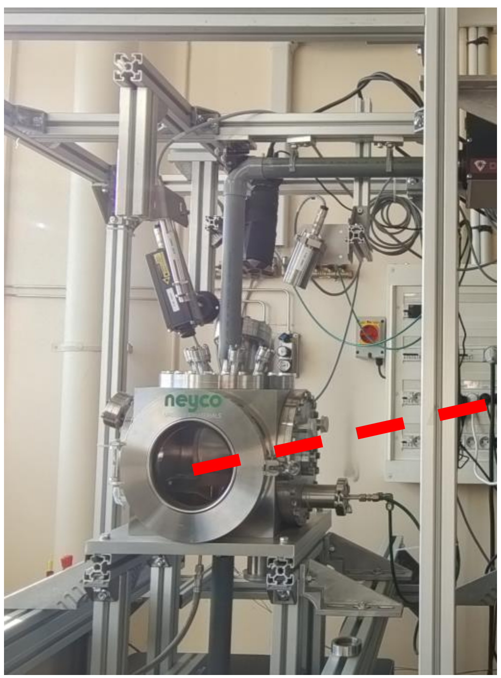
(CNRS-CEMHTI)

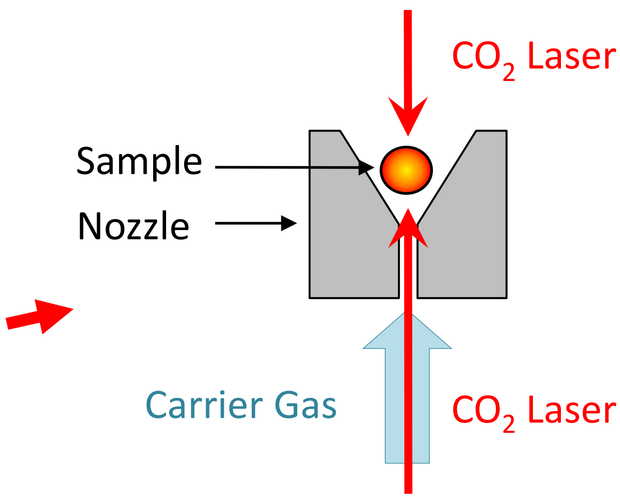
J. Mater. Chem. C. 2016, **4**, 3238

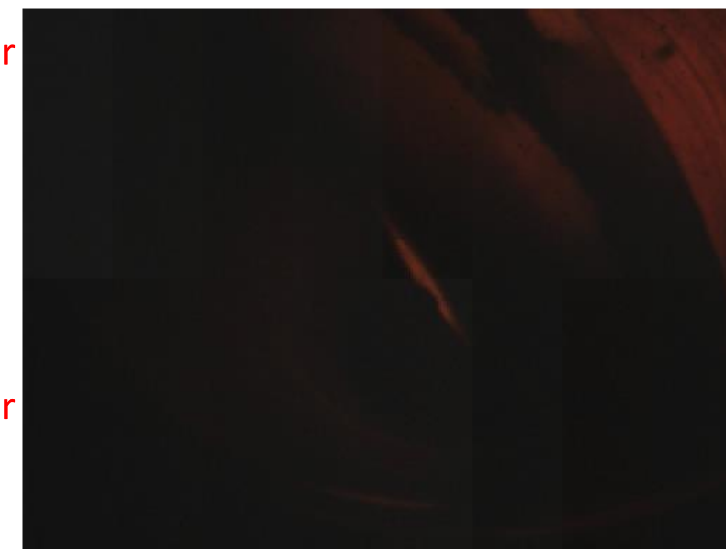
2. Transparent melilite electrolytes. Aerodynamic levitation synthesis method

Aerodynamic Levitation + CO_2 lasers heating

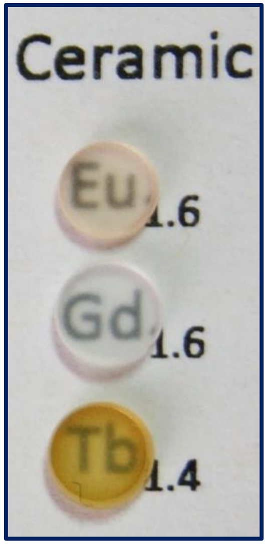
- Up to ≥ 3000 °C
- Contactless
- High quenching rate ≈ 300 °C/s→ metastability!

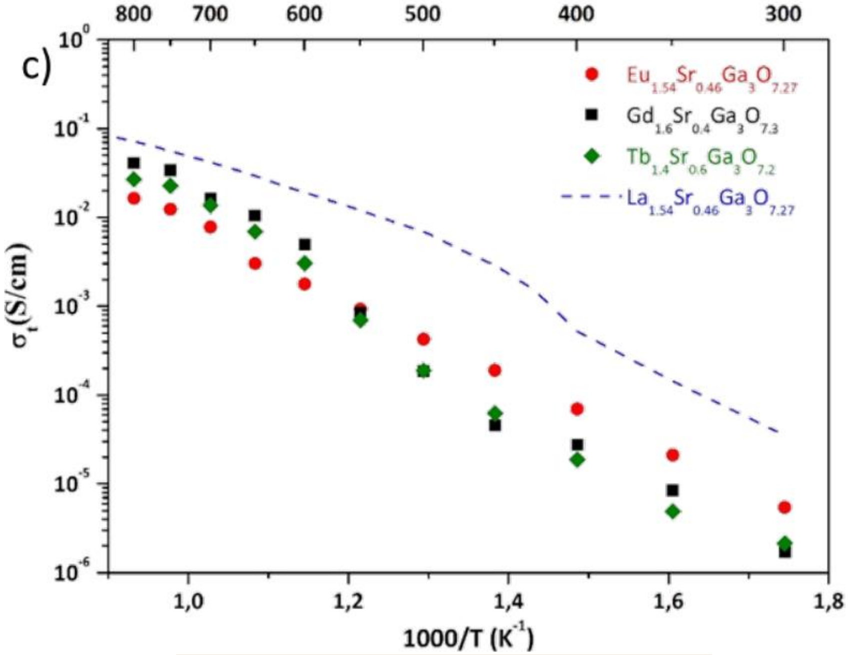


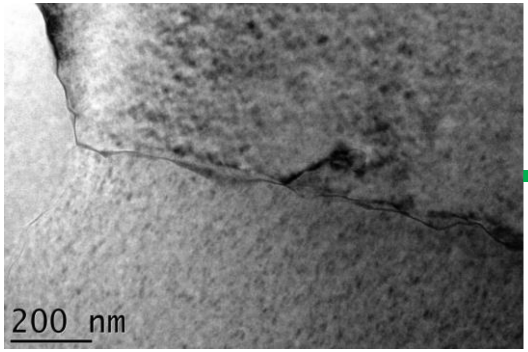




2. Non-stoichiometric melilite compounds. $RE_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$







- ✓ No amorphous (glassy) phase
- ✓ **No porosity**
- ✓ Micrometer scale grain size
- ✓ Thin grain boundaries

J. Mater. Chem. A. **2018**, **6**, 5276

2. $La_{1+x}Ba_{1-x}Ga_3O_{7+0.5x}$ Melilite

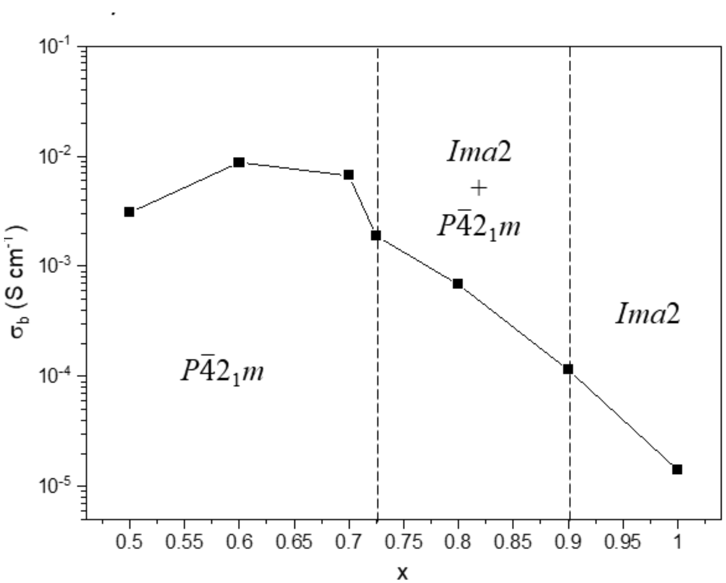
Solid state reaction route

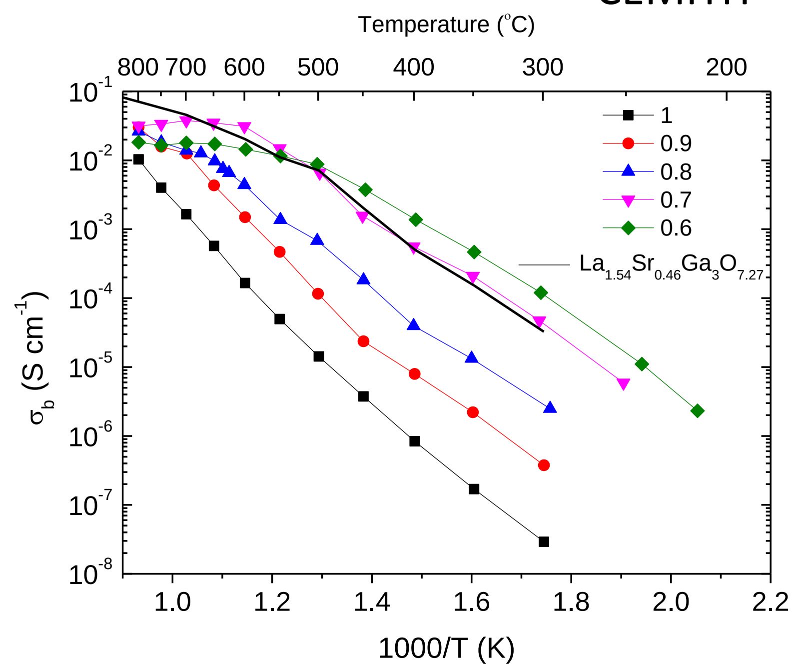
Composition	Solid solution limit (tetragonal melilite)	
	Solid state	Levitation
$La_{1+x}Ba_{1-x}Ga_3O_{7+0.5x}$	x = 0.35	x = 0.725

