Dense Membranes for Anode Supported all Perovskite IT- SOFCs

Rambabu Bobba

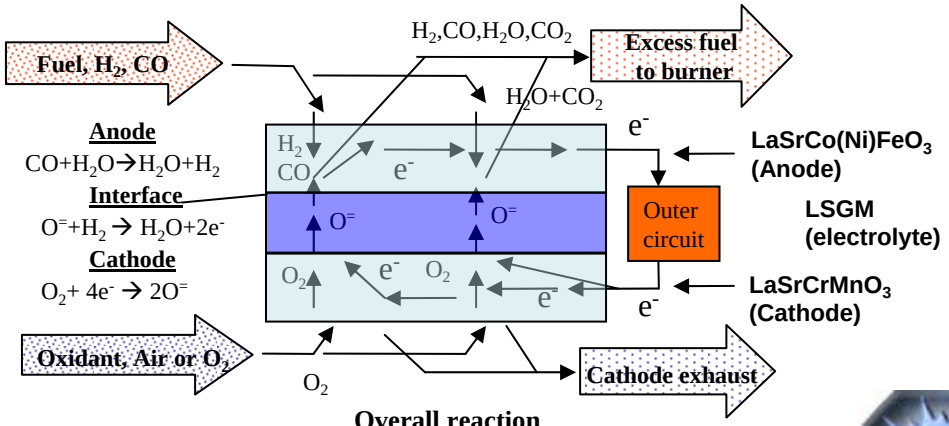
Weichang Zhao, S. Ghosh, Y. Li, Viany B. Reddy and Kourtney Jackson, S. Mitchell, Carhamma Quiett

Solid State Ionics Laboratory, Department of Physics

Southern University and A&M College, Baton Rouge, Louisiana-70813

The intent of the project is to develop inexpensive oxygen permeable, dense and high surface area membranes in the form of bulk and highly oriented thin films using soft solution chemical routes and pulsed laser deposition (PLD) techniques for fabricating natural gas fuelled anode supported all perovskite based intermediate temperature (IT)-SOFCs with planar architecture.

All Perovskite SOFC

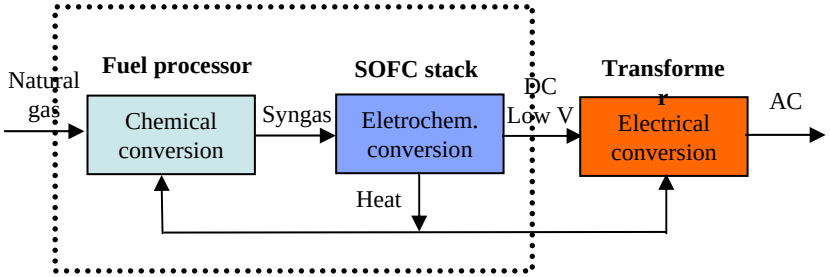


Overall reaction

$H_2+1/2\ O_2 \rightarrow H_2O$

$CO+1/2\ O_2 \rightarrow CO_2$

Natural Gas Fueled SOFC



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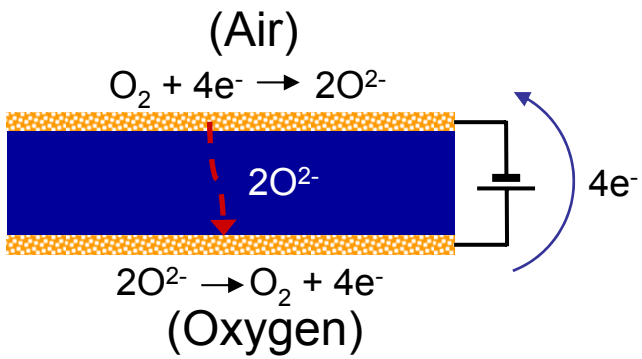
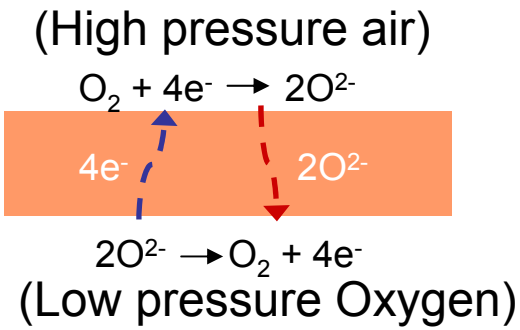
Dense Oxide Conducting Membranes

- O_2 permeable (oxide ion conductors), H_2 permeable (proton conductors)
  - Electrically driven , Mixed conducing





- Dense membranes have high conductivity than thin films (σ = 0.17 S/cm at 800°C), better mechanical strength
  - Electrolyte membranes essentially should be impervious to gases, dense membrane with improved microstructure is must, this can be achieved by adopting wet chemical methods of preparation
- Cathode is mixed (ionic + electronic) conducting, microporous

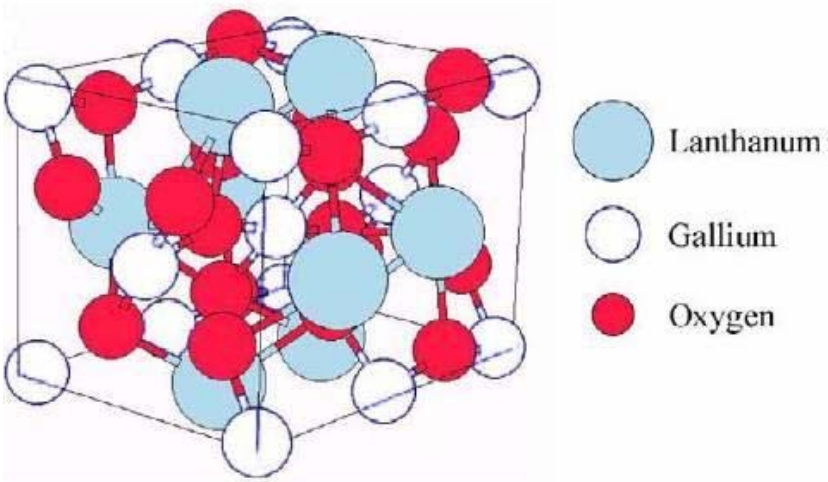
Ionically and Electronically Conducting Oxide Perovskites

