



# The influence of the sintering temperature and synthesis method on the structural properties of doped perovskites

like:  $(La_{0.75}Sr_{0.25})_{0.95}(Cr_{1-x}Fe_x)O_{3-\delta}$  (LSCF) and Ce doped  $Ba(Zr_{0.8-x}Ce_xY_{0.2})O_{3-\delta}$  (BZCY)

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## Why Intermediate Temperature PCFC electrodes?

Proton conducting fuel cells (PCFCs) are considered of interest as one of the cleanest and most efficient chemical-to-electrical energy conversion systems [1-2]. Since PCFCs can directly convert chemical energy to electricity, they have increasingly attracted worldwide attention in recent years due to their remarkable characteristics such as high efficiency and significantly low emission levels of pollutants. However, this type of fuel-cell has an important technical concern related to its operation temperature, which should be held between at 750–1000K, the so-called "Intermediate Temperature (IT)" regime. A novel kind of PCFC is being developed which has the potential to convert methane to longer chain hydrocarbons while generating power. In order to realize this device, it is crucial to understand the electronic and ionic conduction mechanisms of PCFC anode materials in detail, it is particularly important to discuss the valence and oxygen content, chemical state, bond length/angle and coordination related to the B-site atoms [3].

## Preparation of Samples

**Sol gel synthesis:** easy & efficient way to obtain pure and homogeneous sample

- Dissolving all metal nitrates in diluted water
- Jelling & drying (overnight) to get foam formation
- Decomposition and annealing at various temperatures and sintering times
- LSCF & BZCY mixture slurry with binder solution
- Grinding of resulting powder after drying
- Making Anode disk by using a Die with 1" diameter



## Characterization of LSCF and Ce doped BZY samples

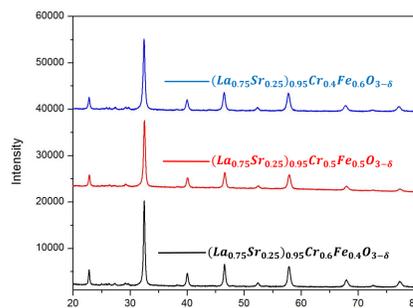


Figure 1: XRD pattern of 3 LSCF samples (Fe ratio changes from 0.4 to 0.6)

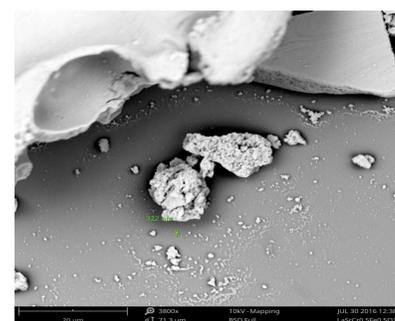


Figure 2: SEM image of  $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$  sample, the grain size of particles like spherical is changing from 50nm to 400nm

Best value of x is known as 0.5 for Fe & Cr, because; according to the literature;

- Cr ratio ↑ --- means --- ↓ Electrochemical Activity
- Fe ratio ↑ --- means --- ↓ Total conductivity

Best sample:  $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$  sintered at 600°C was selected

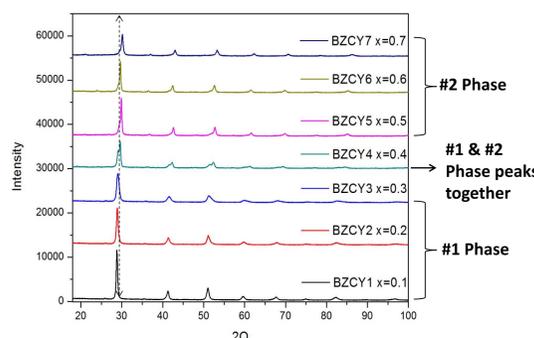


Figure 3: XRD pattern of 7 Ce doped BZY samples (Zr ratio (x) changes from 0.1 to 0.7)

