

4^{èmes} Réunions plénières de la Fédération H₂
La Grande Motte | 7-11 Octobre 2024

S06 : Réactivité redox de surface d'oxydes envisagés comme cathode de piles à combustibles à oxyde solide

Elise Berrier, Valerie Theuns, Siavash Alizadeh, Donovan
Ledru, Marie-Hélène Chambrier



Contexte: Le projet KNOWSKITE-X

Consortium: 10 partenaires



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KNOWSKITE-X
Knowledge-driven fine-tuning of perovskite-based electrode materials for reversible Chemicals-to-Power devices



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- ▶ Industriels: FIAXELL (SW), C2C Newcap (PT)

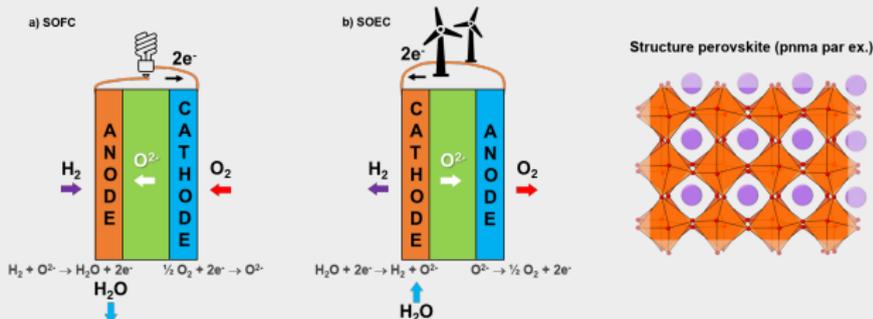


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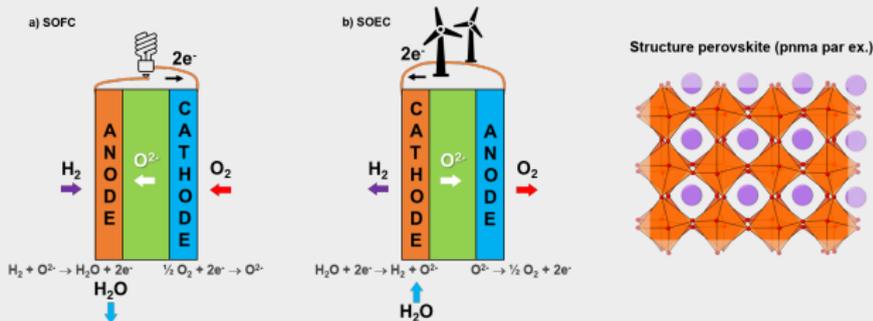
KNOWSKITE-X: Les matériaux

Des oxydes mixtes comme électrodes SOC



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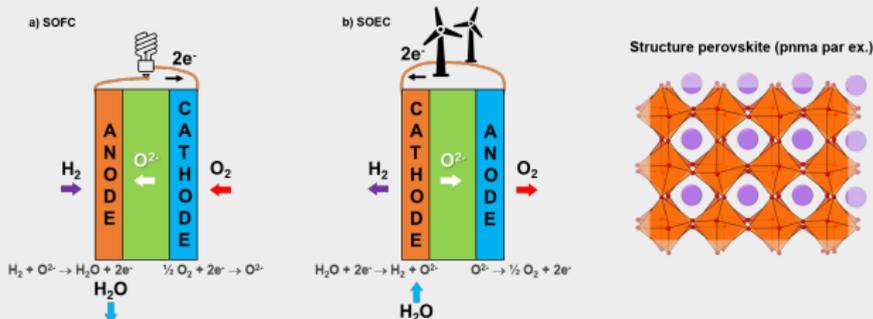
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► formulations $\text{A}_{\alpha-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3\pm\delta}$; $0.7 < \alpha < 1$

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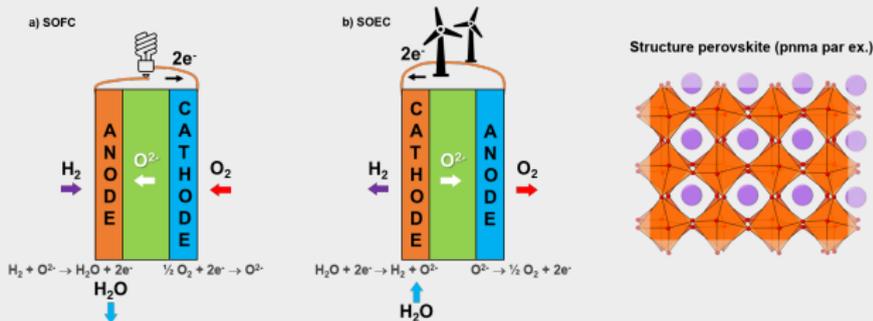
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- ▶ A / A': Ba, Bi, Ca, K, La, Li, Na, Pb, Pr, Sr, Nd, Pr, Tb ...