•Oxide Perovskites (ABO_3)

•Versatile structure

$$t = R_A + R_O / \sqrt{2}(R_B + R_O),$$

t=tolerance factor (0.8 to 0.9)



•Properties can be tailored by substitution at A and B sites and by using suitable synthetic route

•Ionic conductor can be modified to mixed conducting ones (i.e oxide ion to mixed conducting)

Dense LSGM Electrolyte for IT-SOFCs

- **High ionic conductivity (0.12-0.17 S/cm at 800°C) over a wide range of oxygen partial pressures (1-10^{-20} atm), and the conductivity is higher by a factor of over two compared to the existing yttria doped zirconia (YSZ) (0.052 S/cm)**

- **LSGM electrolyte supported configuration, which is usually prepared by densifying the LSGM electrolyte first and then applying the anode and cathode layers afterwards**

- **Very high firing temperatures, 1450-1550°C for example, to be fully densified. There is a need to reduce the firing temperatures.**

- **Reacts with the currently used nickel-based anode during sintering, forming low conductive compounds, for example $LaNiO_3$**

- **Ga depletion; and**

- **Decreasing anode porosity**

Synthetic Routes for Preparing Perovskites

Wet chemical methods : homogeneous mixing, nanocrystalline powders, higher sinter density.

Synthesis from decomposition of complex precursors
(Tartarate, citrate, etc. gel decomposition for $LaGaO_3$, $LaMnO_3$ and doped compositions etc.)

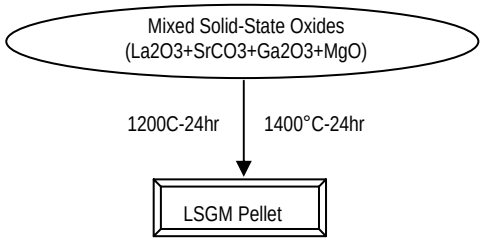
Hydrothermal process
(proton conducting perovskites, $BaZrO_3$, and doped compositions etc.)

Sonochemical assisted reactions
Conventional solid state reaction routes: longer time for product formation, poor homogeneity, microcrystalline product.

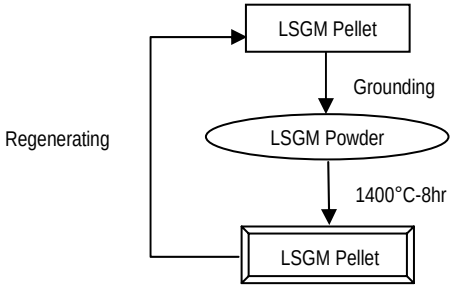
Thin film deposition: pulsed laser deposition (PLD), centrifugation method.

