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Cathode Materials for ITSOFC

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U.S. Department of Energy

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Curators' Professor Emeritus of Ceramic Engineering
Senior Investigator Materials Research Center
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Education
B.S., Ceramic Engineering, University of Utah, 1957
Ph.D., Engineering Science, University of California-Berkeley, 1962

Professional
1999-present, Curators' Professor Emeritus of Ceramic Engineering, UMR
1970-1999, Associate Professor to Curators' Professor of Ceramic Engineering, UMR

Experience
1968-70, Associate Professor, Oregon Graduate Center, Beaverton, Oregon
1962-68, Senior Chemist, Sprague Electric Co., North Adams, Massachusetts

Research Interests
Nonstoichiometry of oxides; sintering behavior of oxides and metals; electrical degradation of dielectrics; methods of preparing high purity oxides from organo-metallics; titanates for use as capacitors and resistors; corrosion of ceramics; perovskites and spinels for use as high temperature electrodes, insulators and catalysts; processing of ceramic materials; multilayer substrates and capacitors; preparation of thin film oxides; sensors and thin film devices.

Honors
Fellow, American Ceramic Society, 1979
Faculty Excellence Award, 1987 and 1988
Curators' Professor, December 1988
Editor, J. American Ceramic Society, September 1992 to July 2002
Emeritus Professor September 1999

Publications
Over 150 refereed publications

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William James	Professor
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Abstract

The overall objective of this study is to gain a fundamental understanding of the parameters and characteristics which are related to SOFC cathode performance in the 500-700ºC range. Initially, we are focusing on determining why Co and/or Fe containing perovskites perform better than Mn based perovskites. This is being accomplished by comparing the electrical conductivity, defect structure and cation valence states of these perovskite compositions. Early results show that one of the primary differences in these oxides is the levels of oxygen vacancy concentrations present at a given temperature and oxygen activity. This suggests that the degree of mixed ionic and electronic conductivity is directly related to the cathode overpotential.

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Outline

- Issues Addressed
- Objectives
- Approach
- Results to Date
- Importance to Goals of SECA
- Future Work

Technical Issue Addressed

- **Overpotential of LSM is too high to operate SOFC at T < 800ºC**
- **Need for cathode materials with overpotential low enough to operate in the 500-700ºC range.**
- **The question to be answered is: What are the properties that a cathode must possess to successfully operate at T < 750ºC?**

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Research Objective

- **The overall objective of this study is to gain a fundamental understanding of the parameters and characteristics which are related to SOFC cathode performance in the 500-700ºC range. That is, what material parameters must an oxide have to possess to perform well as a cathode?**
- **And with this knowledge develop an appropriate cathode material.**
- **We are focusing on answering the question of why Co and/or Fe containing compositions perform better than (La,Sr)MnO_3?**

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- **The primary goal will be to compare the electrical conductivity, defect structure and cation valence states of the (La,Sr)(Fe,Co)O_3 compositions to these of $La_{0.8}Sr_{0.2}MnO_3$ as function of temperature and oxygen activity.**

- **These results will be compared to the overpotential measured on electrode/YSZ electrolyte structures.**

- **To test the hypothesis that the cathode overpotential is related to the oxygen vacancy concentration and the cation valence states in the cathode.**

This will be done by:

- Preparing powders and dense specimens of:

  $La_{0.8}Sr_{0.2}MnO_3$

  $La_{.6}Sr_{.4}FeO_3$

  $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$

- Characterizing each composition using:
  - XRD
  - TGA
  - Electrical Conductivity
  - Neutron Diffraction
  - Mössbauer Spectroscopy

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Results to Date

- **Compositions Prepared:**

  $La_{0.8}Sr_{0.2}MnO_3$

  $La_{1-x}Sr_xFeO_3$

  $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_3$

- **Determination of Oxygen Vacancy Content**
  - **Electrical conductivity**
  - **TGA**
  - **Neutron Diffraction (RmT)**
  - **Mössbauer Spectroscopy (RmT)**
- **Electrical Conductivity in Air**
  - **Measurements**
  - **Simulation**
- **Fe Local Chemistry**

- **The determination of oxygen deficiency is of important for evaluation of oxides for use as cathodes. In addition to chemical analysis and TGA, two techniques are employed:**
  1) ***Neutron Diffraction*** **not only resolves structural and magnetic properties, but also allows an accurate and rapid determination of oxygen deficiency levels;**
  2) ***Mössbauer spectra*** **allow studies on the valence state of Fe, therefore an** ***in situ*** **spectroscopy study of the reaction between the ferrite cathode and oxygen is feasible.**
- **Our studies plus other results suggest that ferrite compositions are candidates for use as cathodes in IT SOFCs**

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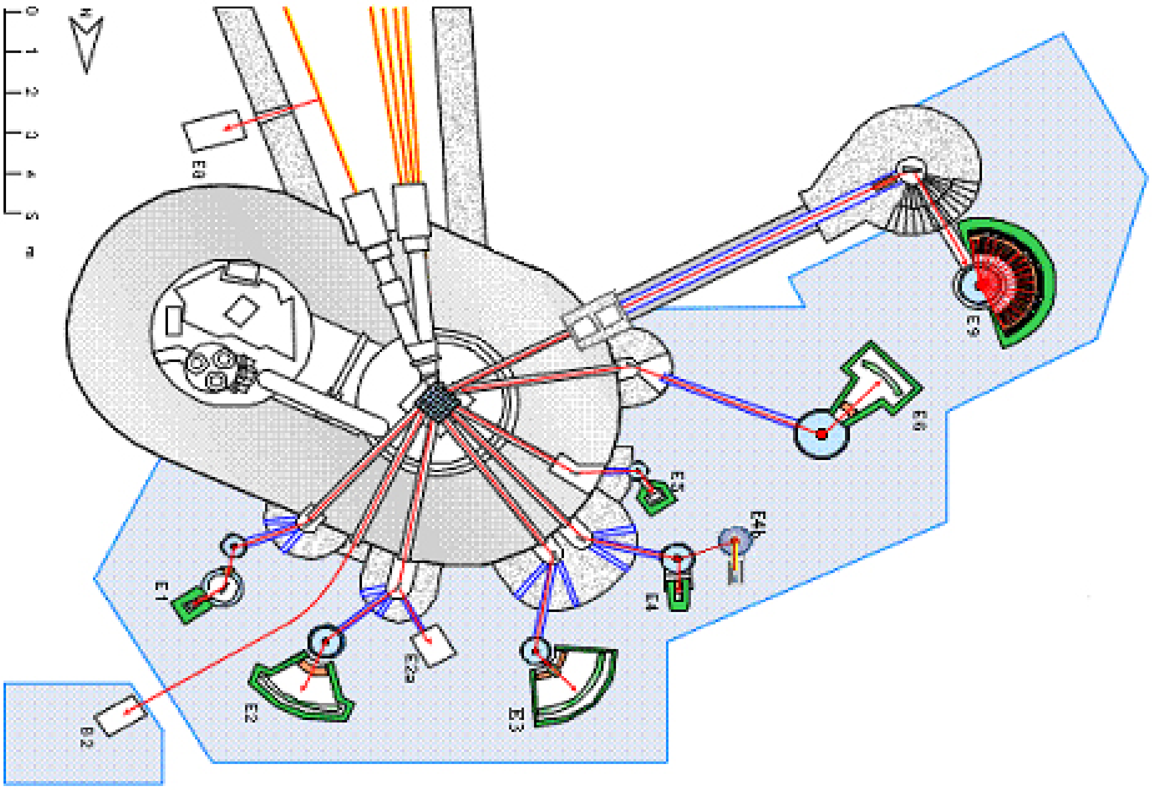
The University of Missouri Research Reactor Center – (MURR)



- Neutron Powder Diffractometer (HR)
- Neutron Reflectometer
- Residual Stress Diffractometer
- Triple Axis Spectrometers
- SQUID Magnetometer
- Deep Level Transient Spectrometer Monochromators
- Neutron Irradiation …

The Merits of Neutron Diffraction on Studies of the Perovskite-Type Cathodes

- Neutrons have unique scattering amplitudes and scattering is not dominated by heavy atoms;
- Neutron cross sections are isotope dependent
- Neutron energies are comparable to elementary excitations (phonons and magnons). Thus, inelastic scattering substantially changes the neutron energy (wavelength);
- Neutrons have a magnetic moment and can probe the magnetic structures and excitations through a strong interaction.
- Neutrons are scattered by the nuclei (except for magnetic scattering). Thus the form factor is flat.