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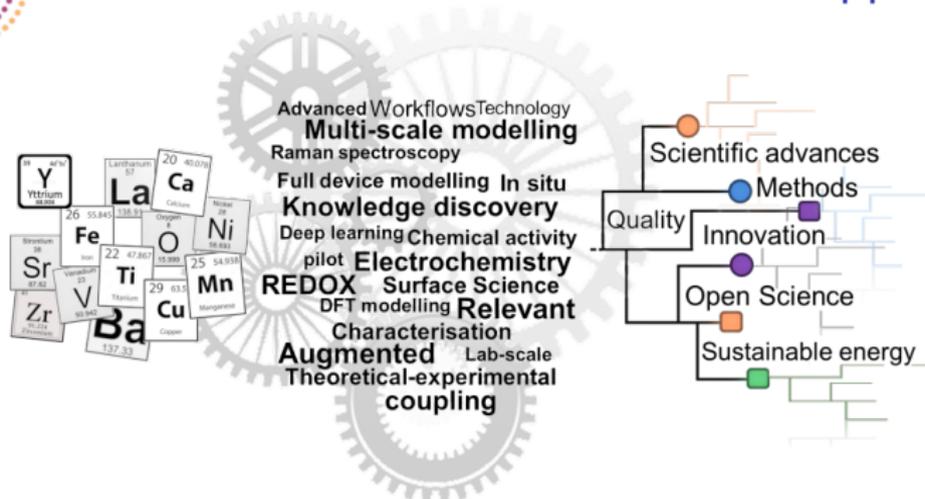
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- ▶ B / B': Na, Te, Fe, Ti, Co, Ru, Mo, Mn, Bi, Nb, Te, Mg, W, Ta, Sb, Al, V, Zn, Hf ...



KNOWSKITE-X: Approche



Elements d'anatomie d'une électrode performante

LSCF + NiO = LSFN

Le système BCTF



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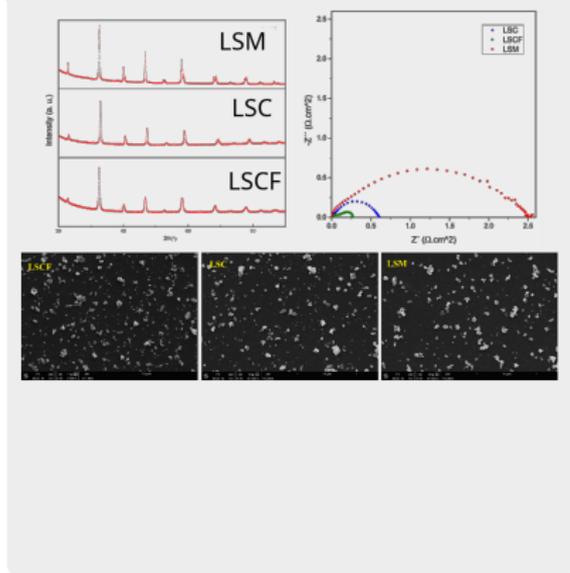
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LSCF, LSM, NiO...

Quelques propriétés physico-chimiques

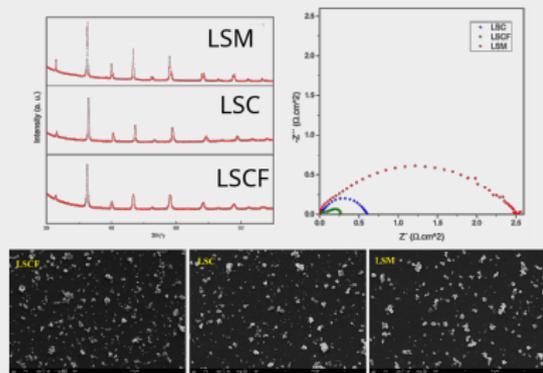
Structure & Morphologie



LSCF, LSM, NiO...