Regenerated Sol-Gel Route of LSGM Preparation

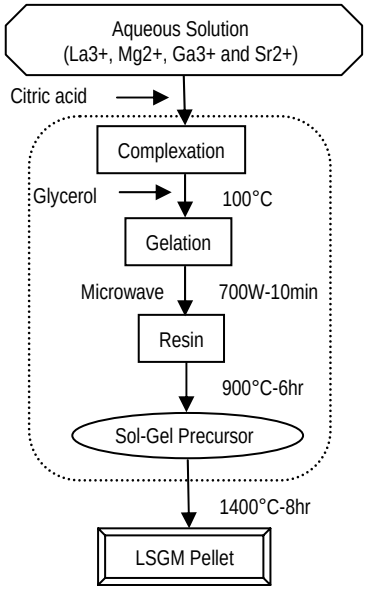
(A) Solid State Route



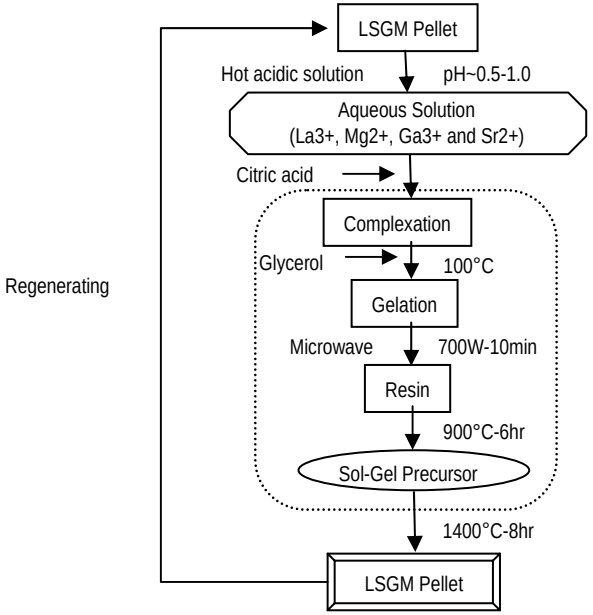
(B) Regenerated Solid-State Route



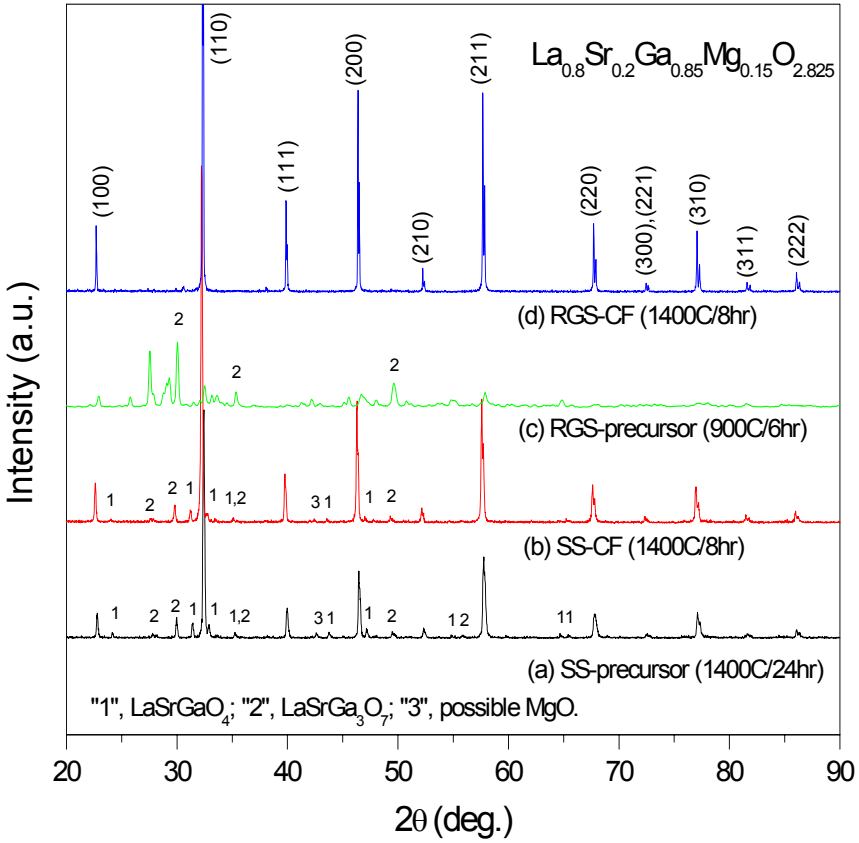
(C) Sol-Gel Route



(D) Regenerated Sol-Gel Route



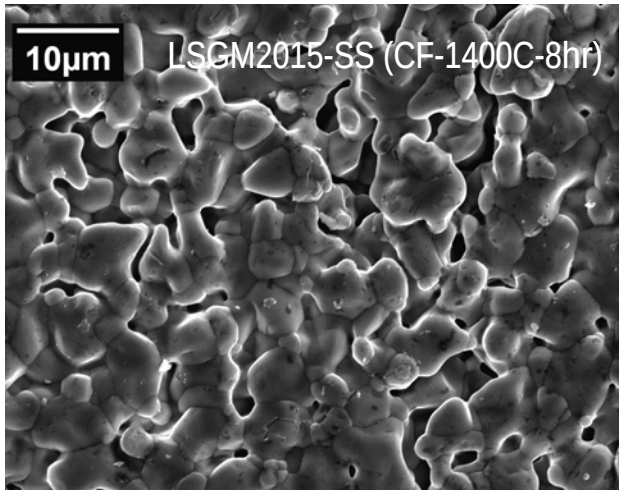
XRD of $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ Prepared in Different Routes

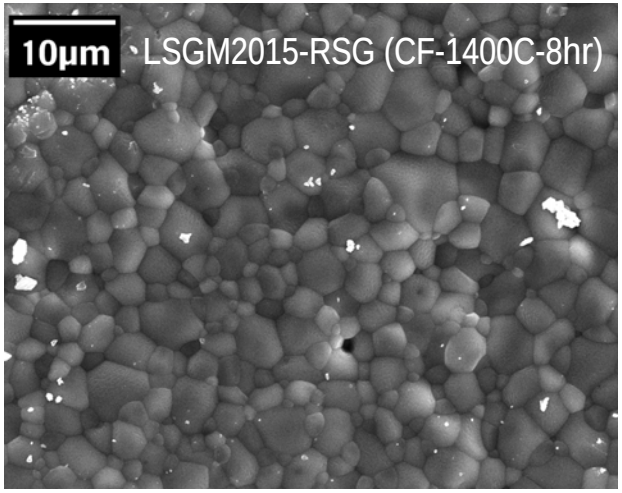


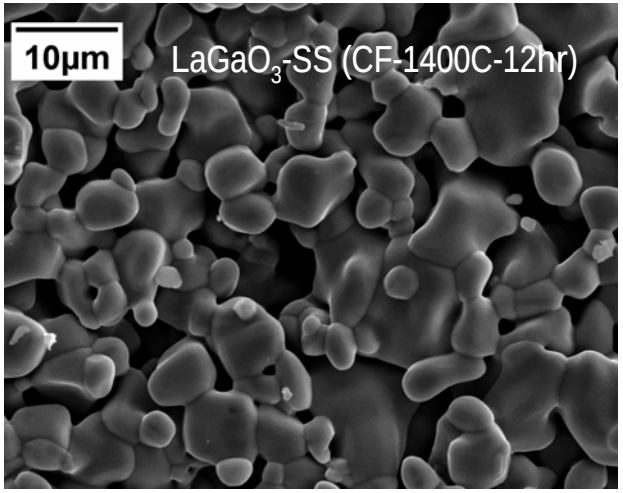
Sample	Preparation	Color	Pellet Density (g/cc)
SS-precursor	SM* heated at 1200˚C-24h, ground and heated again at 1400˚C-24h	white	4.9
SS-CF	CP1 was ground, pelletized and conventionally heated in air at 1400˚C-8h	creamish	5.25
RSG-precursor	An aqueous solution obtained by recycling of CP1 was gelled by pechini-type sol-gel process and charred in air at 900˚C-6h	white	5.10
RSG-MW1	SP1 was ground, pelletized and microwave heated in air at 1200˚C-30min	creamish	5.80
RSG-MW2	SP2 was again microwave heated in air at 1200˚C-30min	creamish	5.85
RSG-CF	SP1 was ground, pelletized and conventionally heated in air at 1400˚C-8h	brown	6.46