Dr. Haytem
CEMHTI

Dr. M. Pitcher

Dr. M. Allix





***Oncoming paper**

Outline

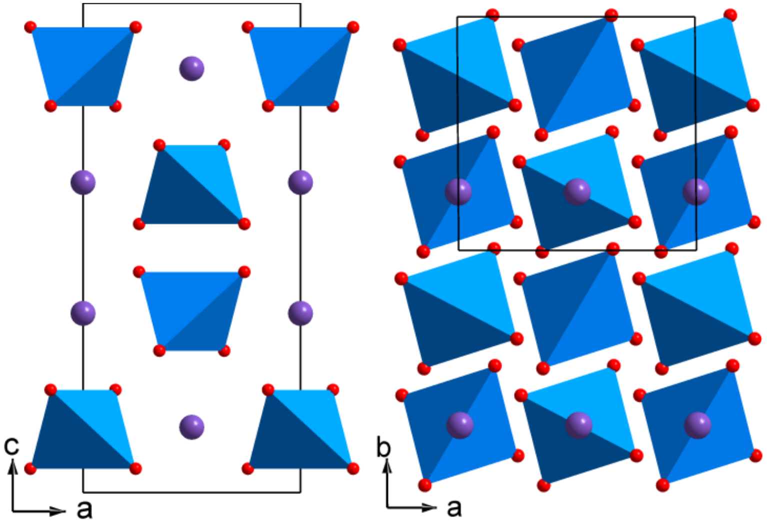
1. Introduction
2. Oxide ion migration in $La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$
3. **Oxide ion migration in $Bi_{1-x}Sr_xVO_{4-0.5x}$**
4. Oxide ion migration in $La_{1-x}Sr_{2+x}GaO_{4-0.5x}$ oxogallate
5. Conclusions

3. $Bi_{1-x}Sr_xVO_{4-0.5x}$ Scheelite. Average structure

$$2SrO + 2Bi_{Bi}^{\times} + O_O^{\times} \rightarrow 2Sr'_{Bi} + V_O^{\cdot\cdot} + Bi_2O_3$$

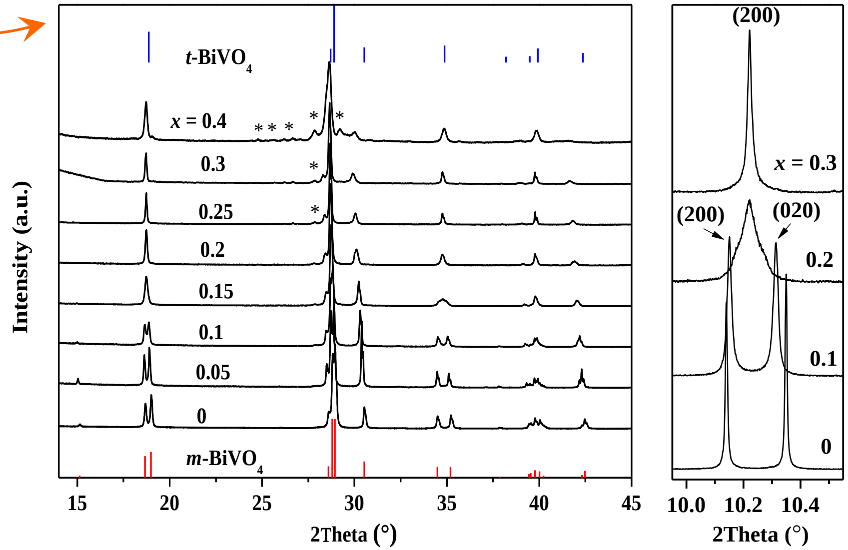
VO_4 tetrahedra

S.G. *I2/b or I4₁/a*



Sample preparation by Aerodynamic levitation method

Enhancement of Sr solubility

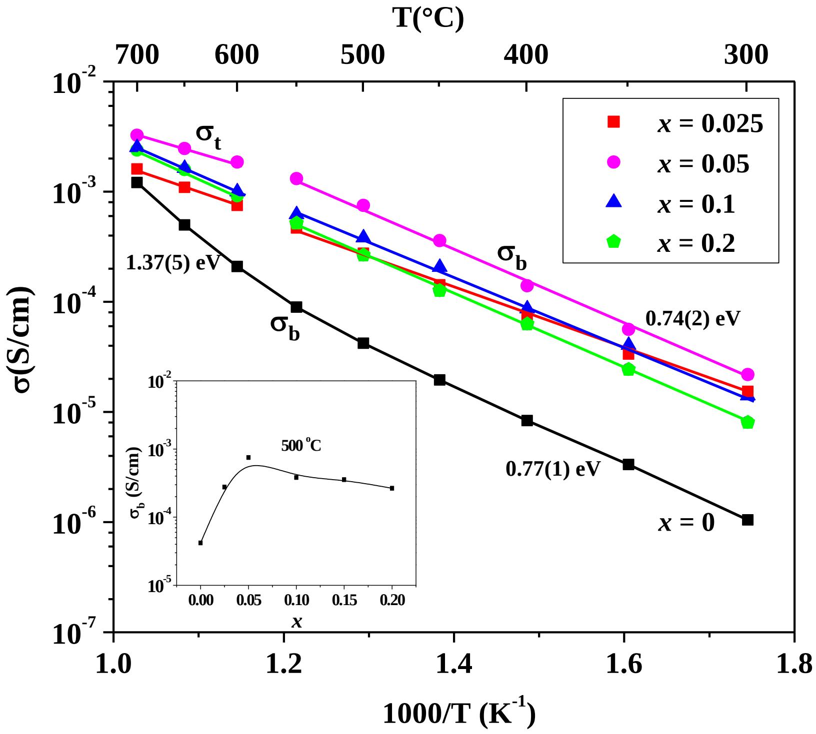


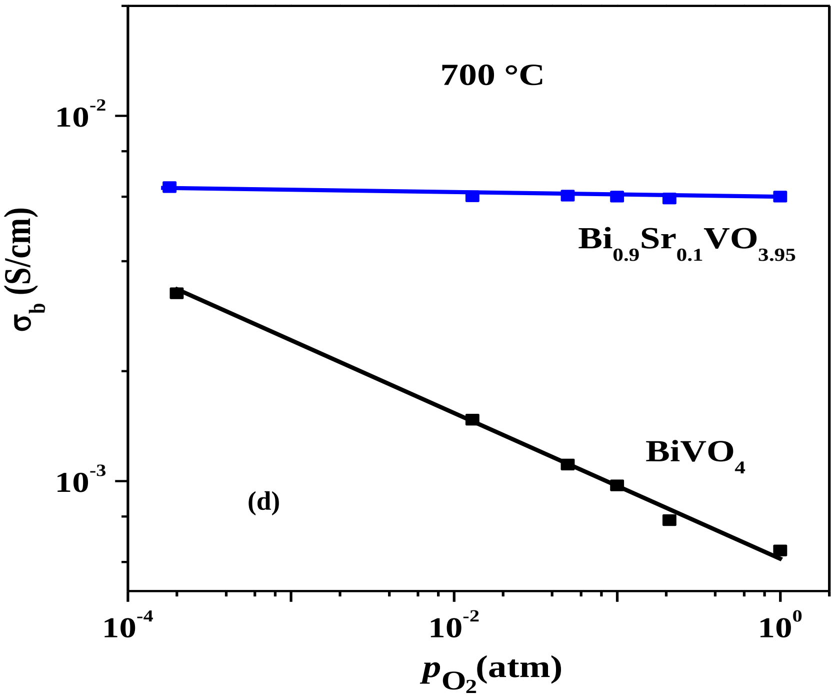
Average structure model
1Bi
1 V
2 O

***Nat. Comm.*, 2018**, *9*, 4484.

3. $Bi_{1-x}Sr_xVO_{4-0.5x}$ Scheelite. Impedance Spectroscopy

$$2SrO + 2Bi_{Bi}^{\times} + O_O^{\times} \rightarrow 2Sr_{Bi}' + V_O^{\cdot\cdot} + Bi_2O_3$$





$t_{O^{2-}} \sim$ **0.88 (700 C)**

Nat. Comm., **2018**, *9*, 4484.