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▶ perovskite majoritaire



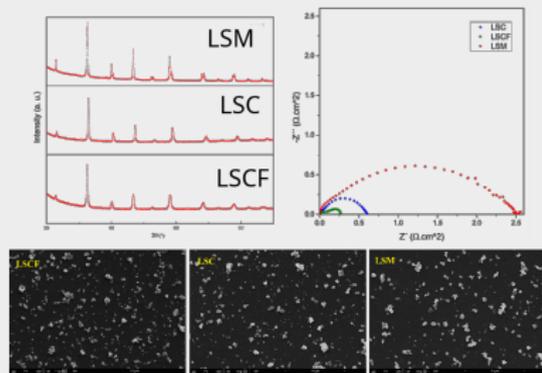
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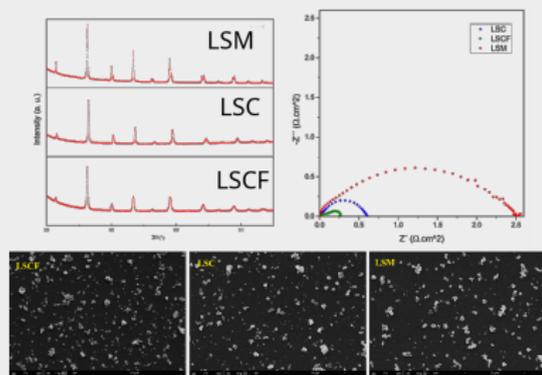
- ▶ perovskite majoritaire
- ▶ morphologies comparables



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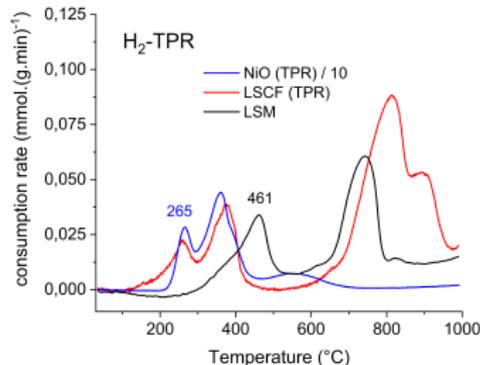
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réactivité redox



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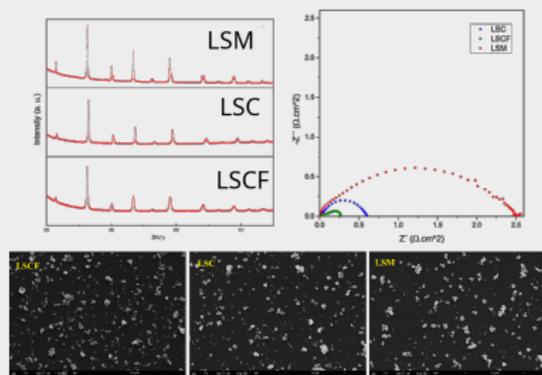




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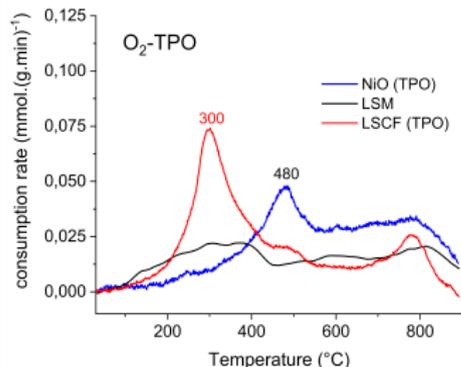
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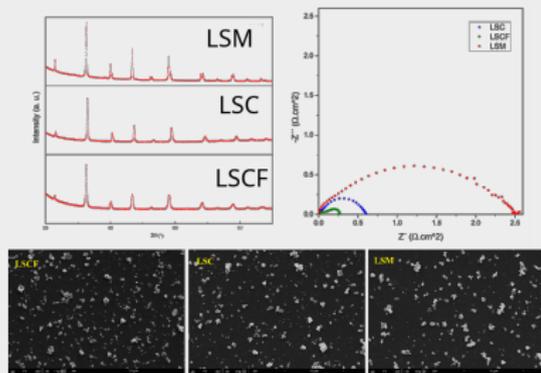
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Structure & Morphologie



- ▶ perovskite majoritaire
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réactivité redox

TPR-TPO

- ▶ NiO réductible sous H₂ (HOR)
- ▶ LSCF re-oxidable sous O₂ (ORR)



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Elements d'anatomie d'une électrode performante

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Le système BCTF



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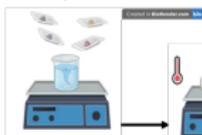
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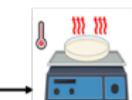


Exploration dans le système LSFN

Mixing starting materials in deionized water at room temperature



$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
 $\text{Sr}(\text{NO}_3)_2$
 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
 Citric Acid
 Glycine



Drying the solution on hot plate until the combustion



The resulting ash-like powder



Grinding with an Agate Pestle

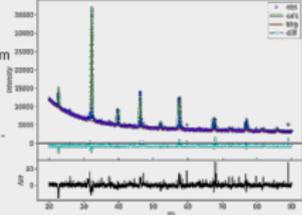


Structure



Rietveld refinement data:

Crystallite size: 176 nm
 $a = 5.5528 \text{ \AA}$
 $b = 5.5288 \text{ \AA}$
 $c = 7.8276 \text{ \AA}$
 Density: 6.725
 Space group: P b n m -
 Orthorhombic