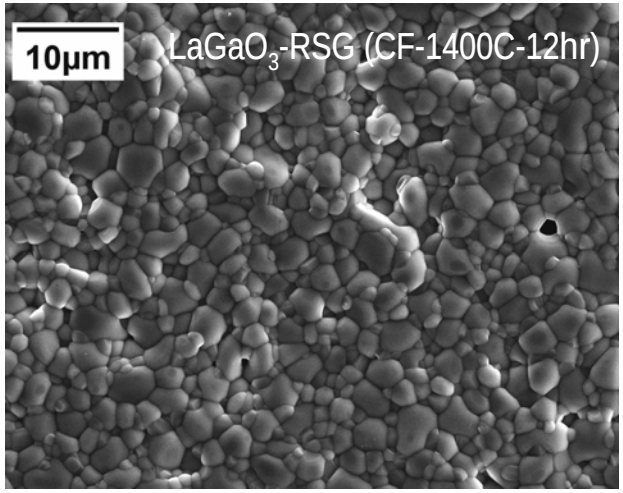
The regenerated sol-gel (RSG) route leads to pure phase LSGM at sintering temperature 1400°C, while the solid-state (SS) route not.

SEM of Doped and Un-Doped Lanthanum Gallate Pellets



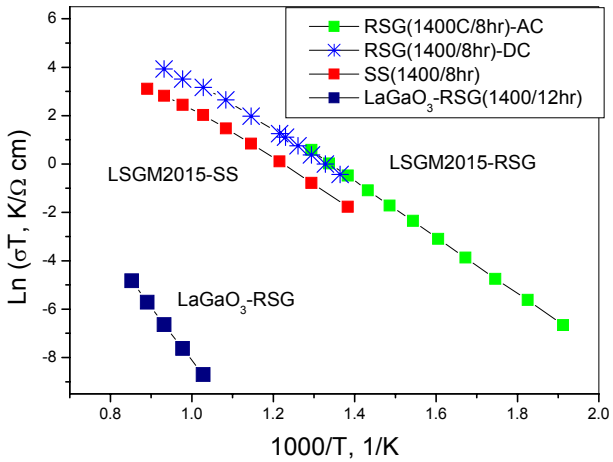


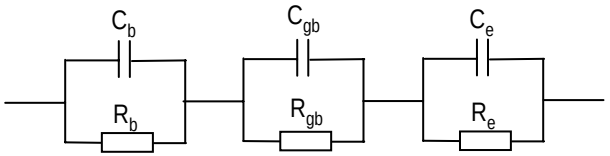




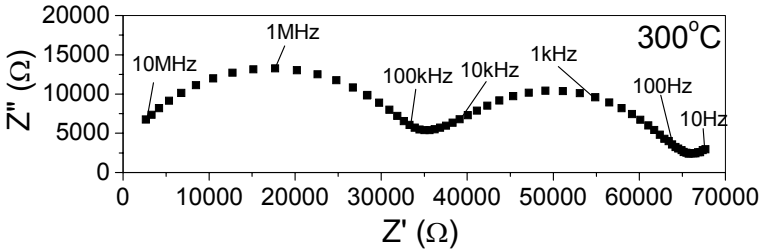
Electrochemical Impedance Spectroscopy (EIS) of Doped and Un-Doped LSGM

Conductivities of different LSGM

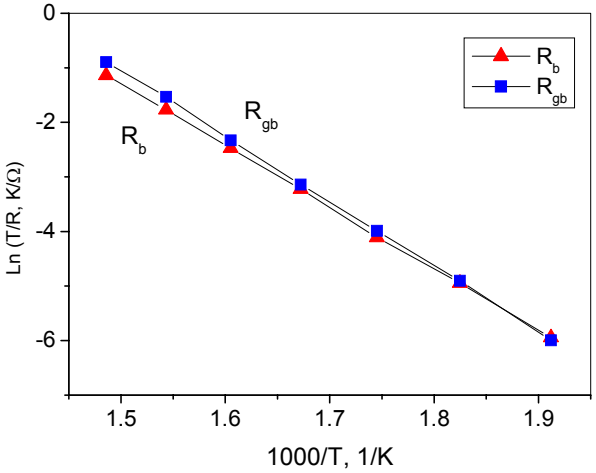




"b": bulk; "gb": grain boundary; "e": electrode.



Bulk and Grain-Boundary Resistances of LSGM2015-RSG



Arrhenius Relation:

$R = (A/T)\,\mathrm{Exp}(-E/k_B T)$,

where

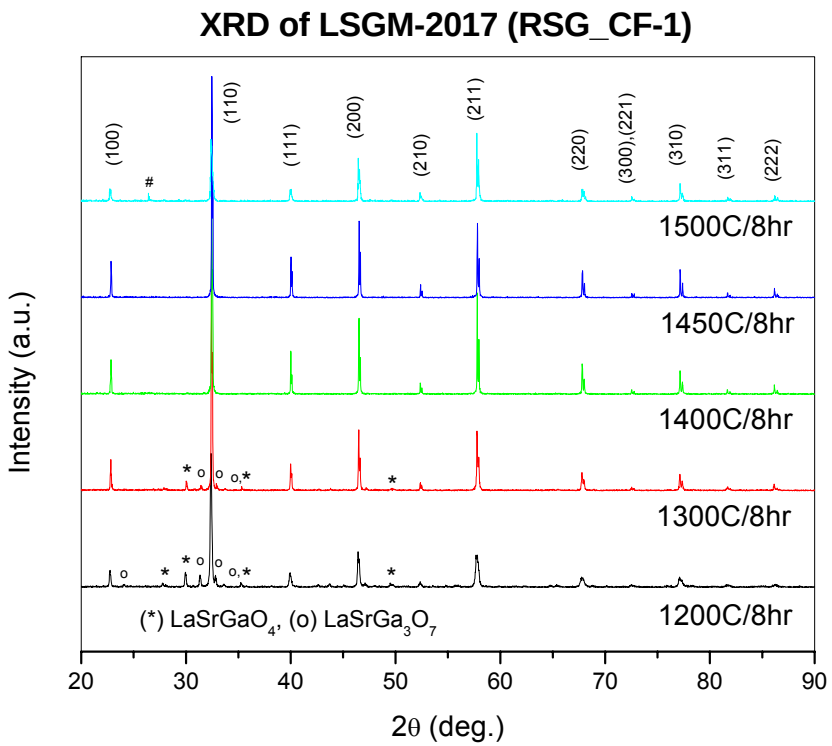
$E = 1.01$ eV ,

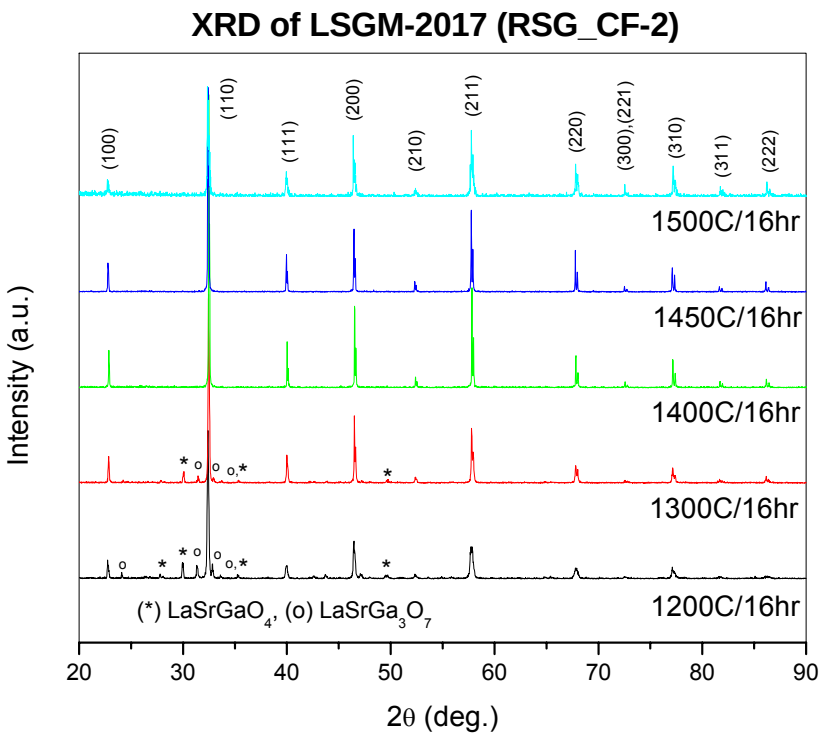
$E_b = 0.97$ eV ,

$E_{gb} = 1.03$ eV

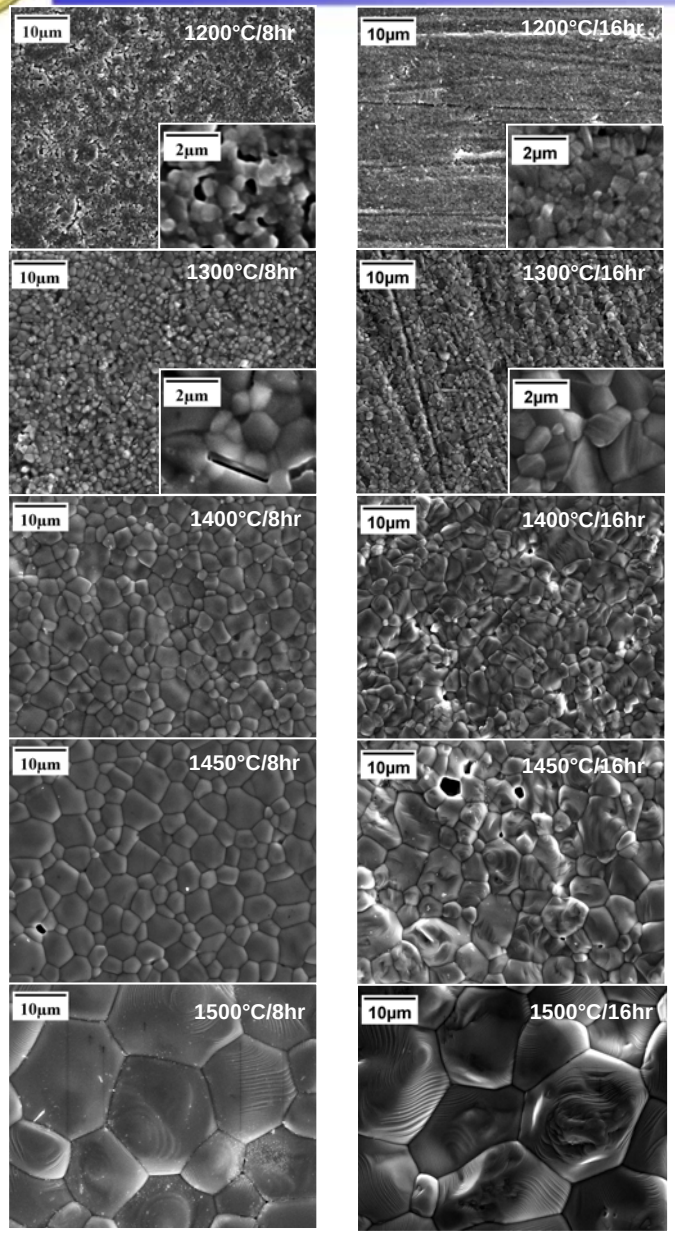
for LSGM2015-RSG.