3. $Bi_{1-x}Sr_xVO_{4-0.5x}$ Scheelite. Impedance Spectroscopy

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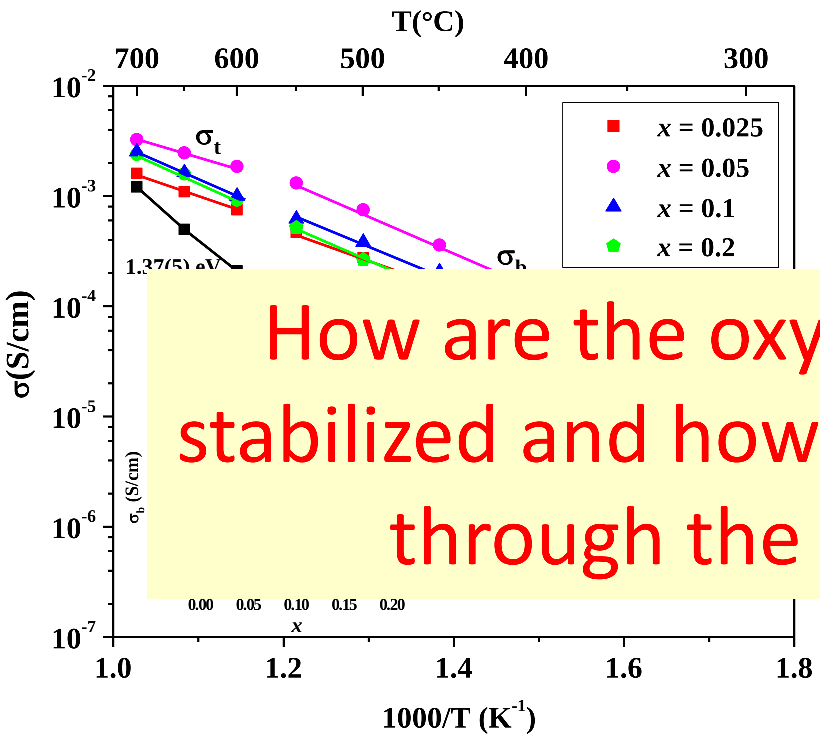
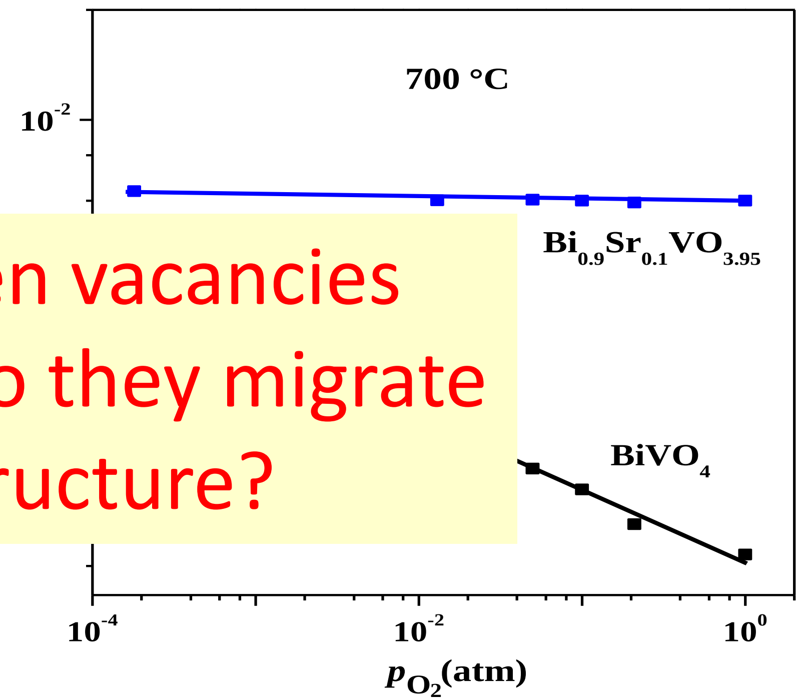




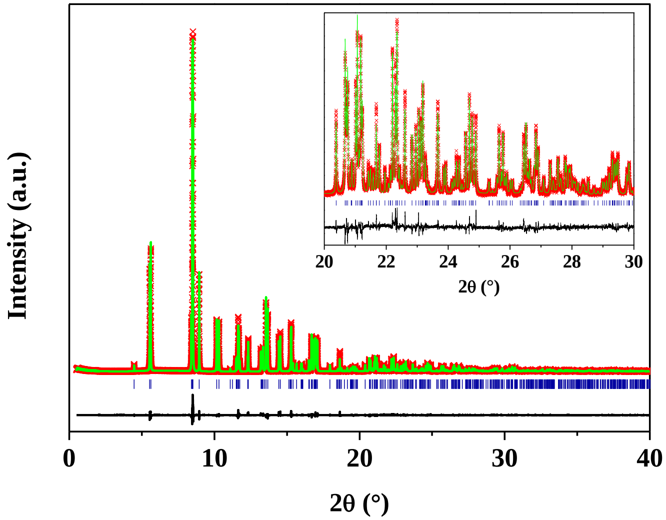
How are the oxygen vacancies stabilized and how do they migrate through the structure?

$t_{O^{2-}} \sim$ **0.88 (700 C)**

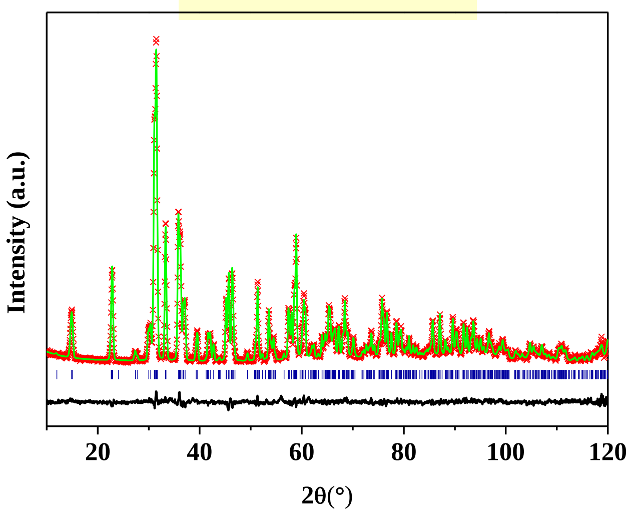
***Nat. Comm.*, 2018**, *9*, 4484.

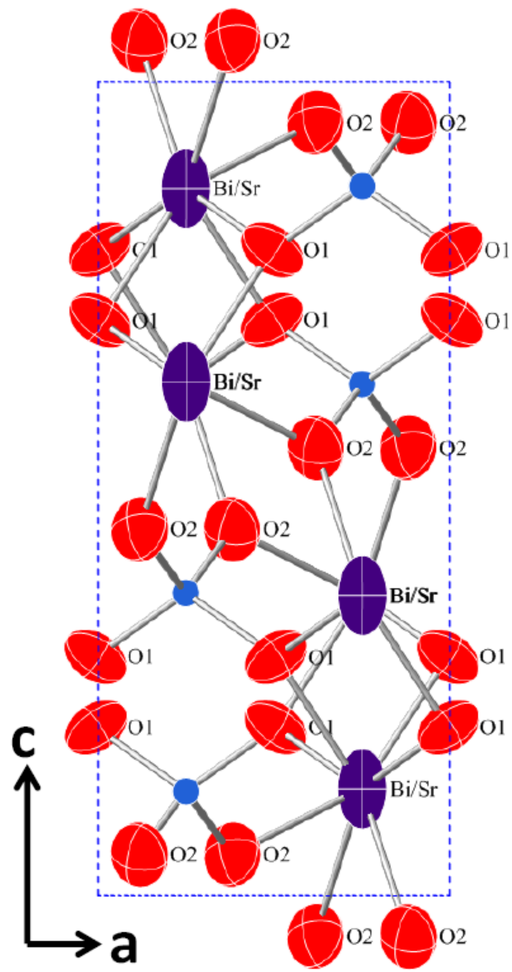
3. $Bi_{1-x}Sr_xVO_{4-0.5x}$ Scheelite. Average structure

Synchrotron XRD data



NPD data





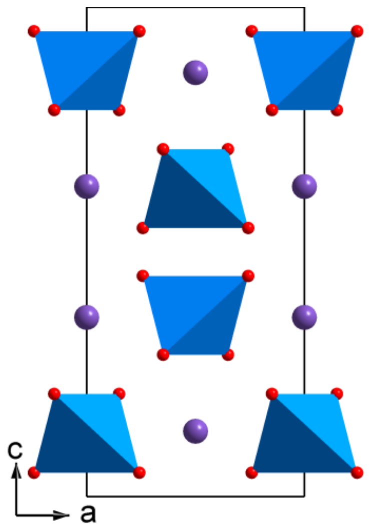
~ 2-3% V_O, positional disorder

Defect structure?
3-coordinate V?

Nat. Comm., **2018**, *9*, 4484.