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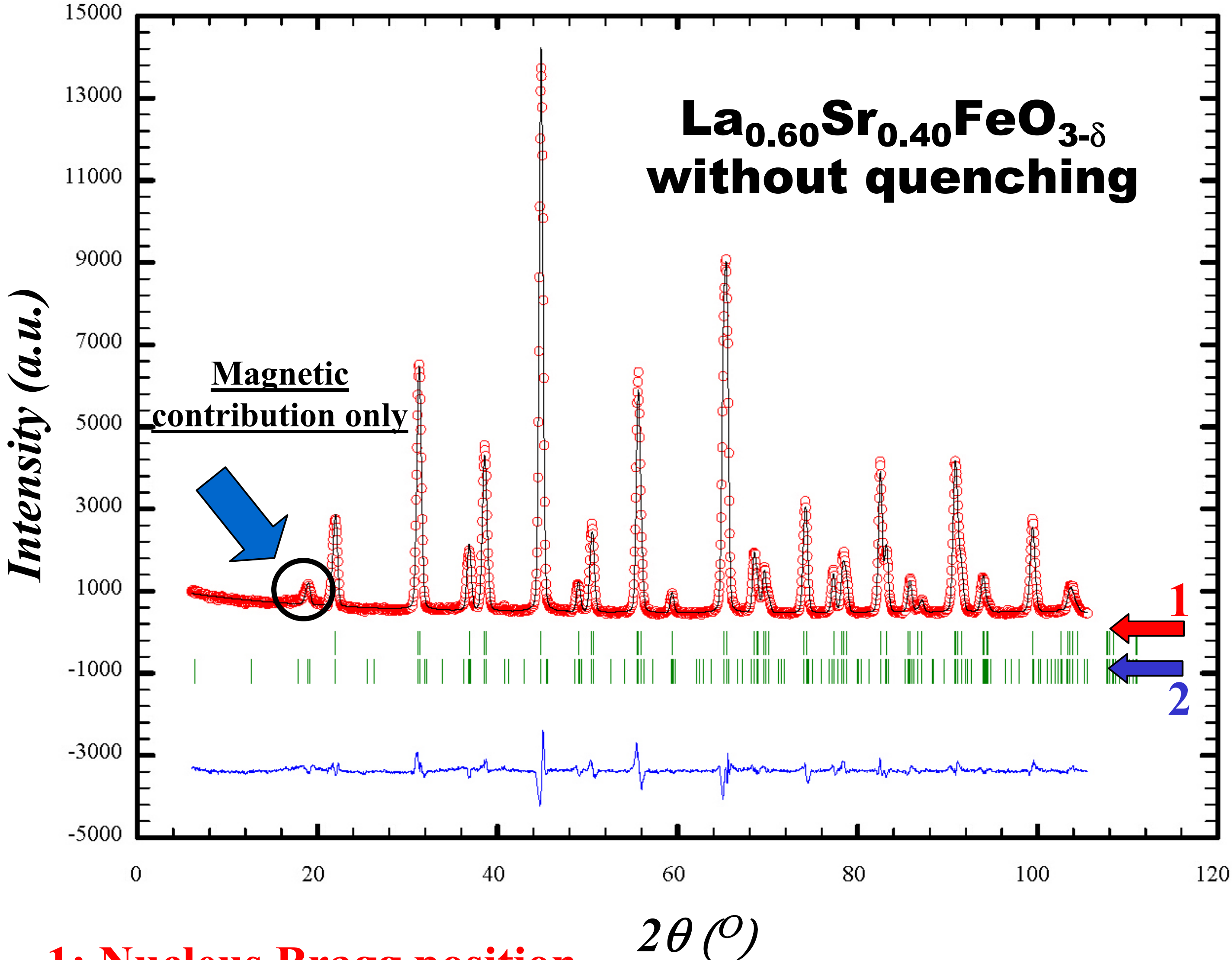
Typical Neutron Diffraction Performed at Room Temperature

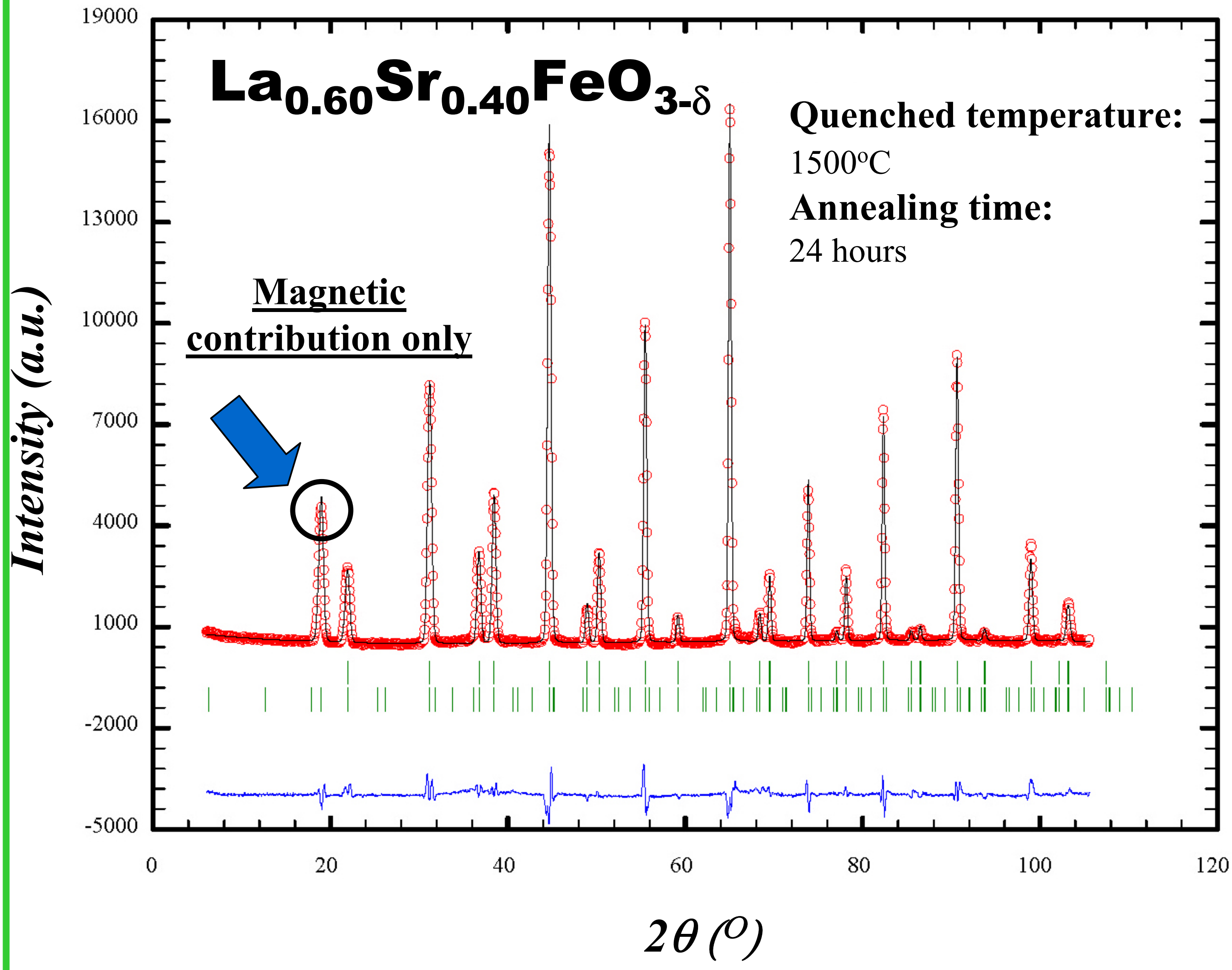


1: Nucleus Bragg position

2: Magnetic position

Nèel temperature of L6SF is around RT, therefore magnetic peak contribution is weak in ND pattern.