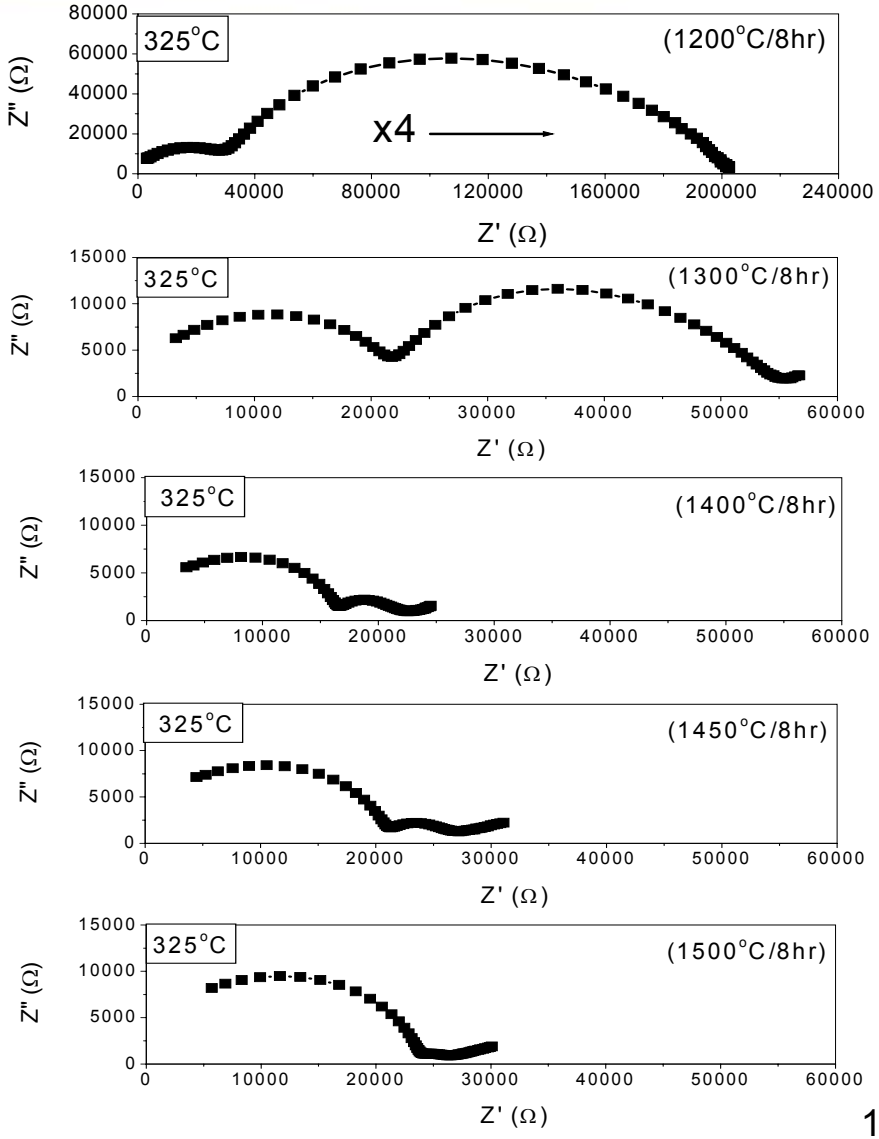
Effects of Sintering Temperature and Duration on Grain Size and Conductivity of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ (LSGM-2017)