3. $Bi_{1-x}Sr_xVO_{4-0.5x}$ Scheelite. ^{51}V NMR – local structure

Diffraction



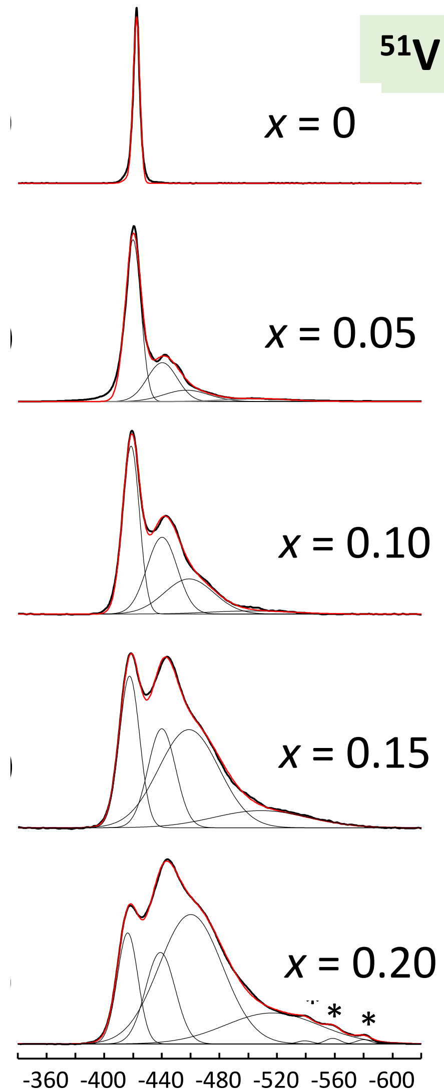
Average structure model

1Bi

1 V

2 O

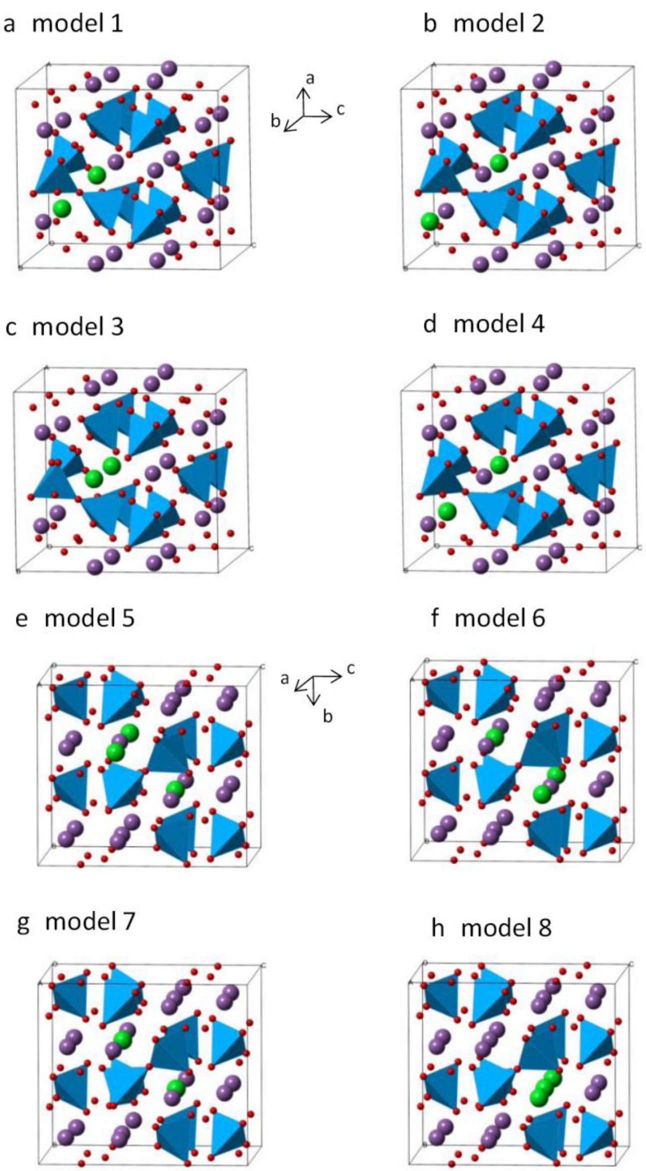
^{51}V NMR



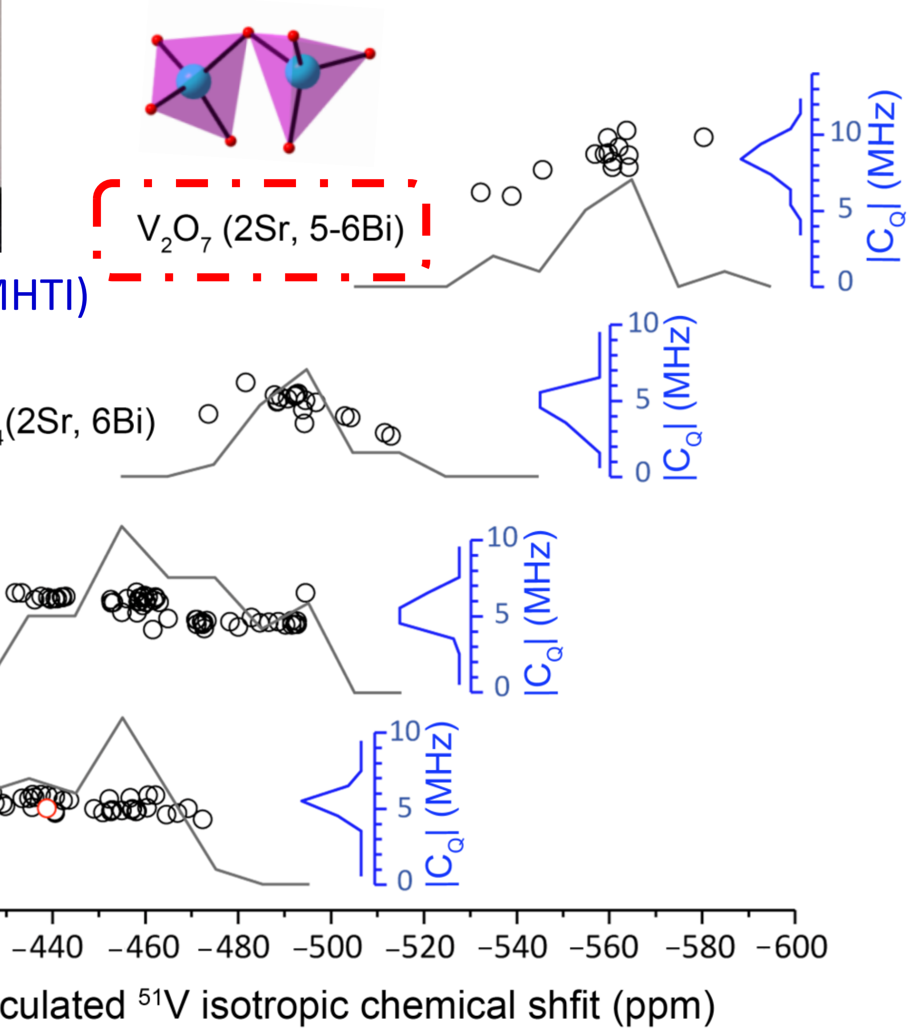
4 types of vanadium local environments!!!

***Nat. Comm.*, 2018, *9*, 4484.**

3. $Bi_{1-x}Sr_xVO_{4-0.5x}$. DFT calculation of ^{51}V NMR parameters

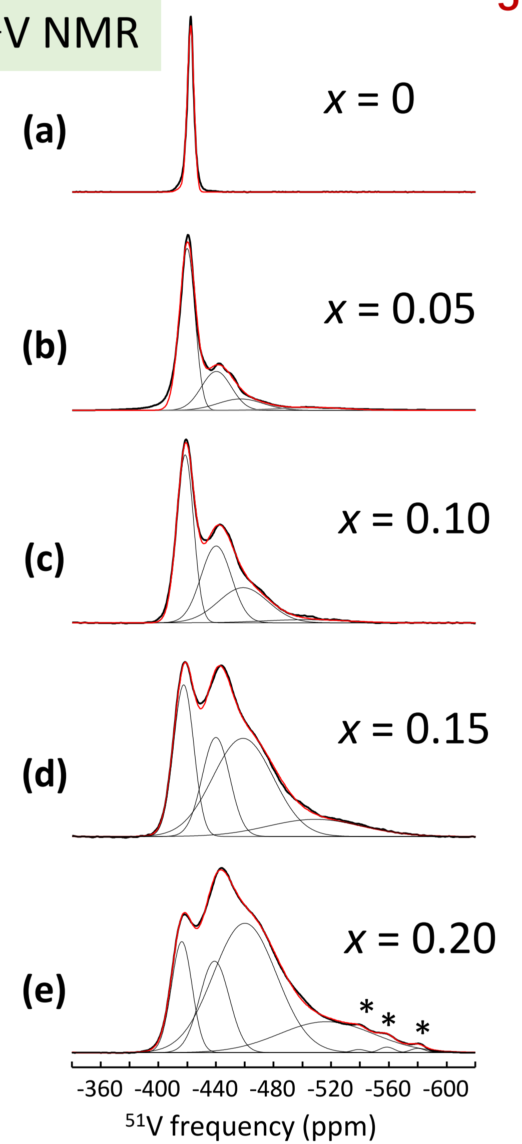


Dr. Fayon, (CEMHTI)

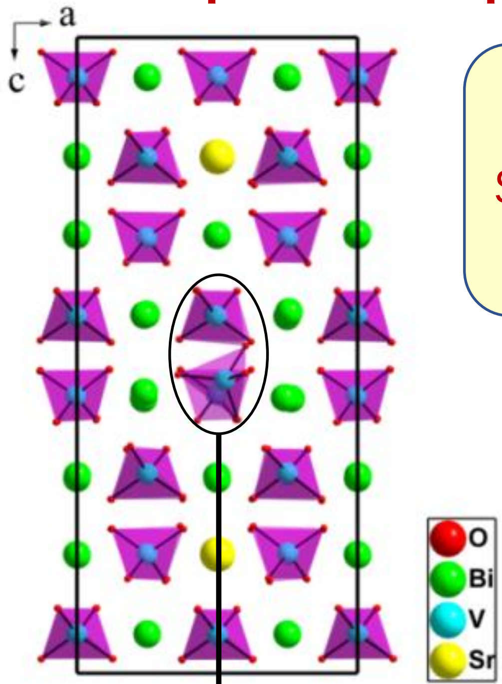


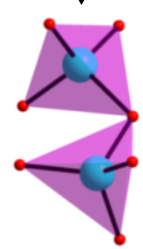
Nat. Comm., **2018**, *9*, 4484.

3. $Bi_{1-x}Sr_xVO_{4-0.5x}$ Scheelite. ^{51}V NMR



^{51}V NMR Spectra to probe defect structure





V_2O_7

Oxygen vacancies are stabilized by formation of V_2O_7 dimers.