High Nèel Temperature and Strong Magnetic Contribution in Quenched $La_{0.60}Sr_{0.40}FeO_{3-\delta}$



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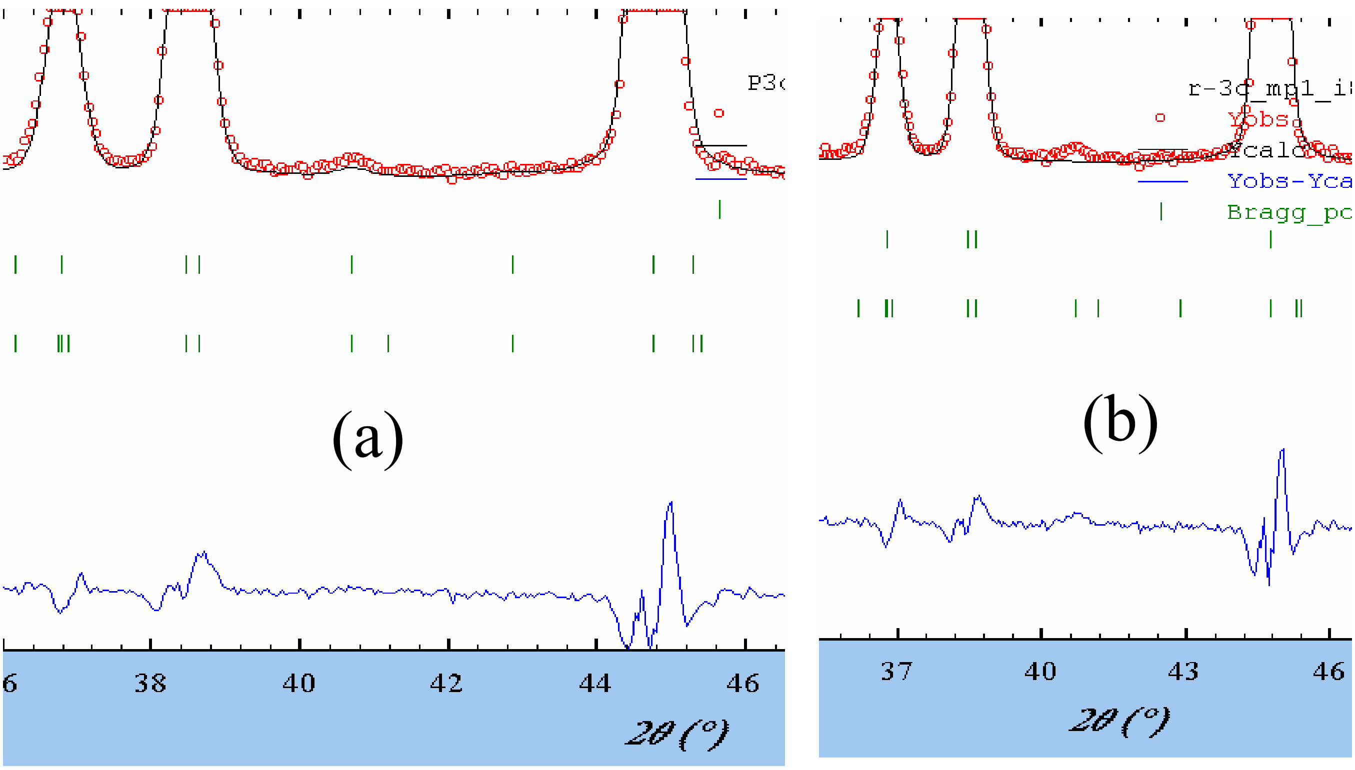
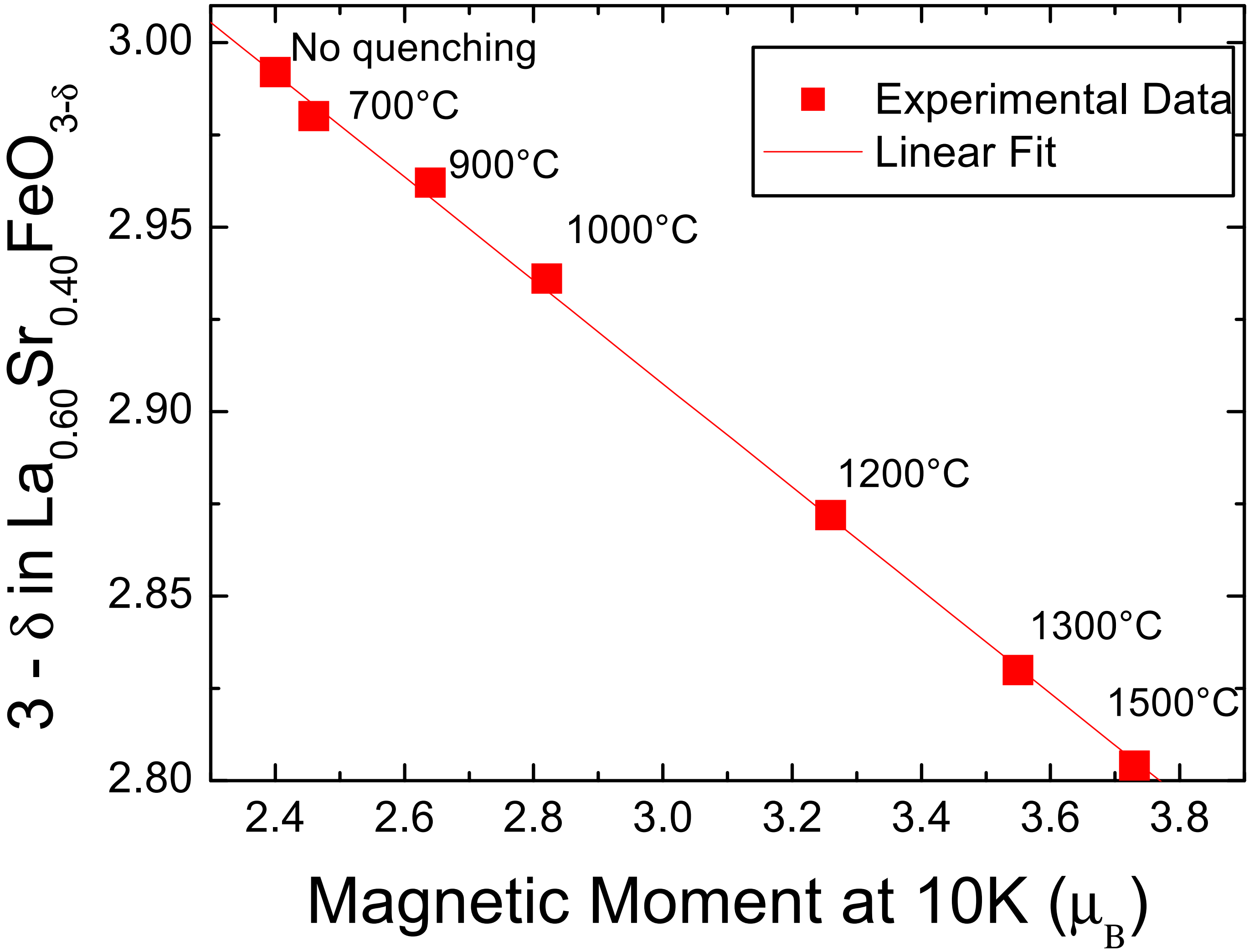
Space group of P – 3c1 improved ND refinement



(a) Refined with P-3c1 space group
(b) Refined with R-3c space group

The green marks are the Bragg peak positions of each phase. Specimen was quenched in air at 1000°C and ND was performed at RT.

$3-\delta$ vs. μ_B for $La_{0.60}Sr_{0.40}FeO_{3-\delta}$ quenched at various temperatures



- **Saturation moments for all specimens**
- **Fe^{3+} (moment ~ 3.8 m_B)**
- **Only Fe^{3+} contributes to antiferromagnetic moment in this system**

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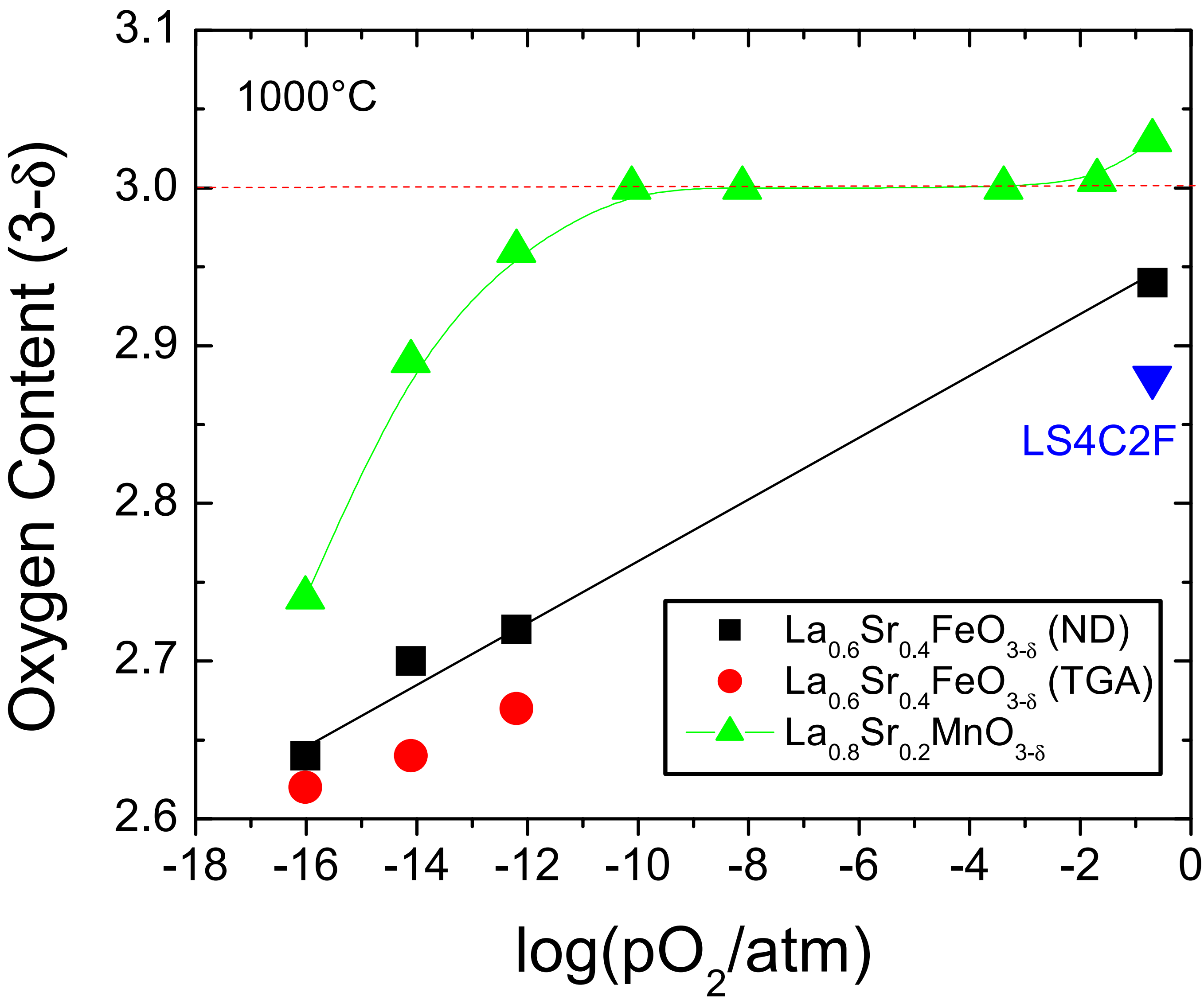
Oxygen Content determined by TGA and ND for LSM, LSF and LSCF