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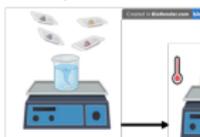


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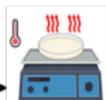
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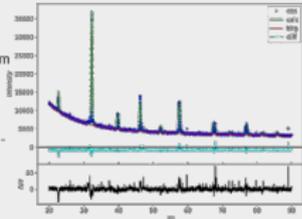


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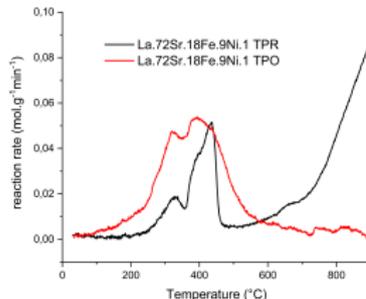


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activité redox



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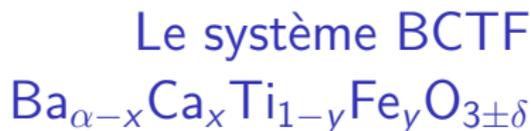
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Motivation et Approche

cation	rayon ionique
Ba^{2+}	1.61 Å
Ca^{2+}	1.34 Å
Ti^{2+}	0.605 Å
Fe^{3+}	0.645 Å

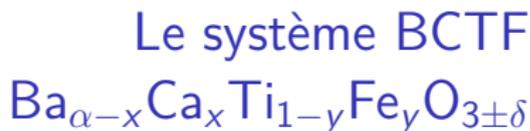


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Motivation et Approche

- ▶ Métaux abondants, non toxiques et non critiques

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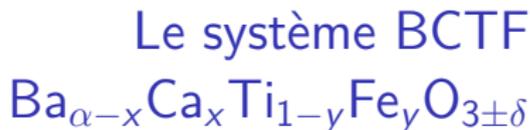


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Motivation et Approche

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- ▶ Couple redox $\text{Fe}^{3+} / \text{Fe}^{2+}$

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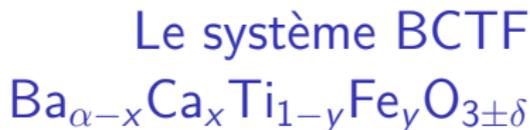


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Motivation et Approche

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- ▶ Couple redox $\text{Fe}^{3+} / \text{Fe}^{2+}$
- ▶ Perovskite de base: BaTiO_3

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Ti^{2+}	0.605 Å
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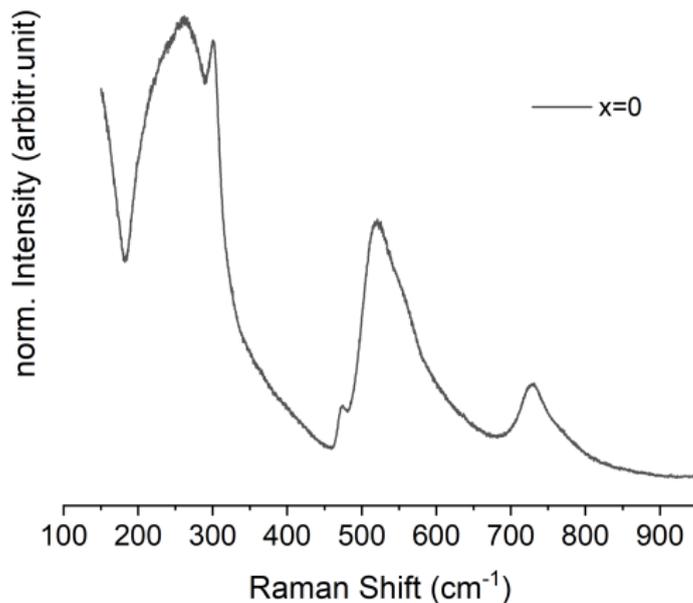
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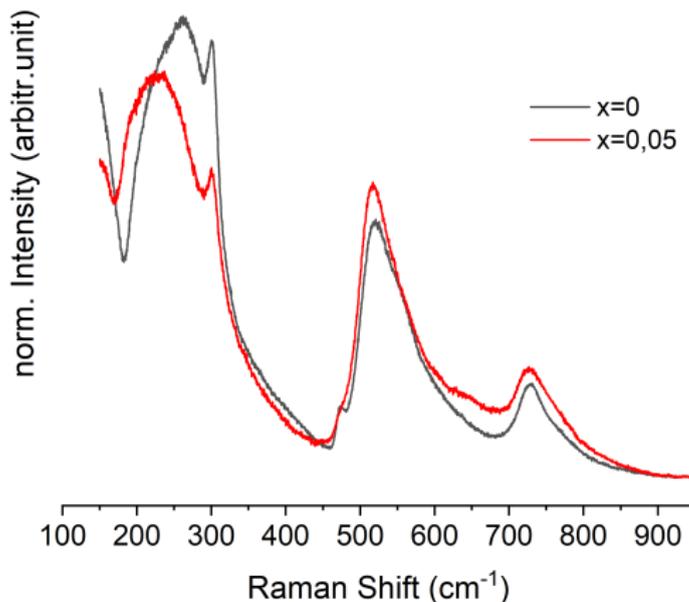