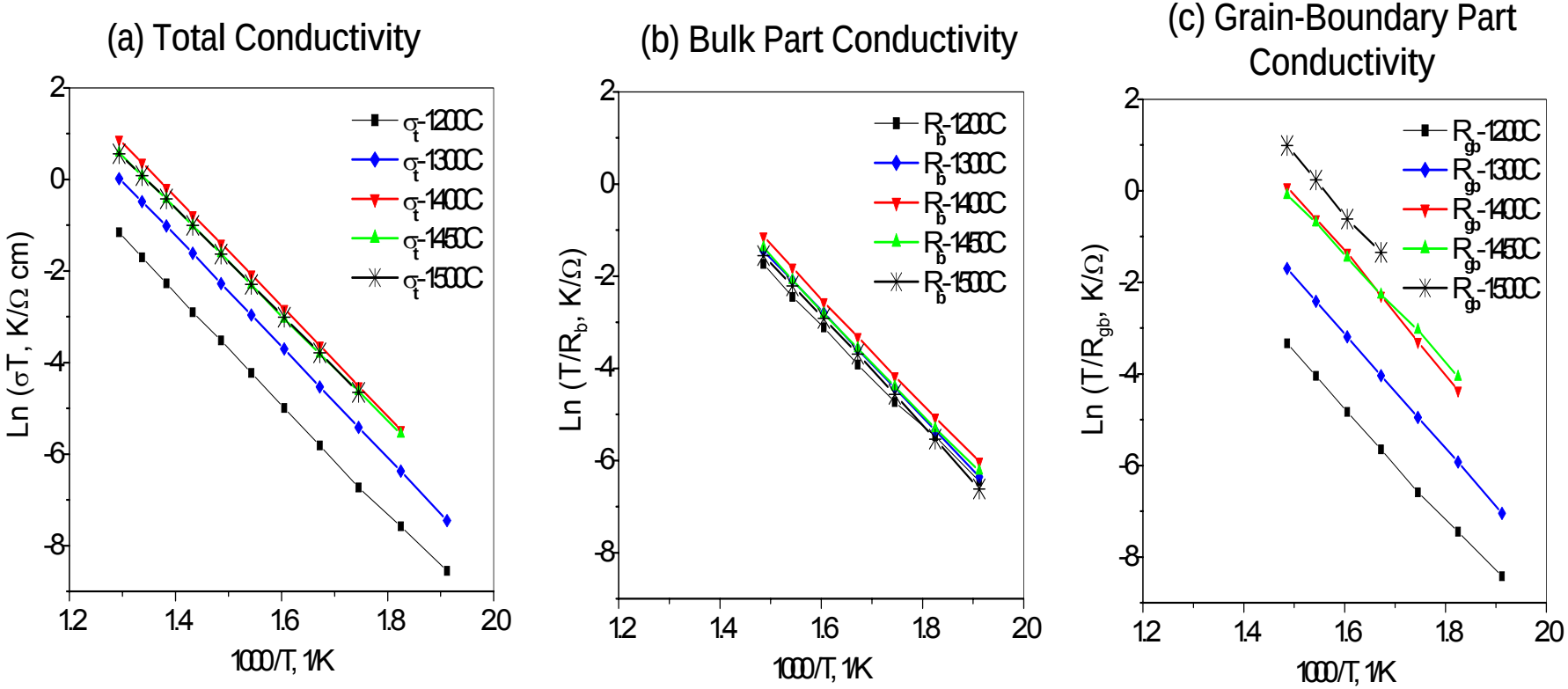


SEM and EIS of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$





Arrhenius Relation of $La_{0.8S}r_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ Deduced by EIS

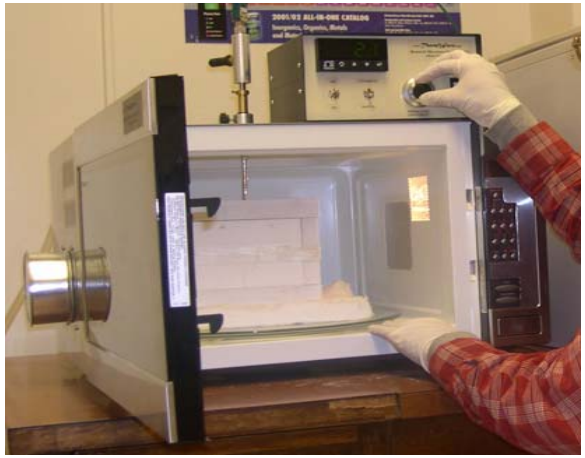


- The pellets sintered at 1400-1500°C got similar high conductivities, the one at 1400°C got the highest, ref. (a).
- All the pellets got similar bulk resistance, ref. (b).
- The lower temperature lead to higher grain-boundary resistance because of smaller grain sizes, ref. (c) 1200-1300°C.

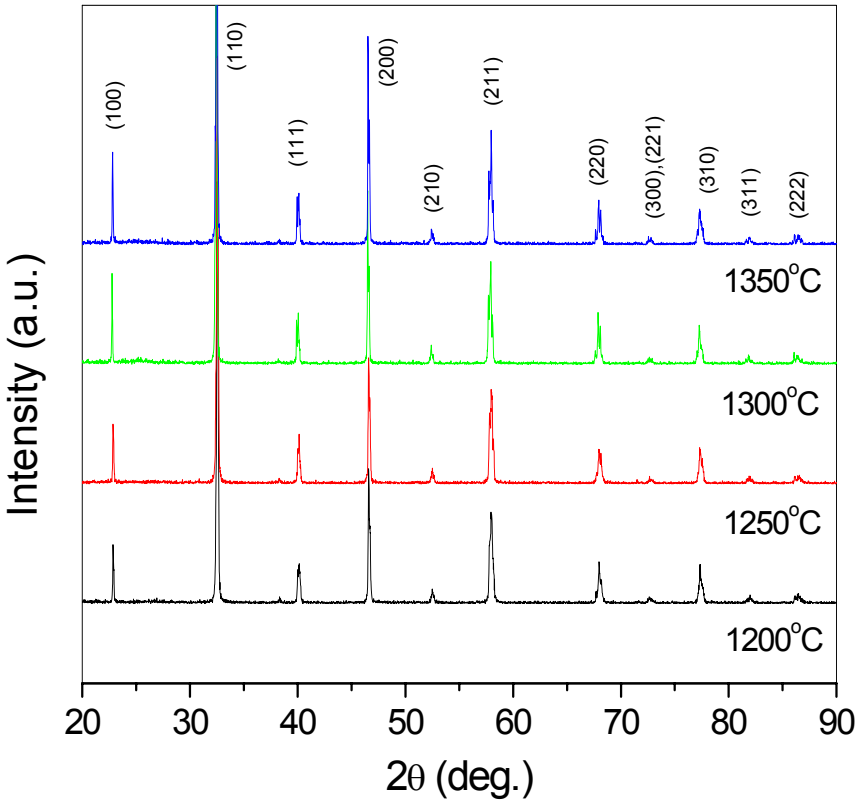
Microwave Sintering of $La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{2.9}$

Microwave Instrument

(Panasonic-2.45GHz-1200W and Research Microwave Systems-ThermWave Mod.III Controler)