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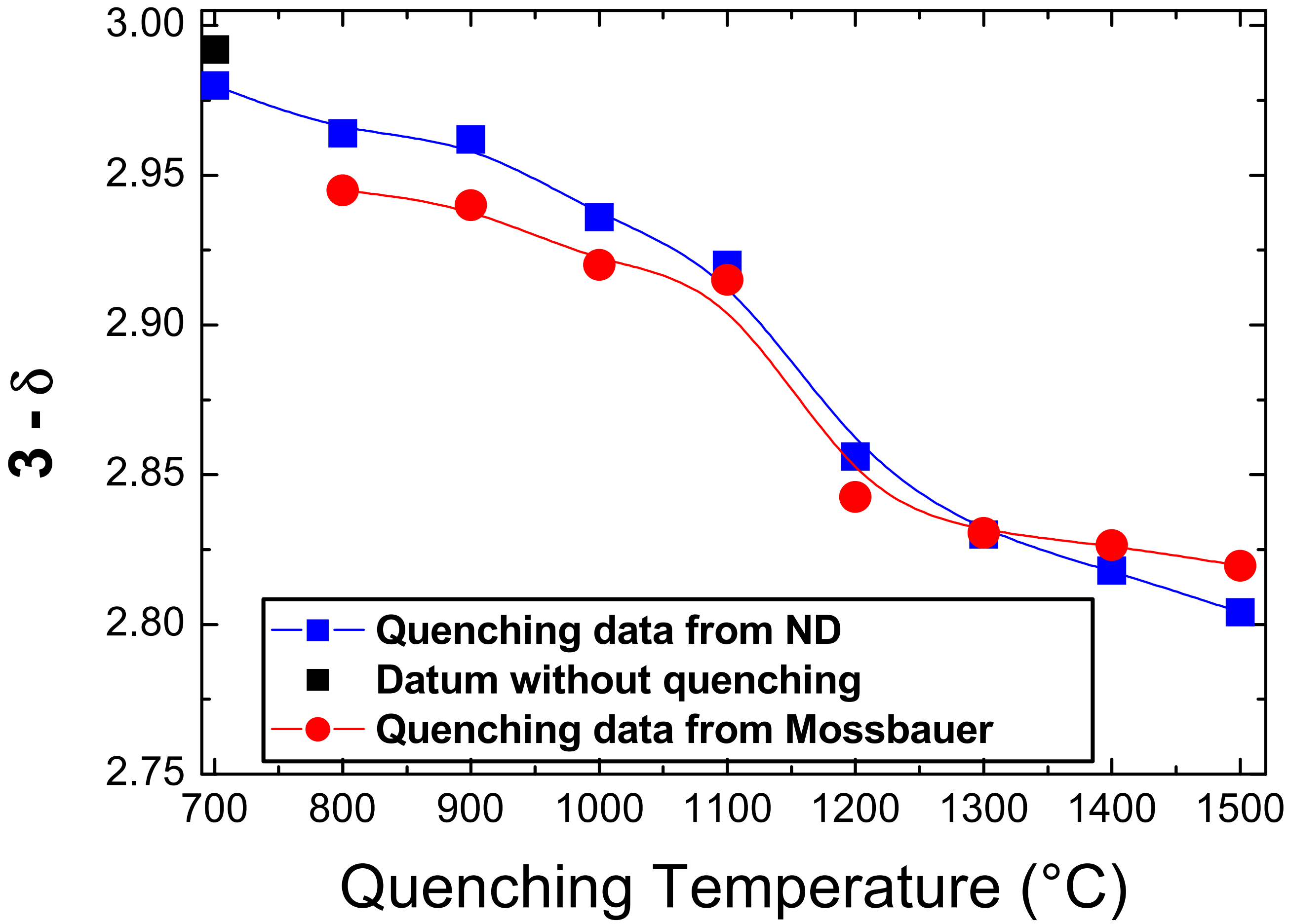
Oxygen Content (3-δ) for Quenched $La_{0.60}Sr_{0.40}FeO_{3-\delta}$



$$O_O^\times \rightarrow V_O^{\circ\circ} + \frac{1}{2}O_2 + 2e'$$

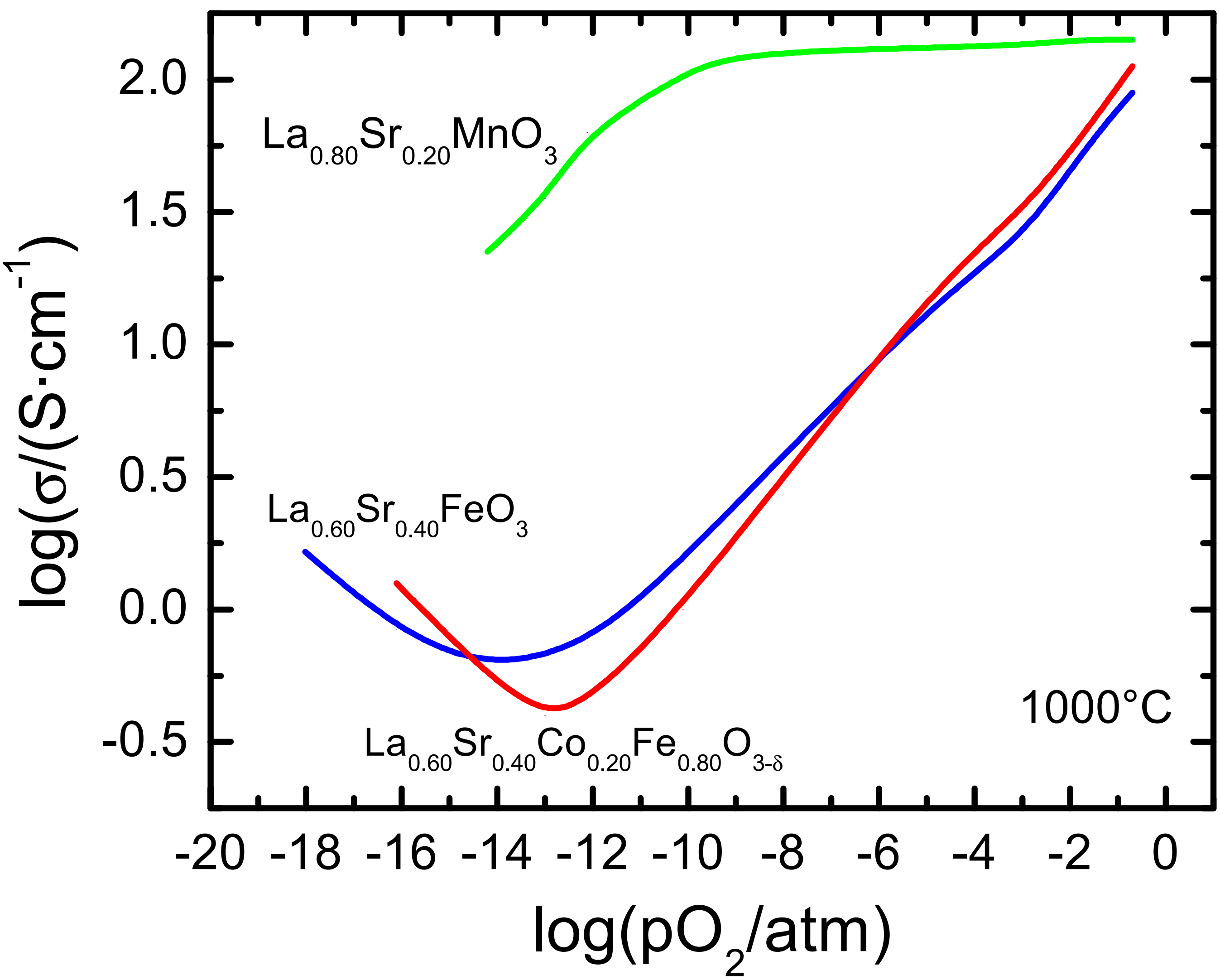
$$K_1 = [V_O^{\circ\circ}]\, pO_2^{1/2}\, n^2$$