***Nat. Comm.*, 2018**, *9*, 4484.

3. Scheelite $Bi_{1-x}Sr_xVO_{4-0.5x}$. Molecular dynamics simulation

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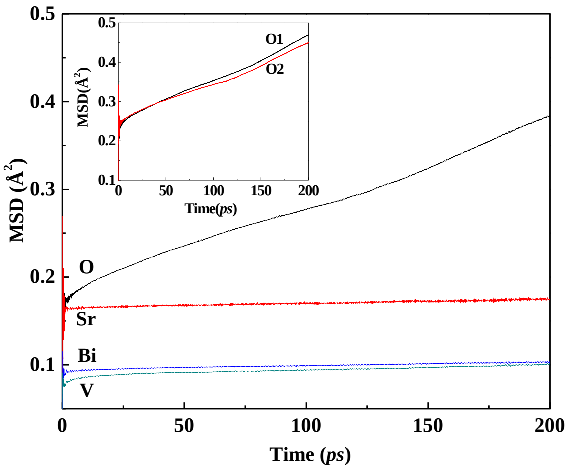
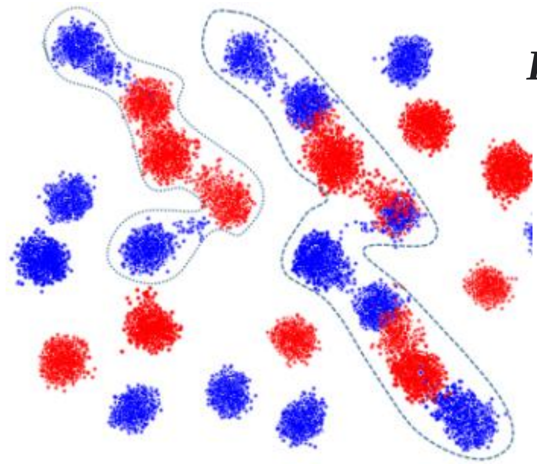
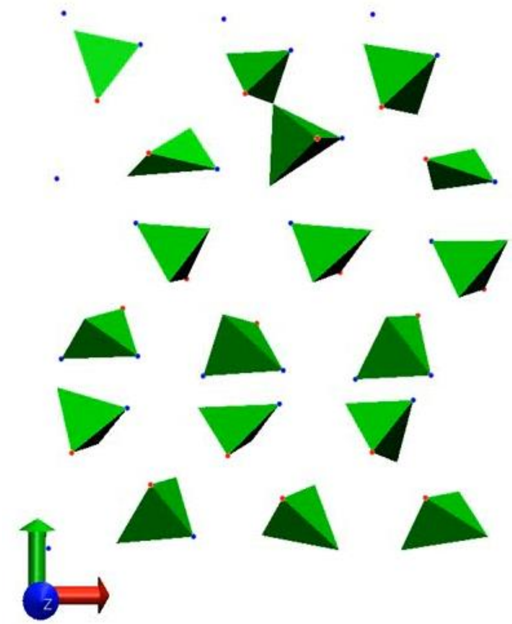
***Nat. Comm.*, 2018**, *9*, 4484.

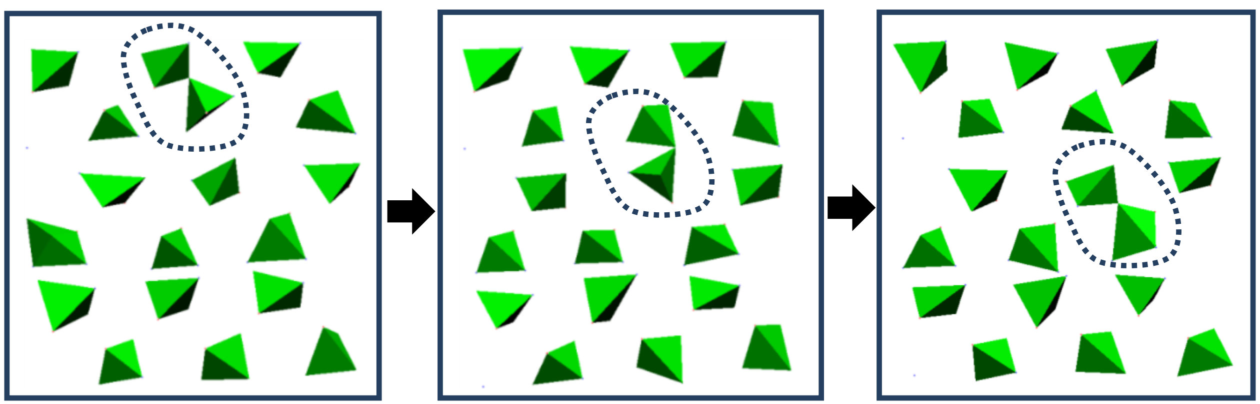
***Inorg. Chem. Front.* 2022** 9, 2644







t = 19 *ps*　　t = 22 *ps*　　t = 23 *ps*



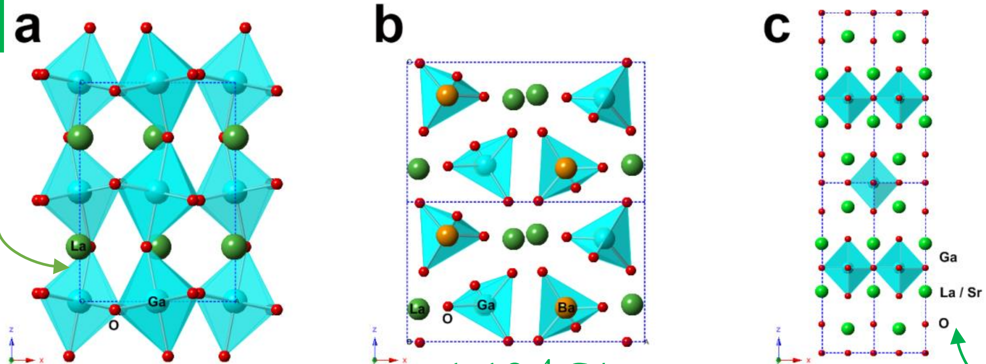
Long-range migration of oxygen vacancies takes place via the continuous breaking and reforming of V_2O_7 dimer.

Outline

1. Introduction
2. Oxide ion migration in $La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$
3. Oxide ion migration in $Bi_{1-x}Sr_xVO_{4-0.5x}$
4. **Oxide ion migration in $La_{1-x}Sr_{2+x}GaO_{4-0.5x}$ oxogallate**
5. Conclusions

4. Oxogallate: $La_{1-x}Sr_{2+x}GaO_{5-0.5x}$

* σ at 500 °C



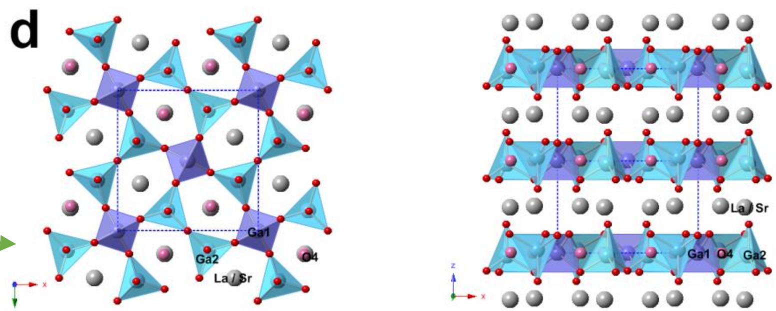
σ ~ $4\cdot10^{-3}$ S/cm

σ ~ $1\cdot10^{-4}$ S/cm

σ ~ $5\cdot10^{-5}$ S/cm

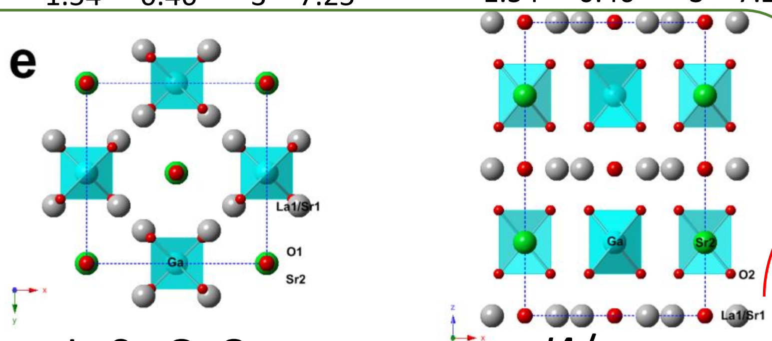
Ga^{3+} exhibits can be stabilized under different corrdination enviroments (CN = 4, 5, 6)

σ ~ $6\cdot10^{-3}$ S/cm



$La_{1.54}Sr_{0.46}Ga_3O_{7.25}$ $La_{1.54}Sr_{0.46}Ga_3O_{7.25}$

Oxogallate



$LaSr_2GaO_5$ *I*4/**mcm**

Highlights

- Moderate mixed p-type/H^+ conductor (2005)
- Structure model *I*4/*mcm* (2000)

4. $La_{1-x}Sr_{2+x}GaO_{5-0.5x}$: Solid solubility

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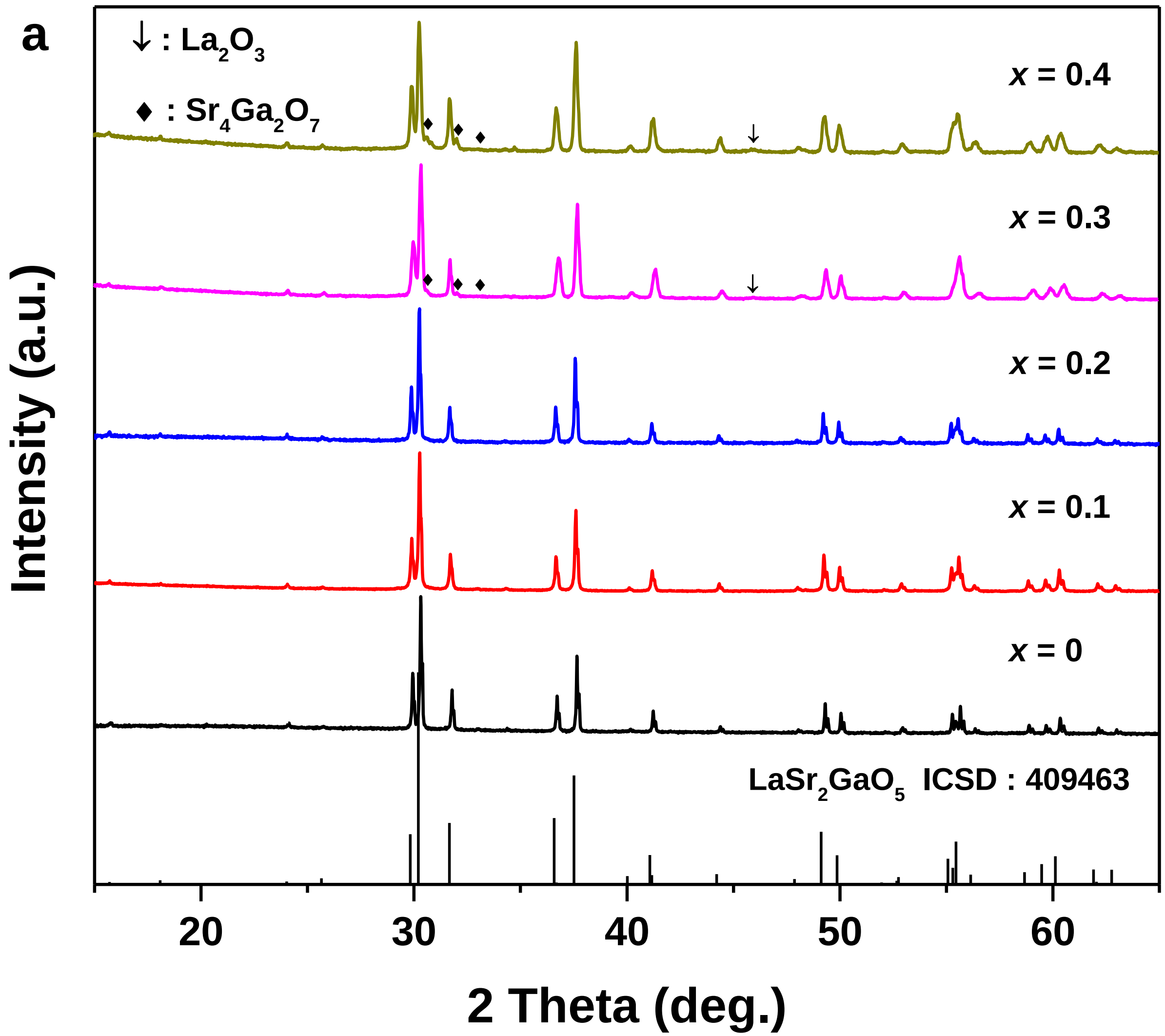