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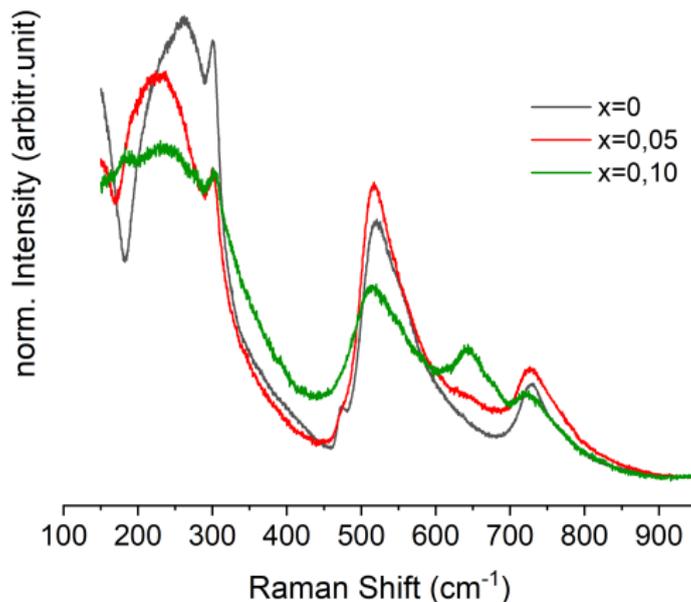
Structure des B85CTF0-20



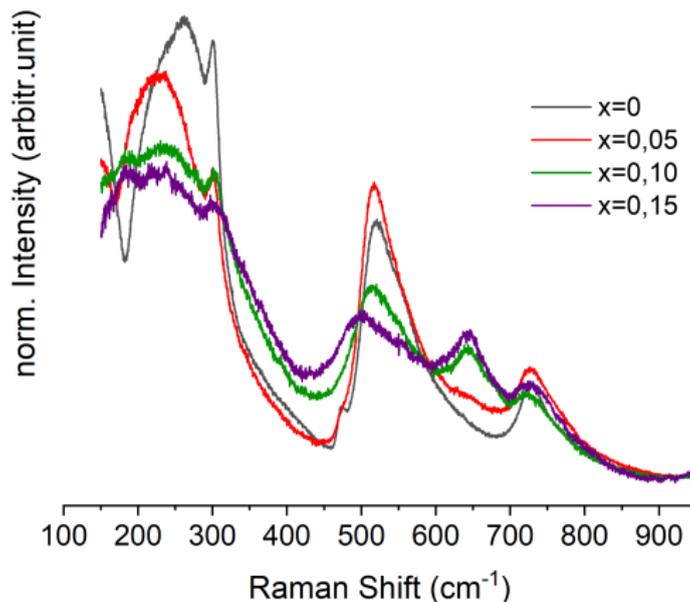
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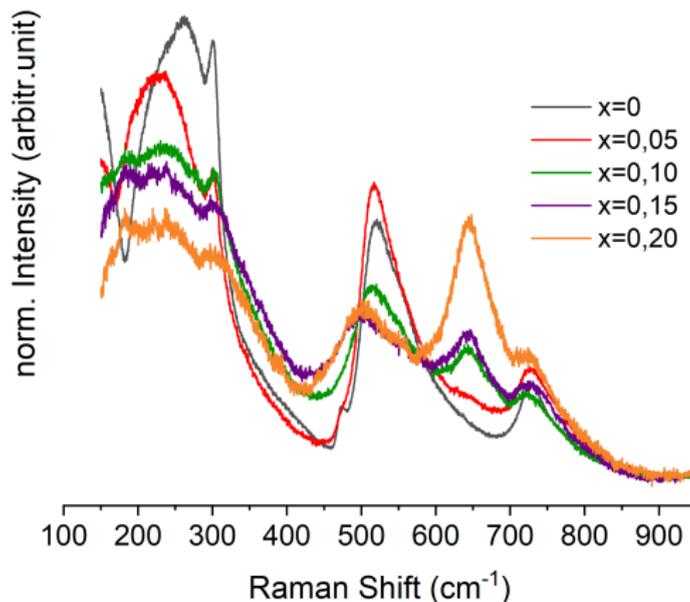
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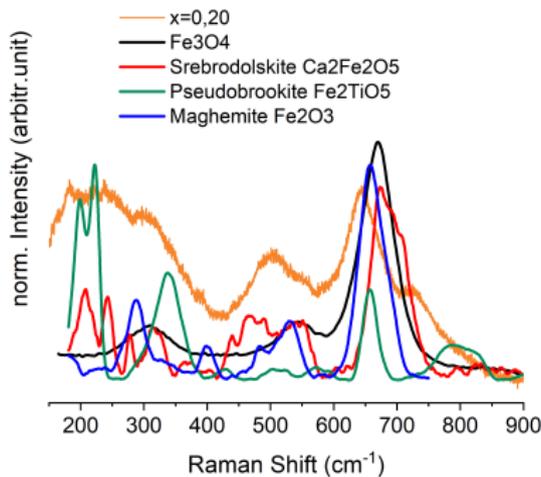
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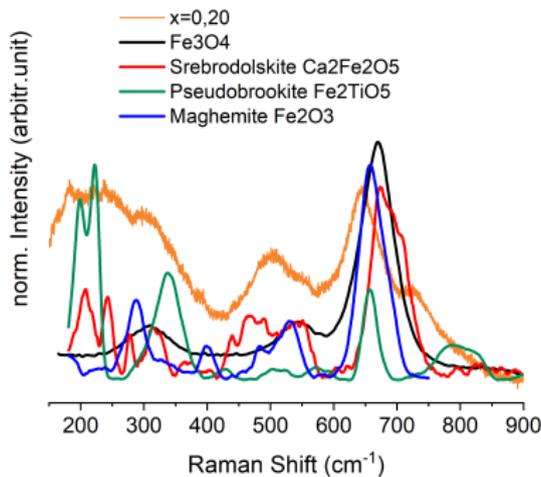