$$n = \frac{K_i}{p} = \frac{K_i}{[Sr_{La}'] - 2[V_O^{\bullet\bullet}]}$$

$$\frac{[V_O^{\bullet\bullet}]}{([Sr_{La}'] - 2[V_O^{\bullet\bullet}])^2} = \frac{K_0}{K_i^2} pO_2^{-1/2} \exp\left(-\frac{E_{V_O^{\bullet\bullet}}}{kT}\right)$$

	$E_{V_O^{\bullet\bullet}}$
Neutron Diffraction	0.6eV
Mössbauer	0.4eV
Conductivity	0.9eV

Log(σ) vs. log(pO_2) for LSM, LSCF and LSF



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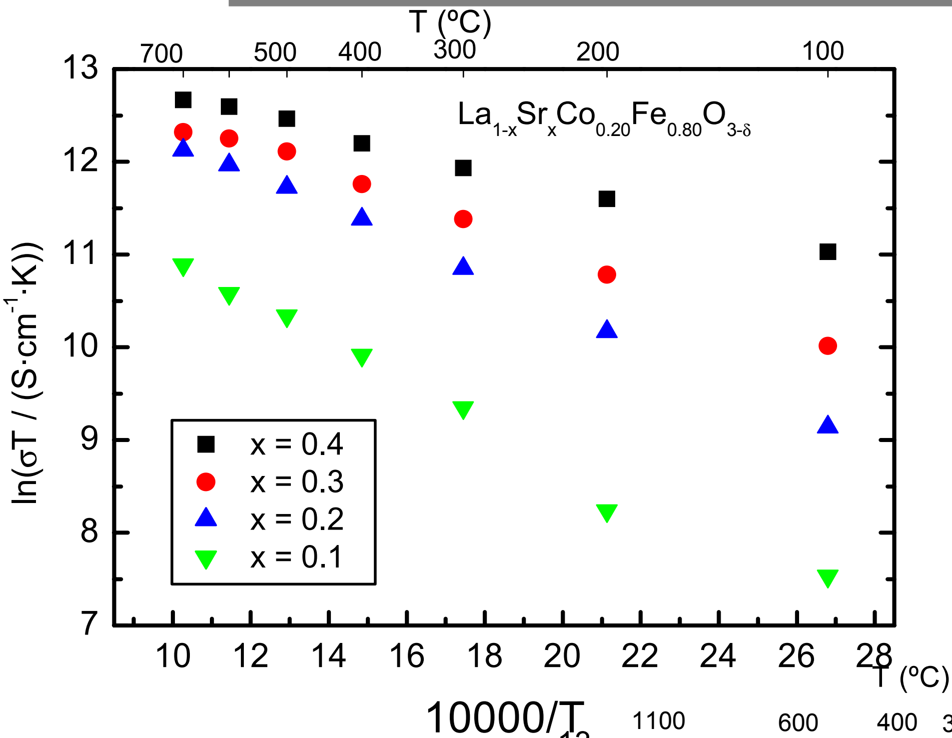
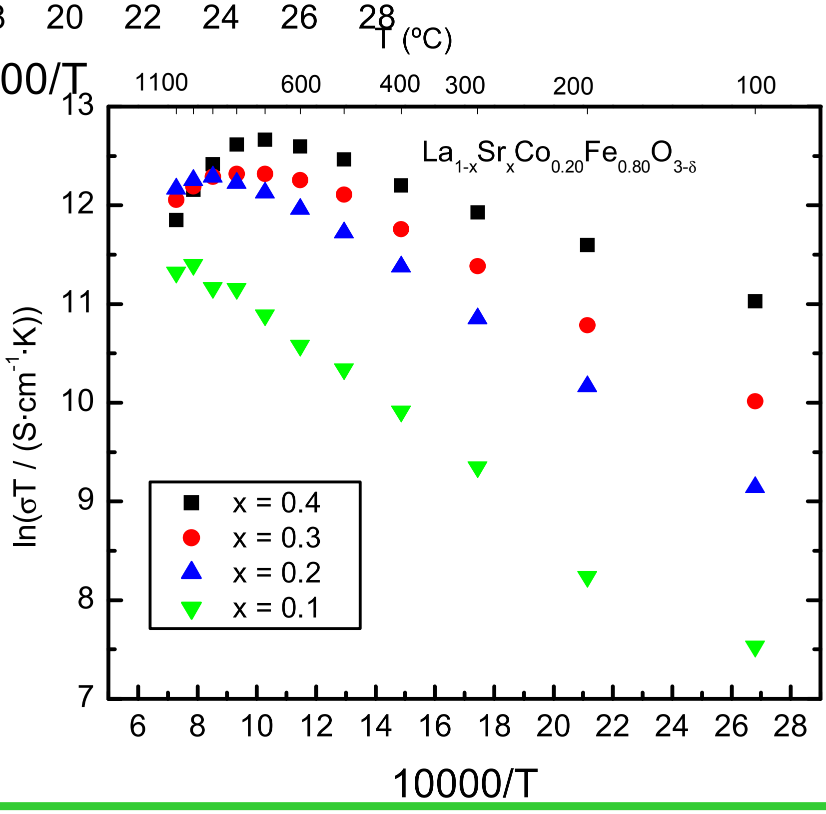
Conductivities of $La_{1-x}Sr_xCo_{0.20}Fe_{0.80}O_{3-\delta}$