Li Jiachen (PH. D)

Solid solubility
Stability range

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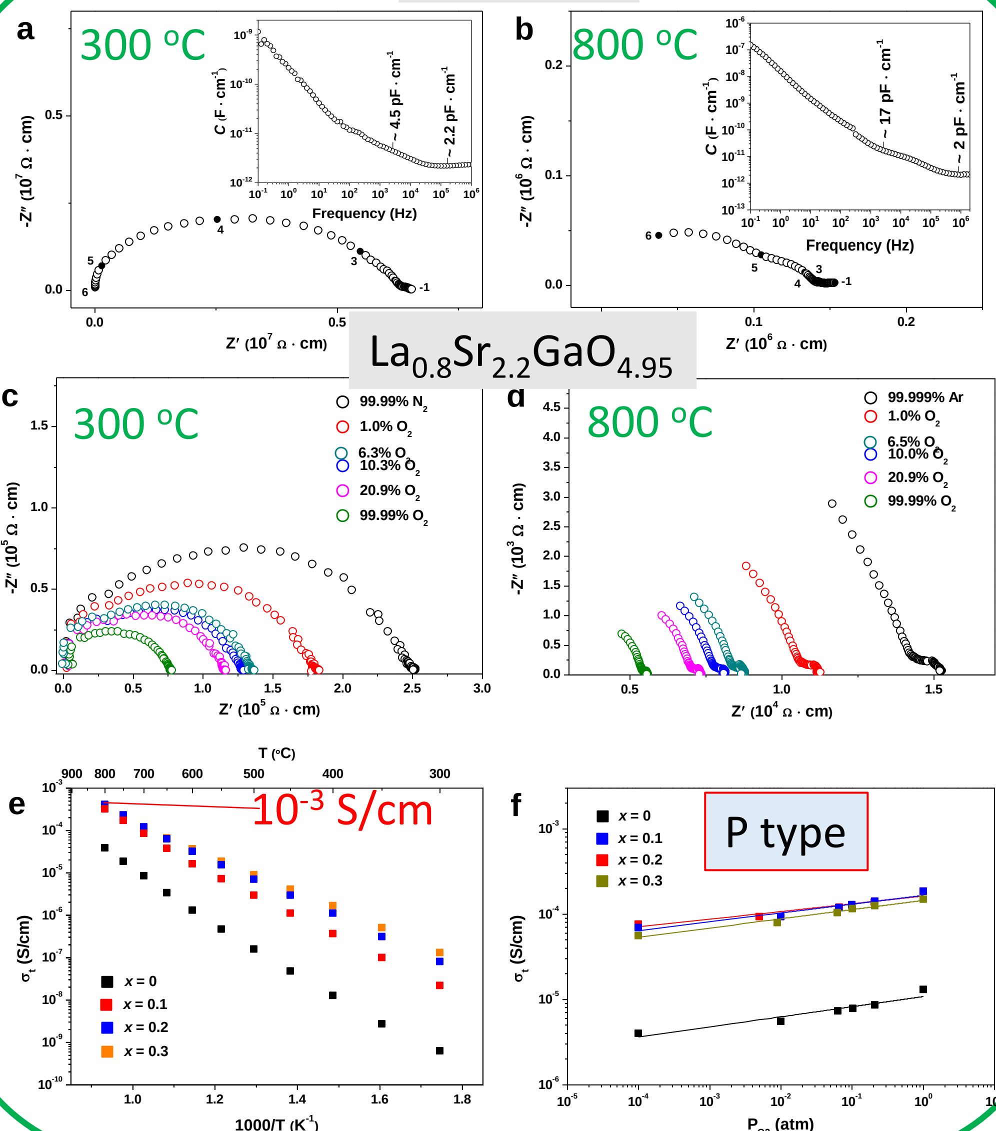
4. $La_{1-x}Sr_{2+x}GaO_{5-0.5x}$. Impedance spectroscopy

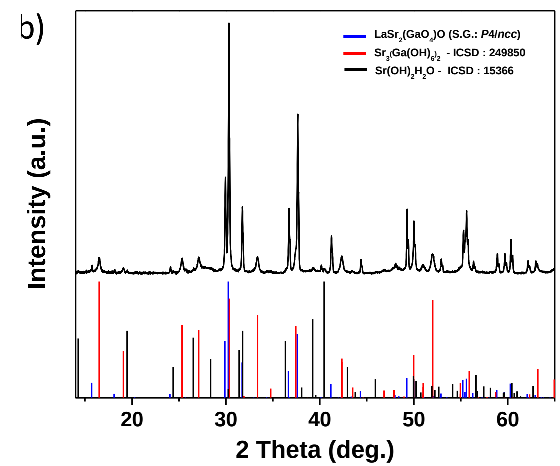
$LaSr_2GaO_5$



The system behaves as a mixed p-type/oxide ion conductor

$t_{o2-} \sim 0.34$ ($La_2Sr_2GaO_5$)

$t_{o2-} \sim 0.15$ ($La_{0.8}Sr_{2.2}GaO_{4.95}$)



Non stable in wet environments

No proton conductor

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4. $La_{1-x}Sr_{2+x}GaO_{5-0.5x}$. MD simulations

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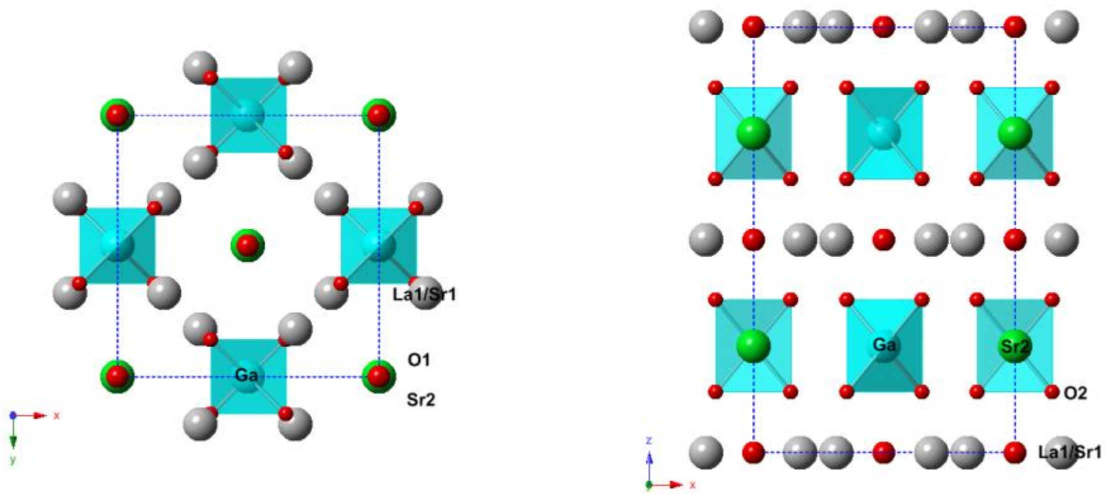
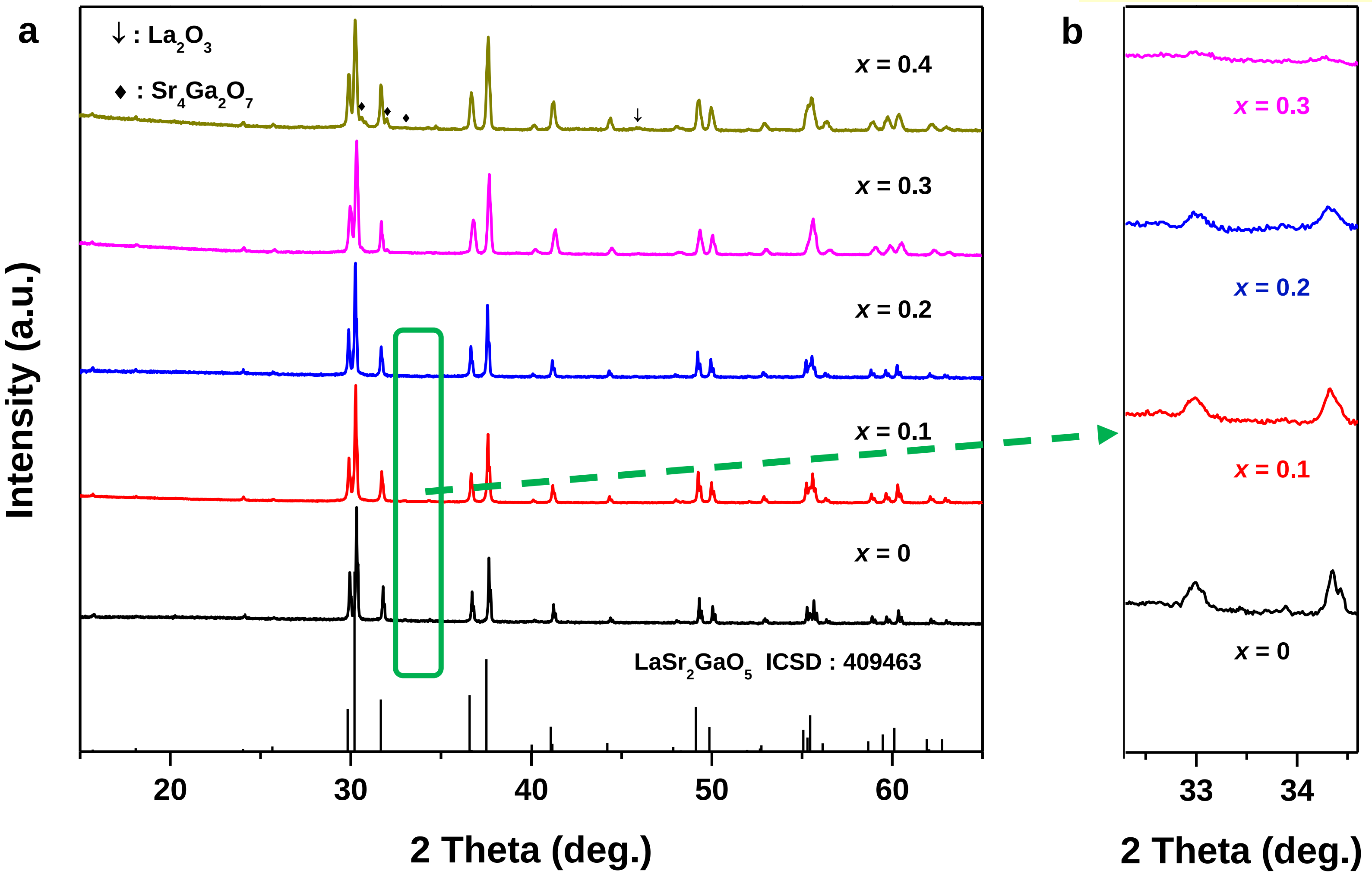