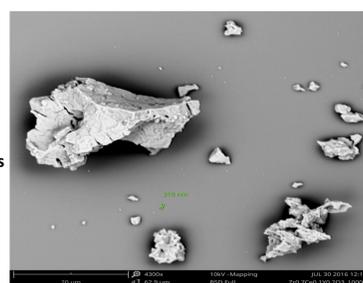
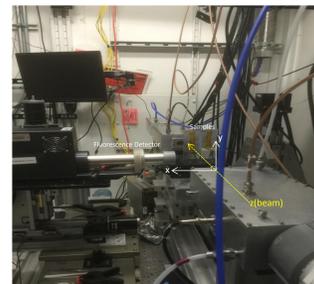


Figure 4: SEM image of  $Ba(Zr_{0.7}Ce_{0.1})Y_{0.2}O_{3-\delta}$  sample, the grain size of particles like spherical is changing from 50nm to 400nm

## The XAS experiment

XAS data was taken at Sector 10 BM line at ANL's Advanced Photon Source. All Cr K-edge data of LSCF samples were taken in fluorescence mode with a 4-element SDD detector due to the small amount of Cr in the sample and the relatively low Cr K-edge energy, whereas Z the K-edge XAS study of all BZCY samples was done in transmission mode. The picture given at right was taken at Sector 10 BM line showing the setup for both transmission and fluorescence measurements. When measuring fluorescence, the sample is turned at 45° to the incident beam.



## X-ray absorption spectroscopy measurement

In this study, we are aiming to determine the valence state, oxygen content and structural model related to transition metals at the B site of Fe/Cr doped LSCF samples and lanthanide series doping atoms at the B site of Ce doped BZY perovskites. These objectives can be achieved by using the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of Cr, Fe, Zr, Y and Ce at the K-edge obtained by simultaneous ex-situ X-ray absorption spectra (XAS) measurements. To deal with this aim, we did the following measurements by using synchrotron X-rays at APS, in Argonne National Laboratory:

- Their valences was estimated by XANES measurements
- Local structure changes in nano-materials was determined by EXAFS measurements.

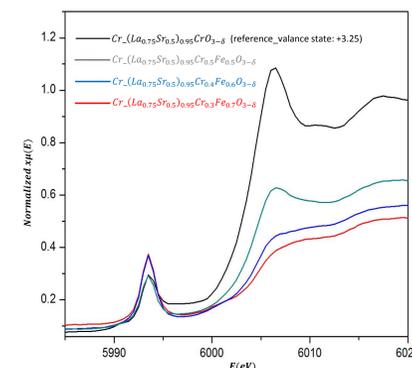


Figure 6: The plotting from ICDD database .cif file of  $La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-\delta}$  with orthorhombic crystal system and Pnma space group

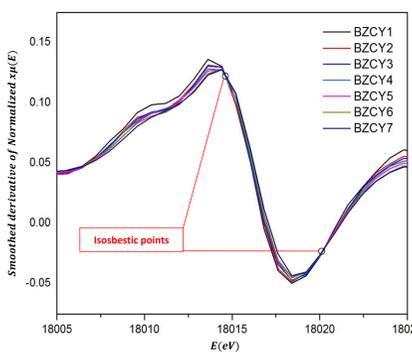


Figure 7: The derivative of XAFS data of  $Ba(Zr_{1-x}Ce_x)Y_{0.2}O_{3-\delta}$  samples

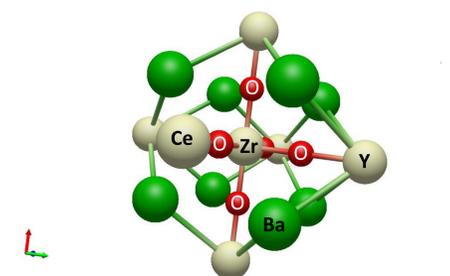


Figure 8: The plotting from ICDD database .cif file of  $BaZr_{0.2}Ce_{0.65}Y_{0.15}O_{3-\delta}$  with cubic crystal system and Pm-3m space group

## XRD fitting and BET-Surface area calculation results

Table 1: The XRD and BET results of  $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$  samples annealed at 600°C, 650°C and 700°C respectively.