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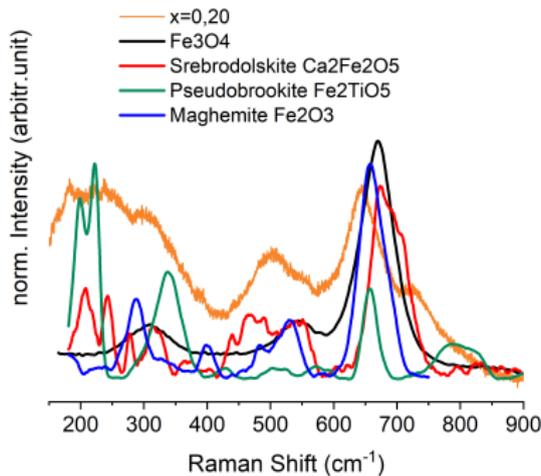
Structure





Structure

▶ Fe en solution?



Structure

- ▶ Fe en solution?
- ▶ DRX accord

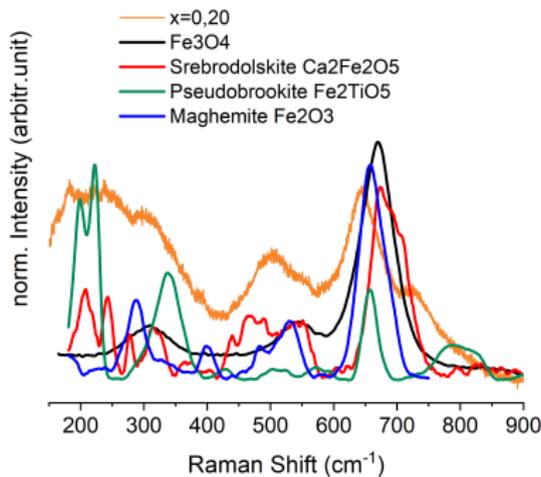


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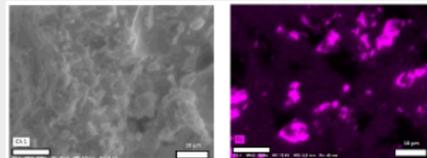