MD simulations and BVSE did not succeed

Any problem with the structure model?

4. Oxide ion conductors. $La_{1-x}Sr_{2+x}GaO_{5-0.5x}$

Non-indexed Extra reflections



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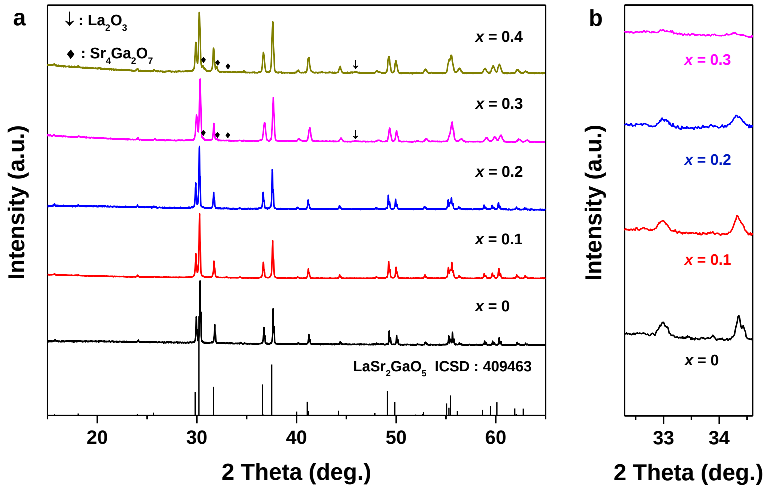
4. Oxide ion conductors. $La_{1-x}Sr_{2+x}GaO_{5-0.5x}$

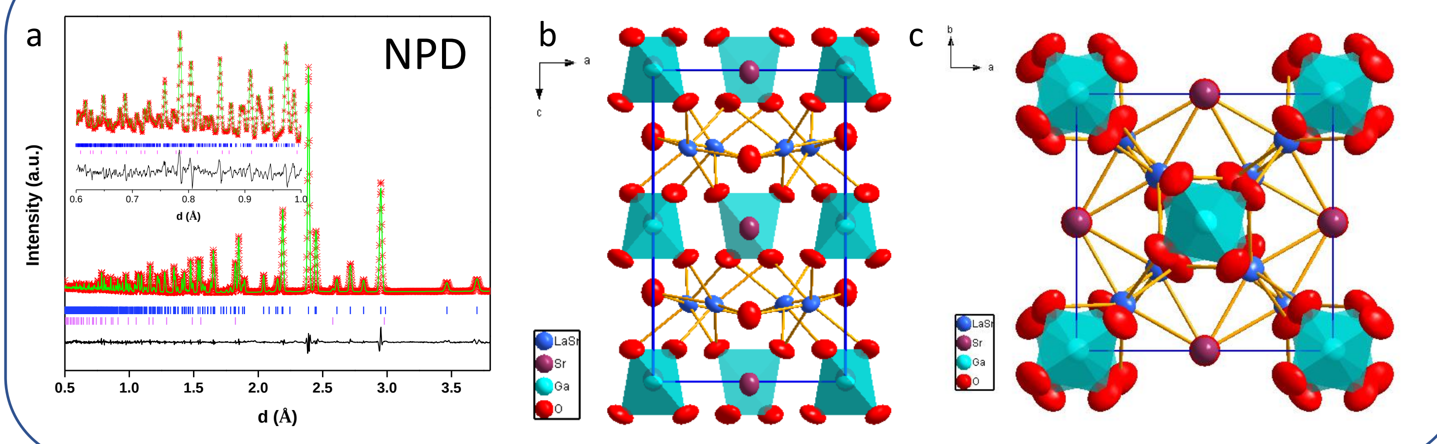
Some extra peaks cannot be indexed according to any known compound



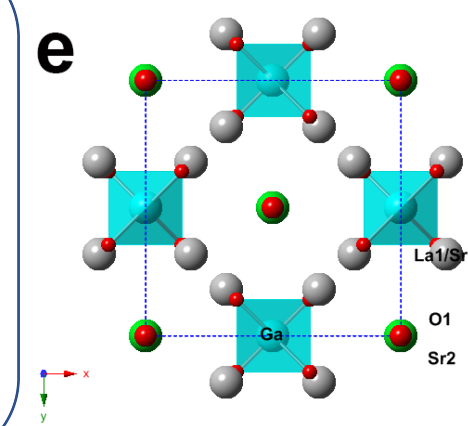
The Extra peaks can be indexed according to a single phase *P4/ncc*

We propose a new structure model differing from the previous centering body structure due to the GaO4 tetrahedra tilting

P4/ncc



*I*4/**mcm**
old



4. Oxide ion conductors. $La_{1-x}Sr_{2+x}GaO_{5-0.5x}$

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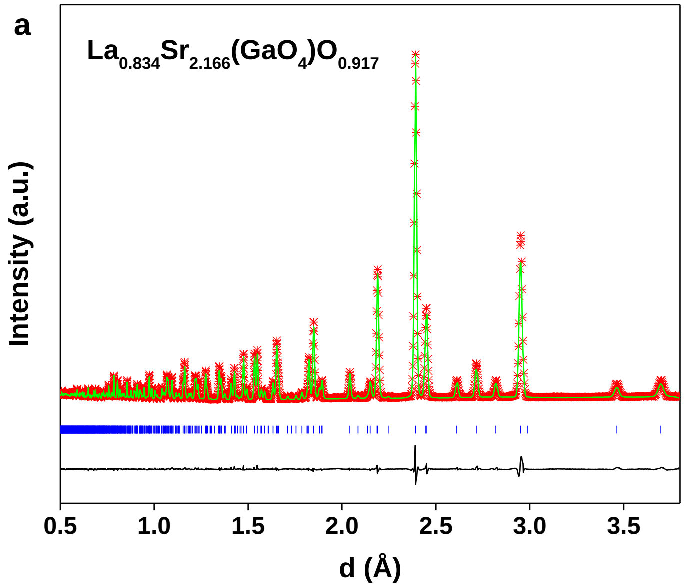
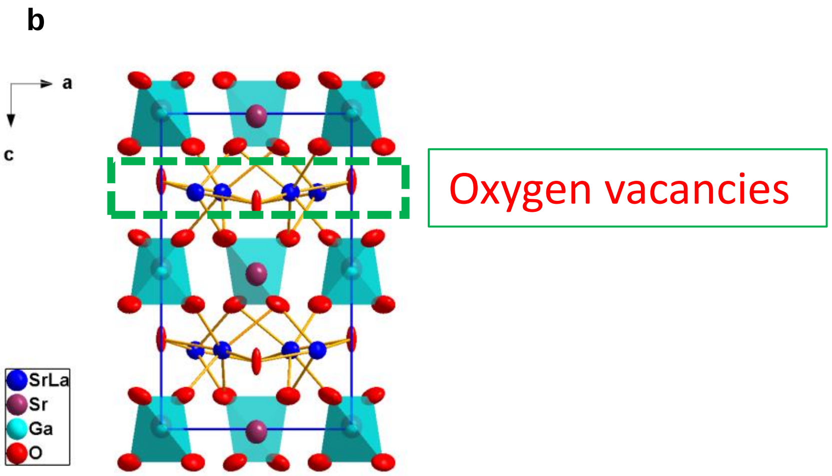
Average structure model $La_{1.8}Sr_{2.2}GaO_{4.9}$