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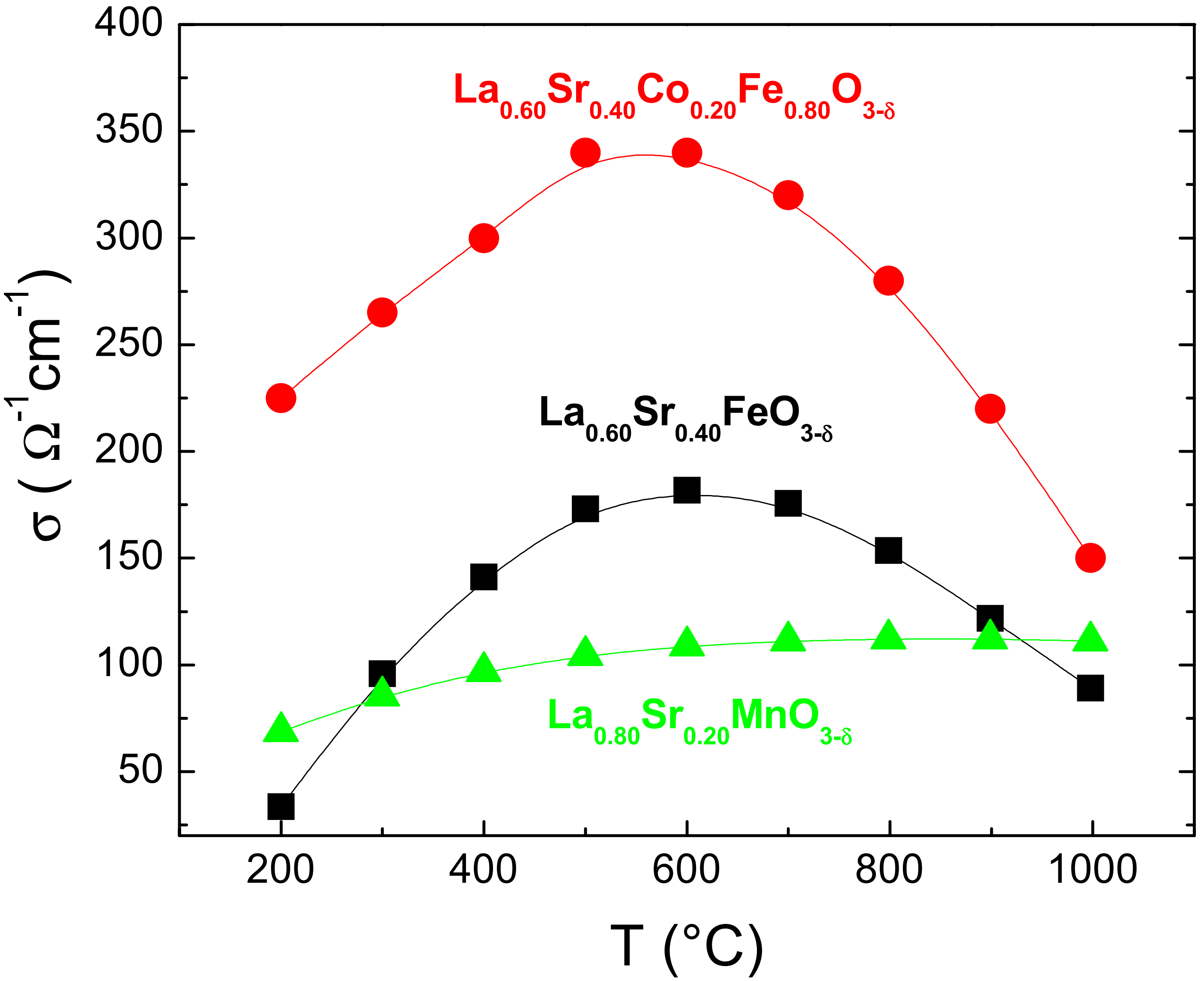
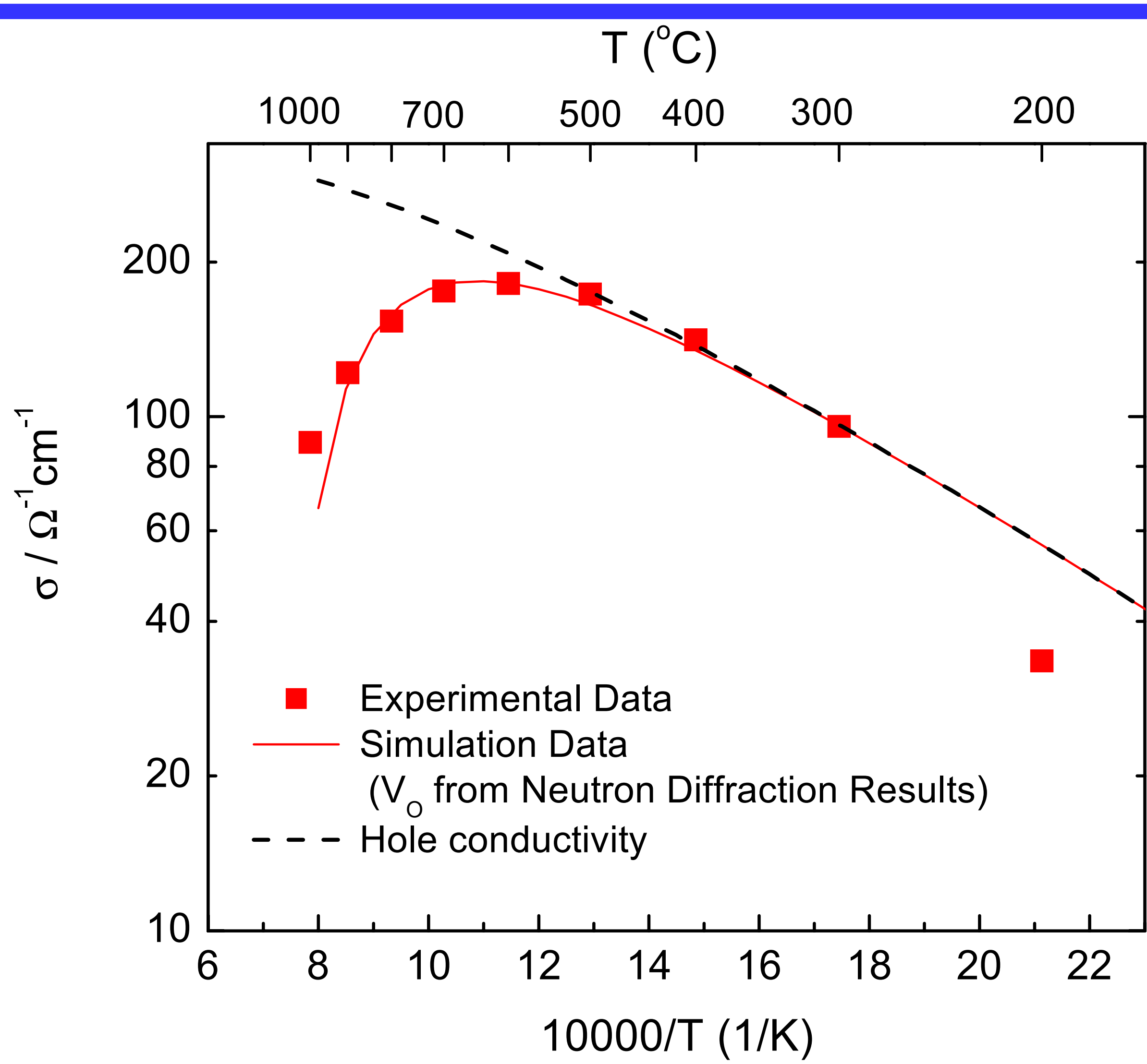
Temperature dependant of σ for LSM, LSCF and LSF



Simulation of σ for $La_{0.60}Sr_{0.40}FeO_{3-d}$ in air, ($[V_o^{oo}]$ from ND)



σ

$$= C[Sr_{La}^{'}]\mu q \text{ at } T < 500°C$$

$$= (C[Sr_{La}^{'}] - 2[V_O^{\bullet\bullet}])\mu q \text{ at } T > 600°C$$

$C \sim 0.3$

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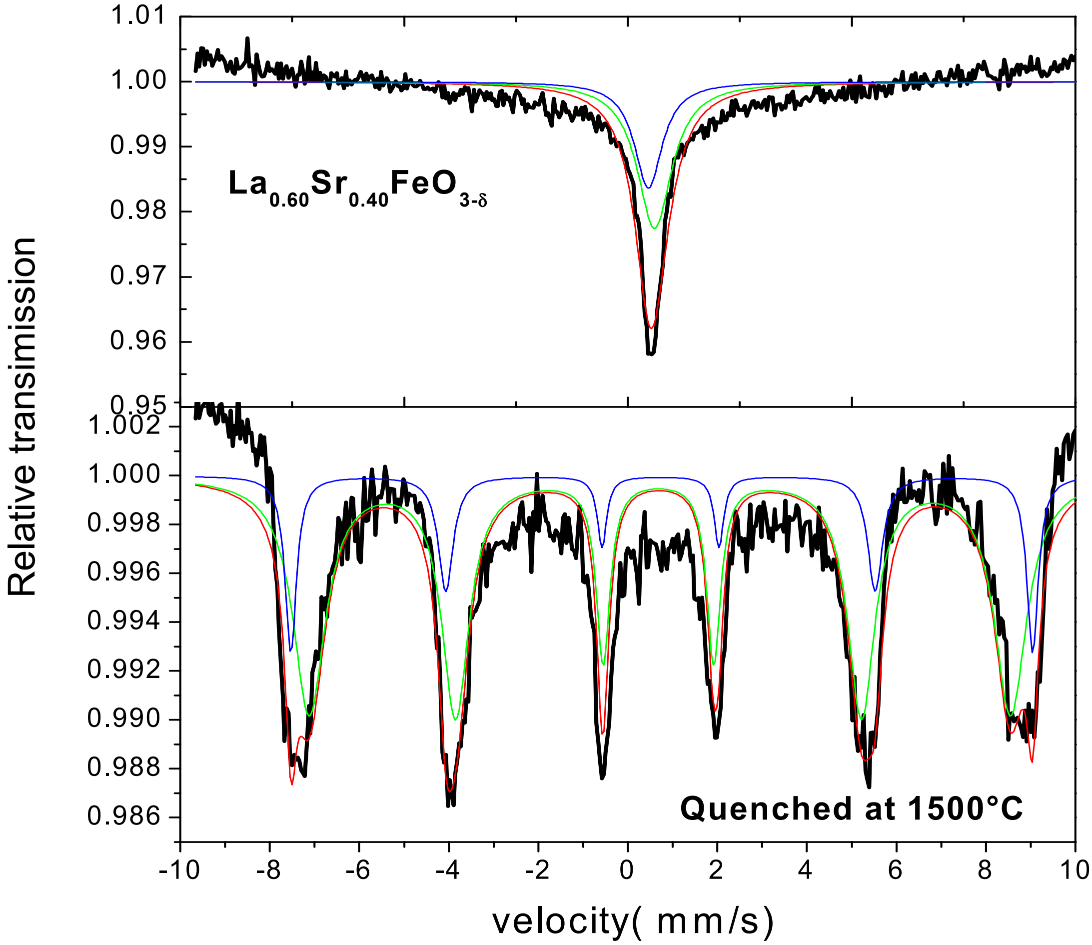
Comparison between $La_{0.80}Sr_{0.20}MnO_{3-\delta}$, $La_{0.60}Sr_{0.40}FeO_{3-\delta}$ and $La_{0.60}Sr_{0.40}F_{0.80}Co_{0.20}O_{3-\delta}$ at 500°C in Air