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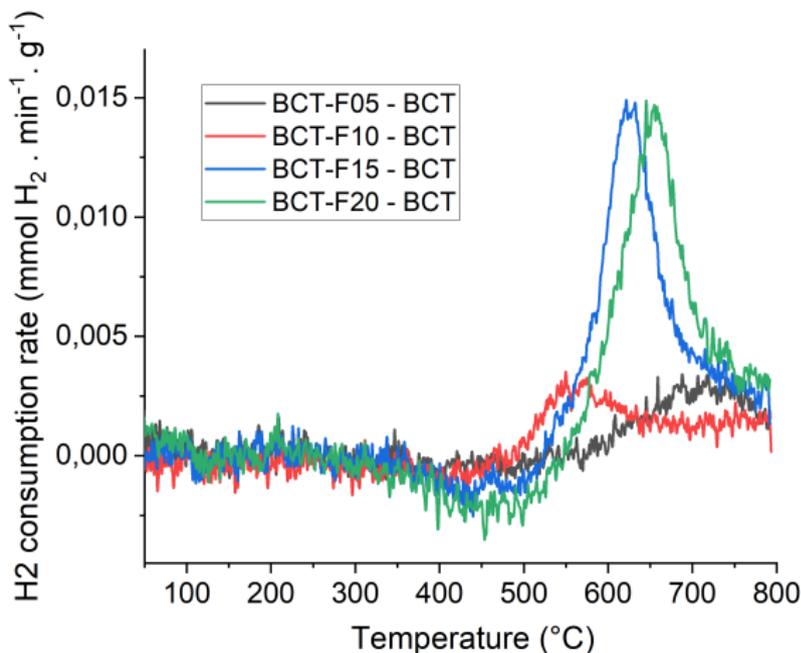


Structure

- ▶ Fe en solution?
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- ▶ EDS (15kV, x2000):



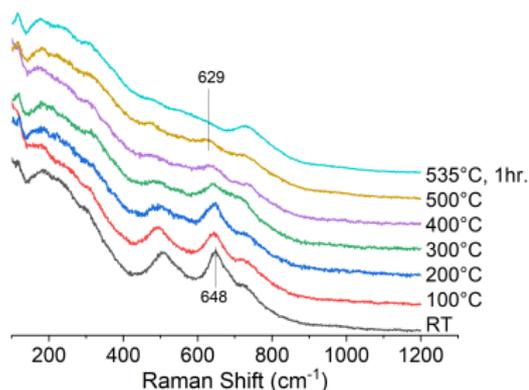
Réductibilité des B85CTF-5 à 20



Cyclage redox de B85CTF-20

exploration structurale de la réduction (HOR)

Spectro. Raman *in situ*
pendant la RPT



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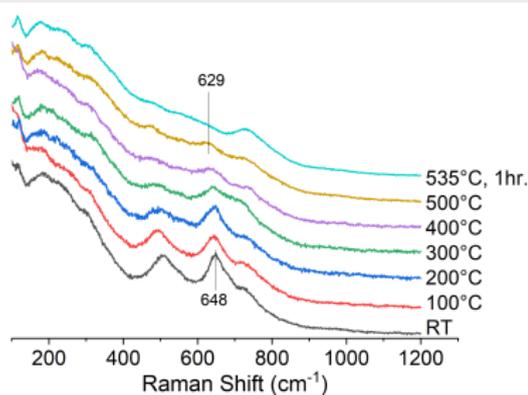


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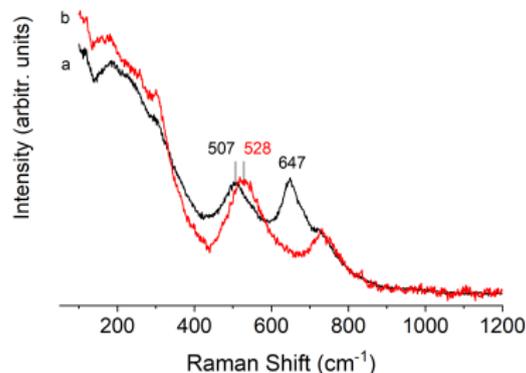
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Retour à Tamb.

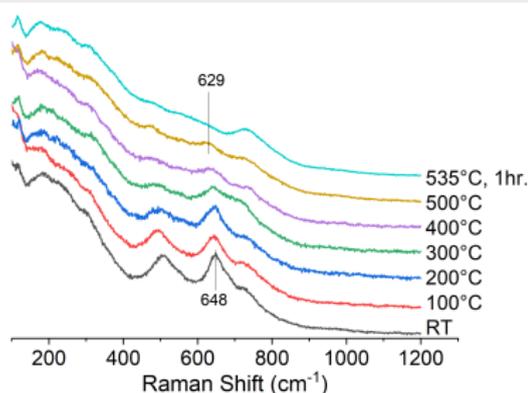




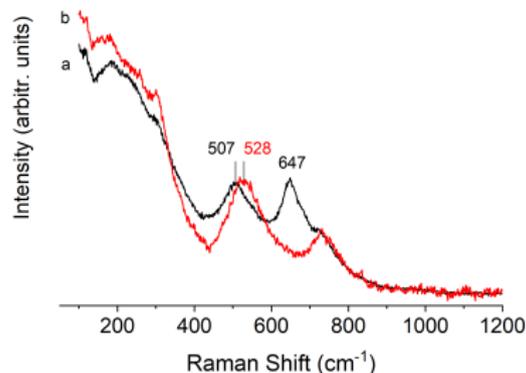
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Spectro. Raman *in situ* pendant la RPT