1 La site
1 La/Sr site
1 G site
2 Oxygen sites: only one of them has vacancies

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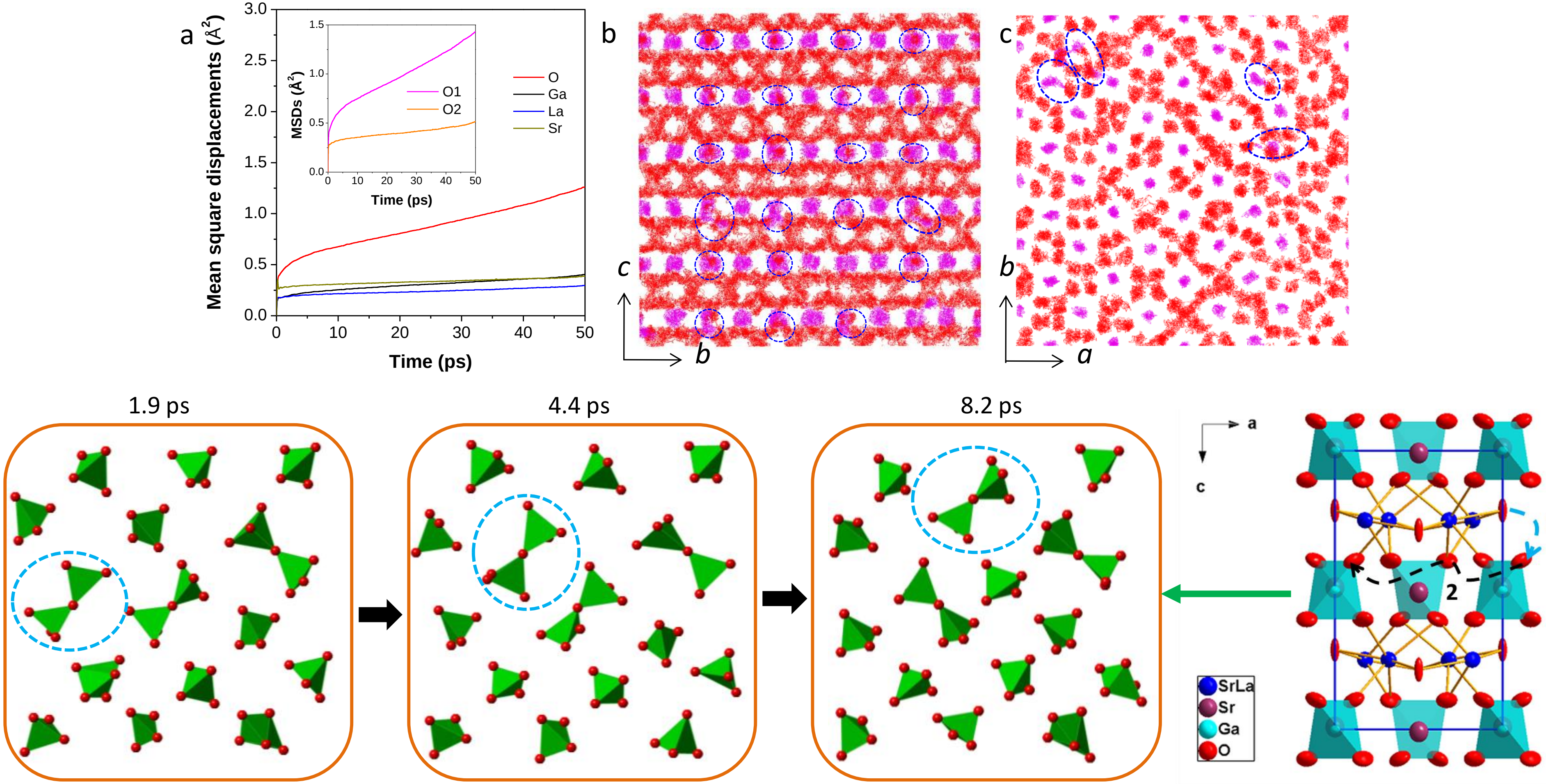
3. $La_{1-x}Sr_{2+x}GaO_{5-0.5x}$. Molecular dynamics simulation



✓Simulations breaking and reforming of Ga_2O_7 dimmers within the *ab* plane
✓Migration facilitated by the subtle GaO_4 tetrahedra tilting.

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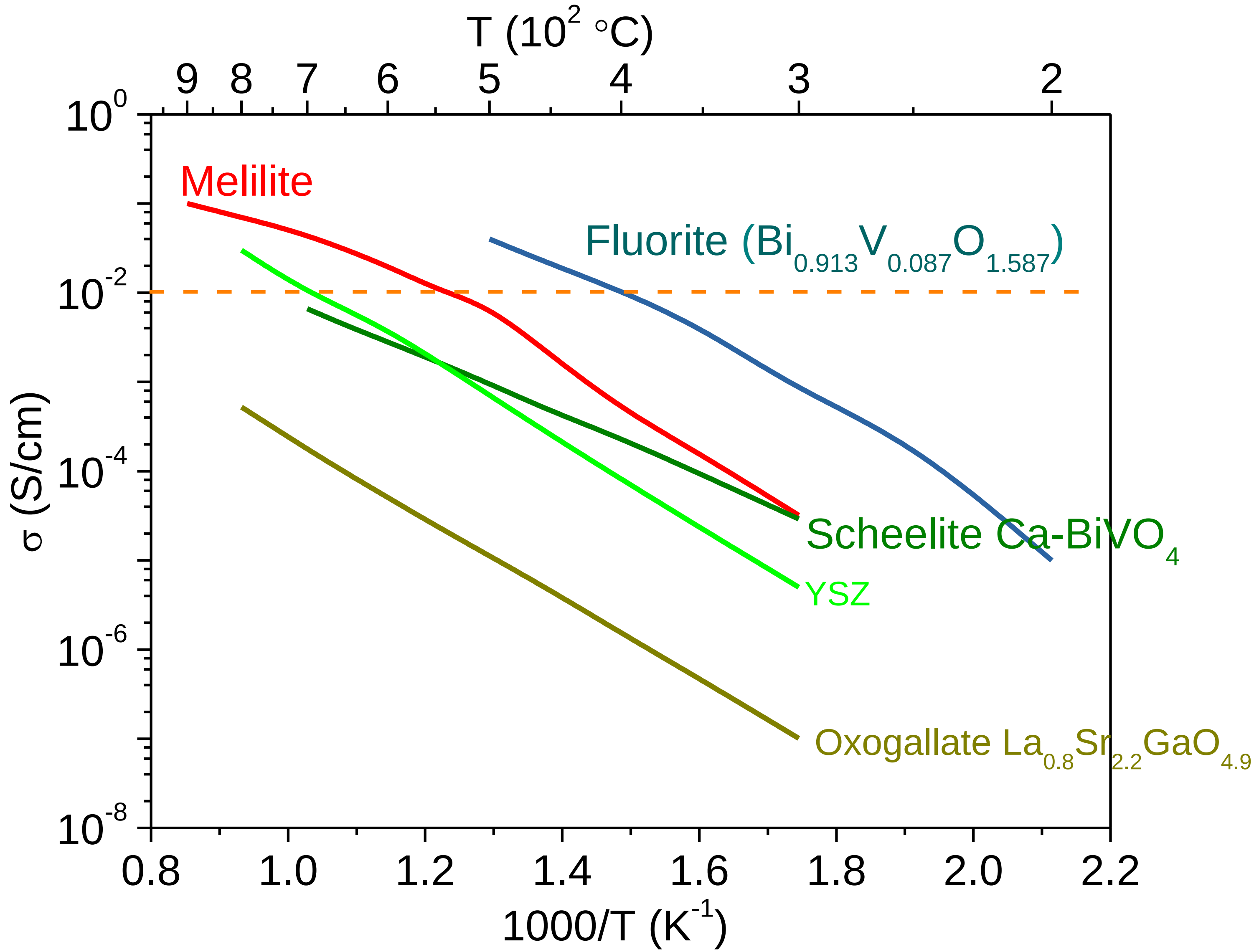
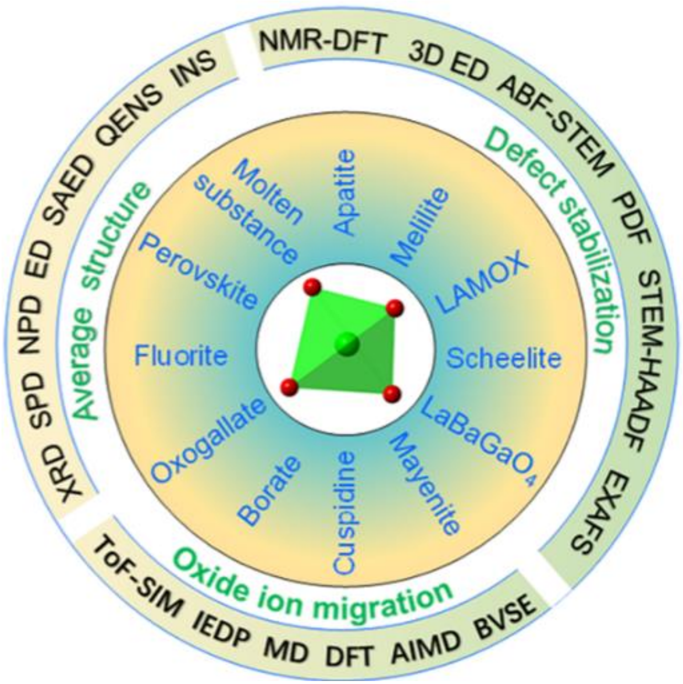
Conductivity comparison



4. Conclusions:



Oxide Ion-Conducting Materials Containing Tetrahedral Moieties

- ✓ Remarkable rotation/deformation flexibility of the tetrahedral units
- ✓ Select metal elements with the ability to tolerate a variable coordination number (Ga^{3+}. V^{5+}, B^{3+}, Mo^{6+}, Ge^{4+})

Acknowledgement

Main collaborators




Dr. X. Kuang | Dr. X. Yang | Dr. M. Allix | Dr. M. Pitcher

Institutions

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