	LSM	LSF	LSCF
σ_p (S/cm)	104	173	340
E_h (eV)	0.095	0.17	0.087
μ_h (cm^2/v s)	0.19	0.16	0.31
$3-\delta$	3	2.997	2.95

Mössbauer Studies



Specimen without quenching

- Singlet spectrum
- Nèel temperature ~ RT
- Fe^{3+} 60%, Fe^{4+} 40%

Quenched Temp. = 1500°C

- Sextet spectrum
- Nèel temperature > RT
- Fe^{3+} two local chemical environments

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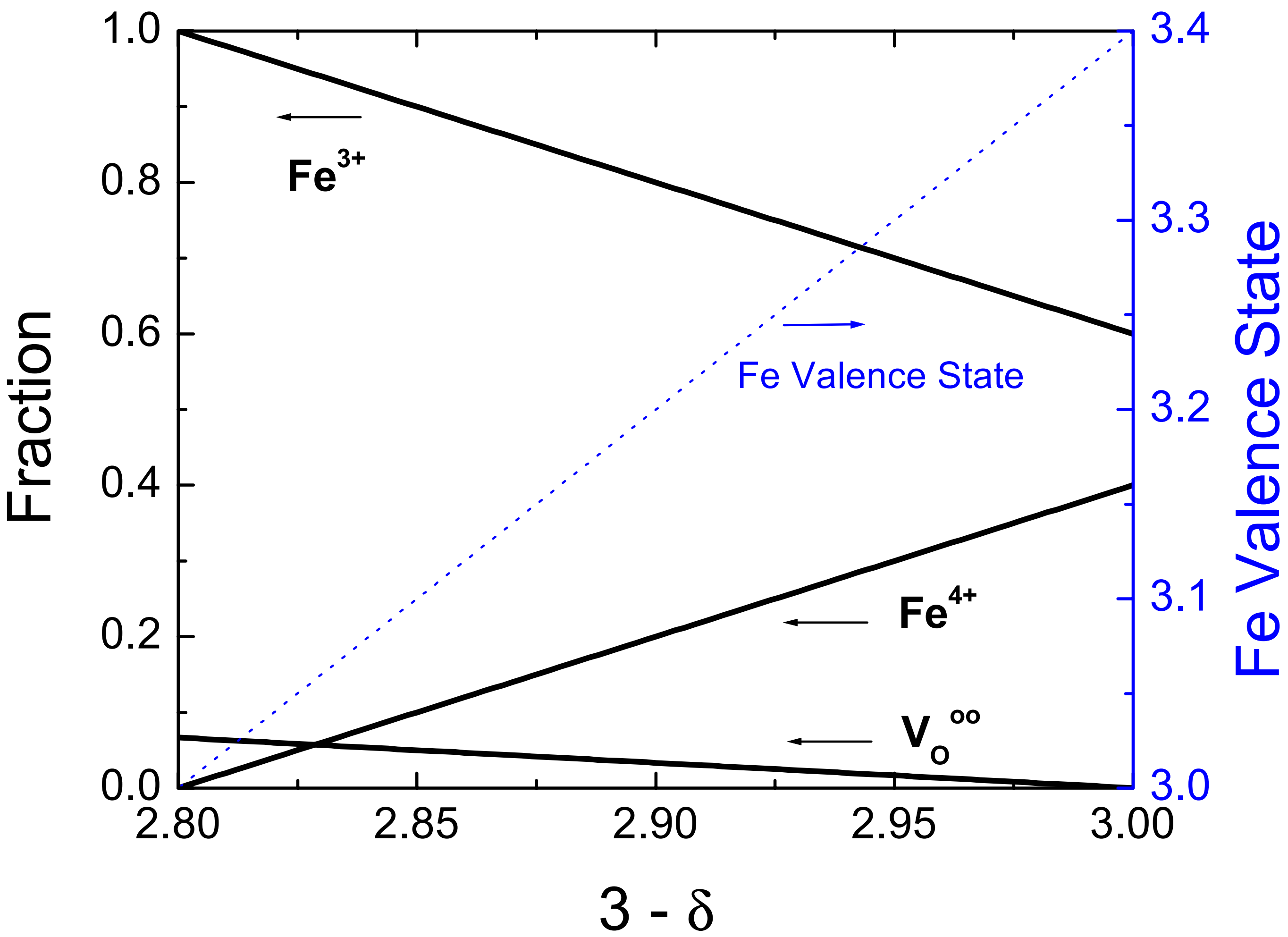
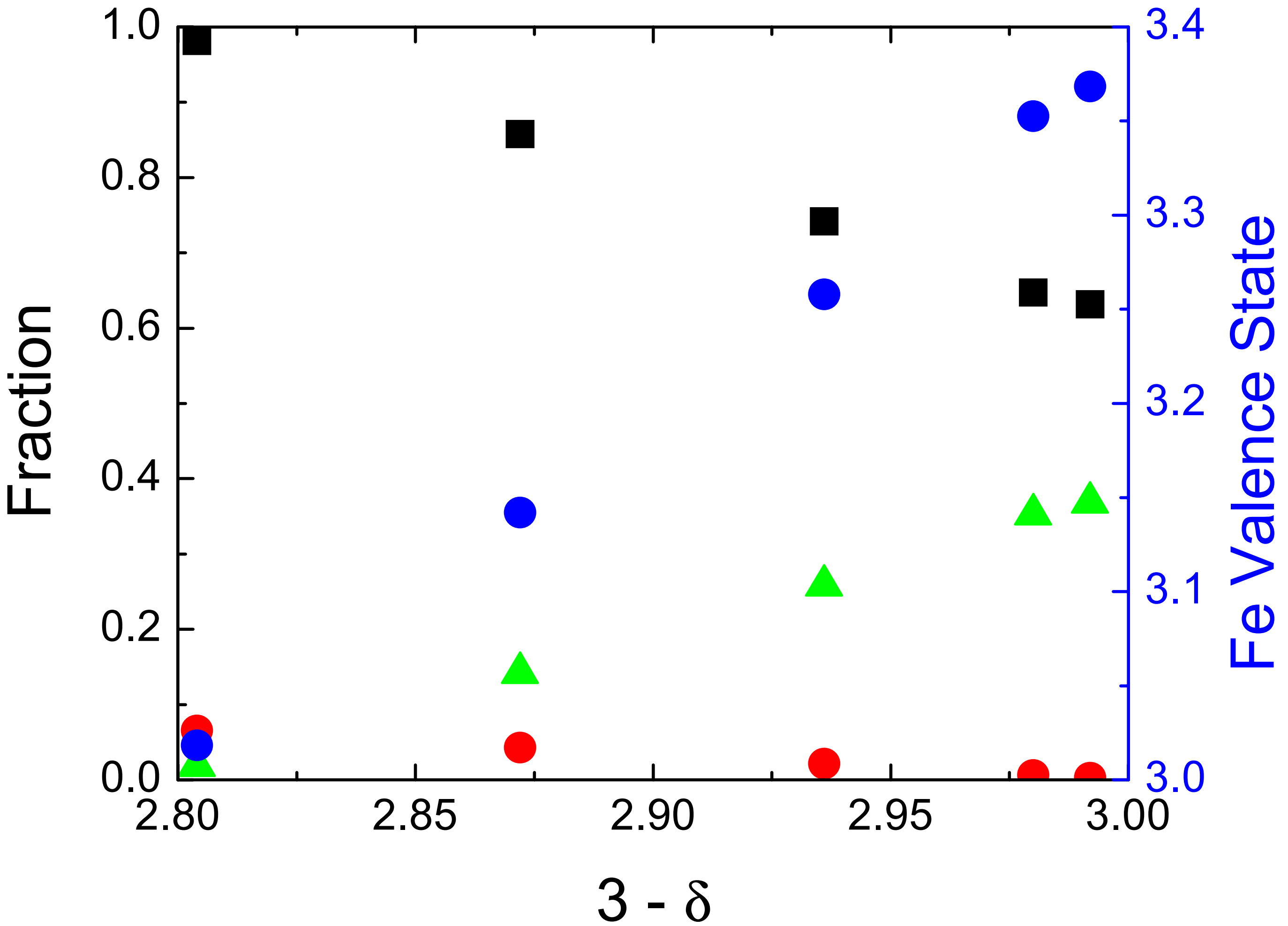
Fe valence state and $[V_o^{oo}]$ vs. 3-δ in $La_{0.60}Sr_{0.40}FeO_{3-\delta}$