Retour à Tamb.



post-TPR

La phase "Fe" est réduite



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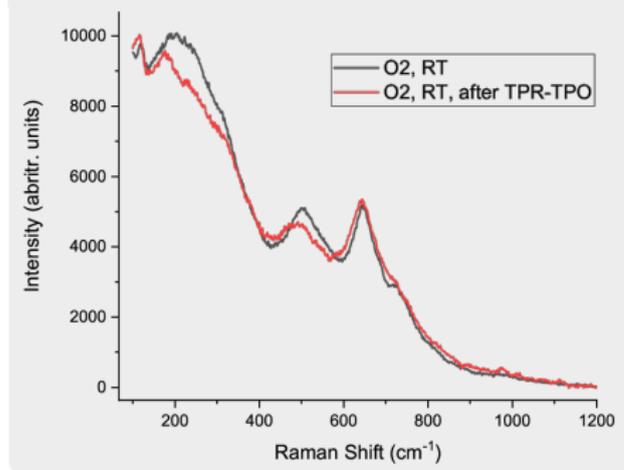
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exploration structurale de la ré-oxydation (ORR)

Spectro. Raman *in situ* après la TPO



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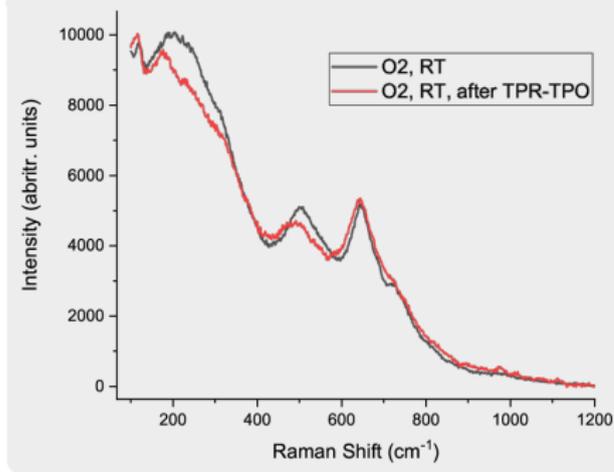
KNOWSKITE-X
Knowledge-driven fine-tuning of perovskite-based electrode materials for reversible Chemicals-to-Power devices



Cyclage redox de B85CTF-20

exploration structurale de la ré-oxydation (ORR)

Spectro. Raman *in situ* après la TPO



- ▶ signature BCTF app retrouvée



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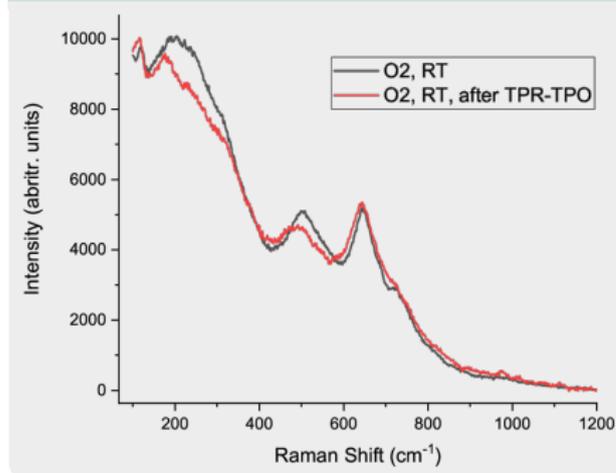
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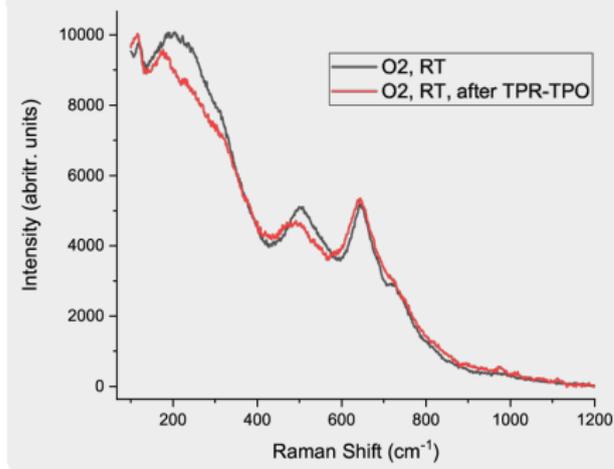
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- ▶ ... à suivre



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Quelques Conclusions

- ▶ Approche "catalyse hétérogène" des matériaux d'électrode:
 - ▶ surface: quantitatif-qualitatif
 - ▶ cyclage redox TPR-TPO
 - ▶ *operando*
 - ▶ réactions modèles (eg. réactivité méthanol, NH_3 , CO_2 ...)



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Merci pour votre attention



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