Samples	Sintering Temp.	Cell Parameters	Crystal System	Space Group	Rp (%)	wRp (%)	χ²	Crystallite Size (nm)	BET (m²g⁻¹)
$(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$	600°C	a = 5.499 b = 7.821 c = 5.535 α = β = γ = 90°	Orthorhombic	Pnma	2.43	3.08	1.716	23.4	21.358
$(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$	650°C	a = 5.515 b = 7.801 c = 5.544 α = β = γ = 90°	Orthorhombic	Pnma	1.95	2.	1.437	24.7	15.665
$(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$	700°C	a = 5.499 b = 7.821 c = 5.535 α = β = γ = 90°	Orthorhombic	Pnma	1.91	2.41	1.295	25.4	11.864

## XRD refinement with GSAS

All powder X-ray data was collected at XRD laboratory in Illinois Institute of Technology(IIT). After all LSCF and BZCY samples were experimentally evaluated, their crystallographic phase analysis was discussed using powder XRD patterns refined with the GSAS (General Structure Analysis System) software. The size of coherently diffracting domains (assumed to be spherical) was evaluated using the Scherrer formula [6]:

$$(1) P(nm) = \frac{1800K\lambda}{\pi(LX - X_{ins})} \quad (\text{From GSAS}) \quad (2) B(2\theta) = \frac{K\lambda}{\cos\theta \cdot \beta} \quad (\text{From XRD pattern})$$

Where K=0.94 is the Scherrer constant, λ is the wavelength in nm, X<sub>ins</sub> the instrumental broadening, and LX the refined Lorentz coefficient for size-type broadening [7].

### LSCF

Rietveld refinement results:

- ❖ Lattice parameters & angles:  
a = 5.499 b = 7.821 c = 5.535  
α = β = γ = 90°
- ❖ Reduced χ² = 1.295
- ❖ wRp = 0.0241
- ❖ Rp = 0.0191

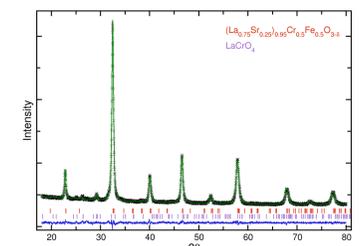


Figure 9: GSAS fitting of  $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$  sample with orthorhombic crystal system and Pnma space group, except the small impurity peaks ( $LaCrO_4$  monoclinic) between around 20° and 30° of 2θ.

### BZCY

Rietveld refinement results:

- ❖ Lattice parameters & angles:  
a = b = c = 4.2905 (Å)  
α = β = γ = 90°
- ❖ Reduced χ² = 2.433
- ❖ wRp = 0.0605
- ❖ Rp = 0.0469

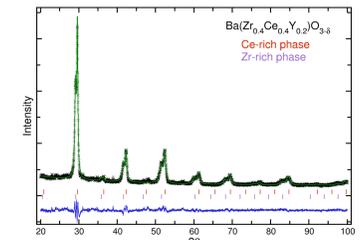


Figure 10: GSAS fitting of  $BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-\delta}$  sample having two main cubic crystal system with Pm-3m space group

## Results

- Greater amount of Cr and Fe has negative effect in SOFCs, so x=0.5 was selected
- $LSCr_{0.5}Fe_{0.5}O_{3-\delta}$  sintered at 600 °C has the highest surface area with minimum crystallite size
- $Ba(Zr_{0.6}Ce_{0.2}Y_{0.2})O_{3-\delta}$  is the best combination of BZCYs in terms of chemical stability and protonic conductivity [5]
- Cr valence state is increasing with decreasing it's ratio in BZCY samples.

## Future work

- 60% LSCF and 40% BZCY will be deposited on Al substrate with CB and binder solution to make an anode disk
- Surface area of BZCY samples will be calculated
- All XAS data will be analyzed with Artemis & Athena Software
- Ce K-edge XAS study will be done with high energy at Sector 10 ID line in APS.

## Acknowledgement

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## References

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