Assumptions:

- Neutrality condition
- Only Fe^{3+} and Fe^{4+} exist if $\delta < 0.2$ in $La_{0.60}Sr_{0.40}FeO_{3-\delta}$

Fe valence state and $[V_o^{oo}]$ vs. 3-δ for L6SF – ND Studies



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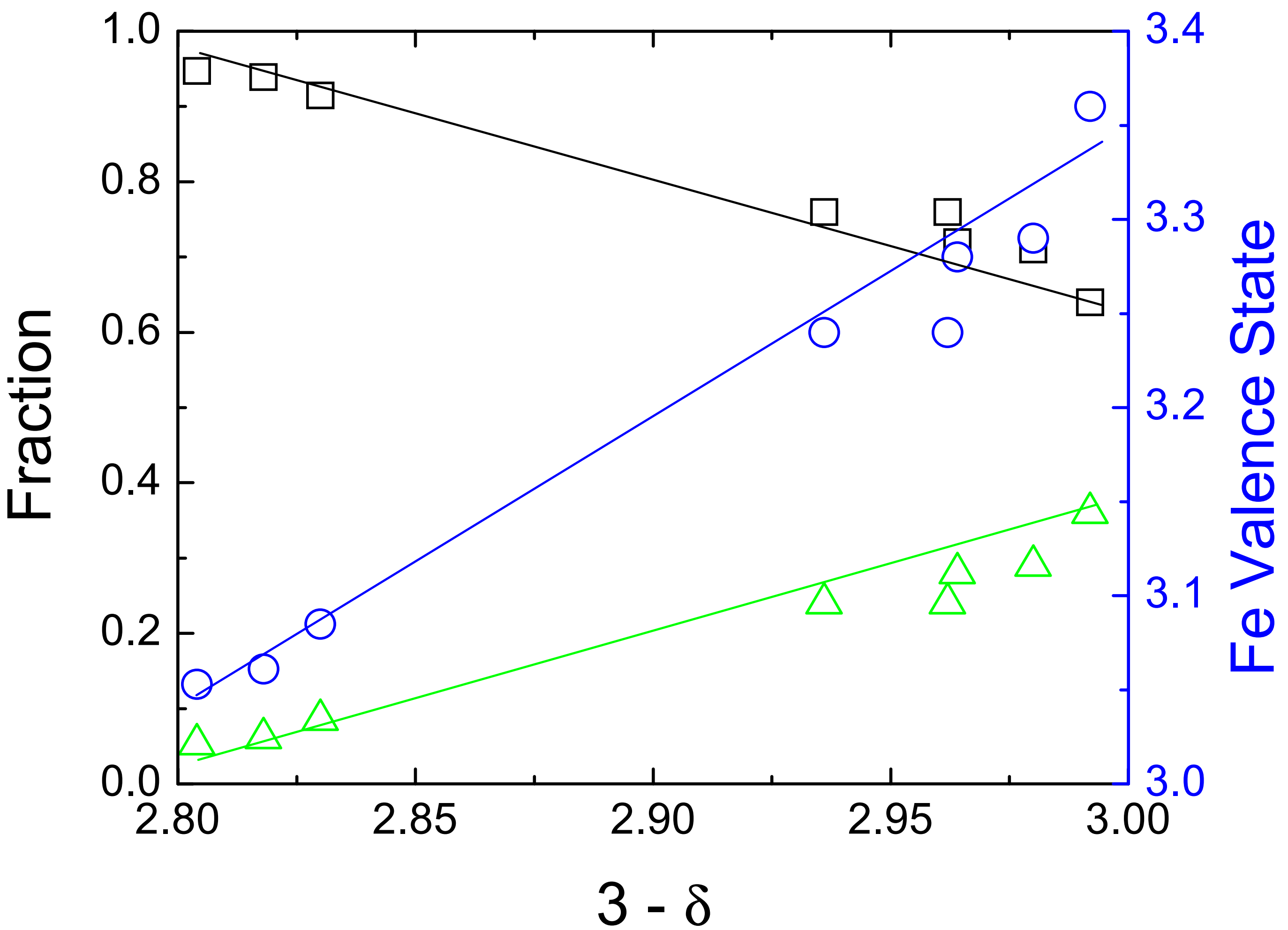
Fe valence state and [V_o^{oo}] vs. 3-δ for L6SF – Mössbauer Studies



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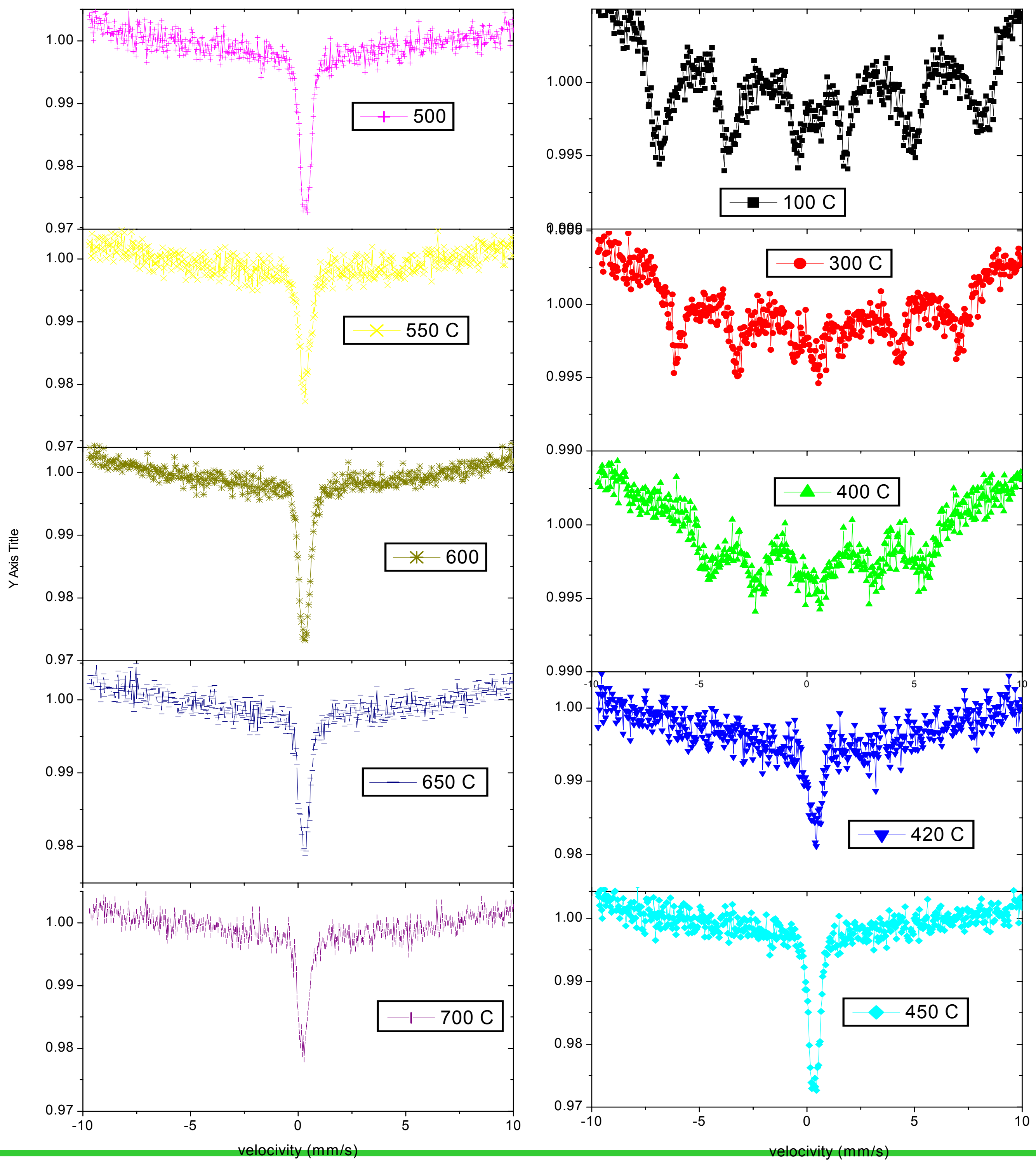
In Situ Mössbauer studies from 100°C to 700°C for L6SF quenched at 1500 °C



Importance to Goals of SECA

- **Currently there are no cathode materials which will perform satisfactorily in a SOFC at temperatures ≤ 700ºC**
- **The development of new cathodes is not trivial and requires a good understanding of both the cathode as well as the cathode/electrolyte interface**
- **The attainment of the goals of this project will yield the fundamental knowledge which aides the development of the required cathode materials**

Future Work

- **Complete current studies**
- **Perform *in situ* studies**
- **Select candidate for Cathodes**
- **Determine cathode/electrolyte over potentials of selected candidates**