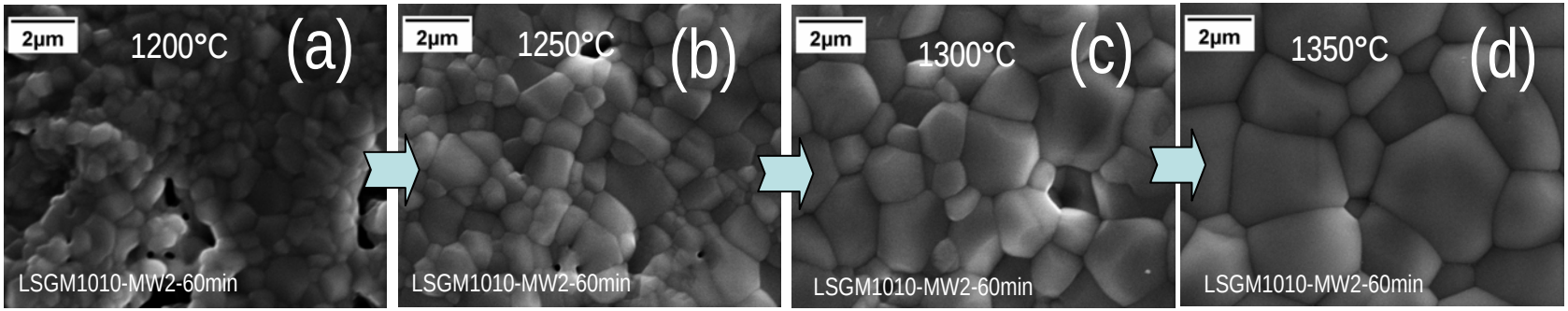


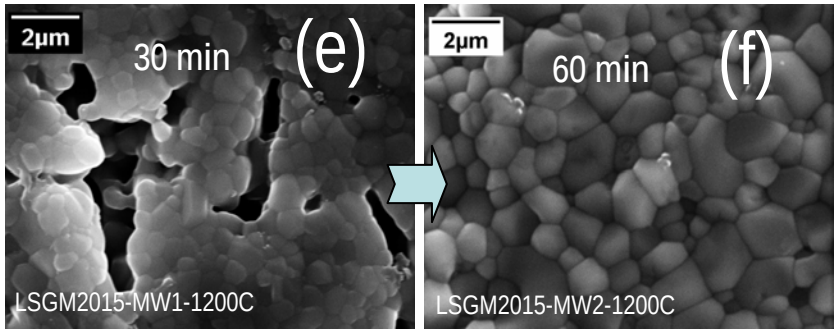
XRD of LSGM1010 (Microwave-60min)

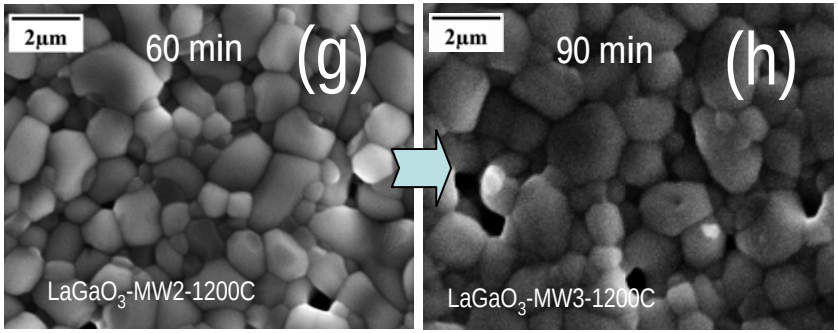


Pure phase! --------The microwave method achieves pure-phase LSGM even at the firing temperature as low as 1200°C.

SEM of Microwave Sintered $La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{2.9}$ (LSGM-1010)

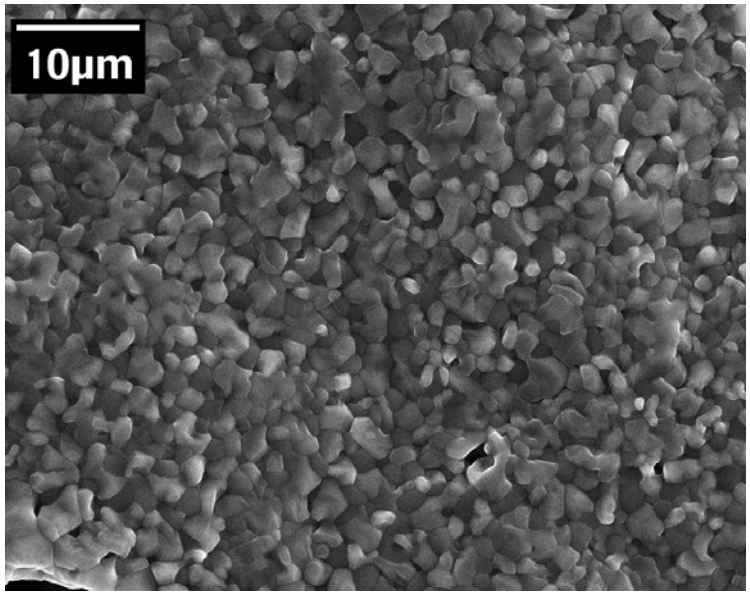




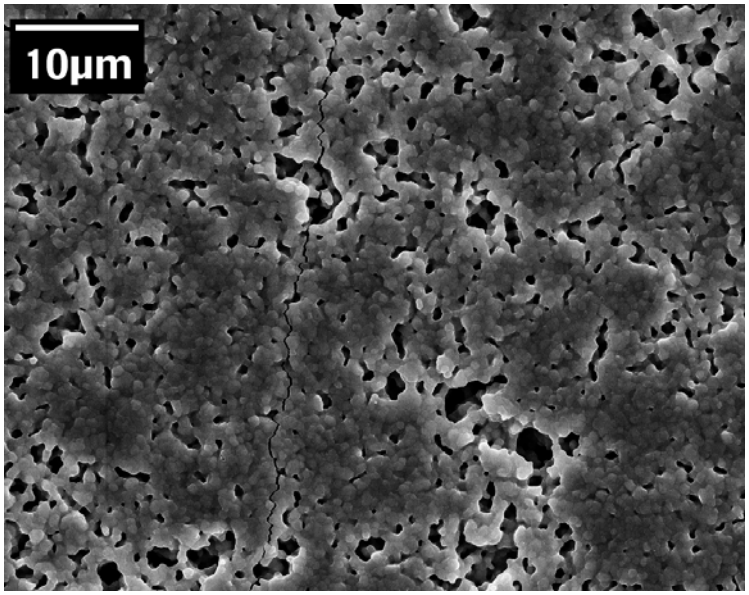


- The LSGM grain size is more sensitive to the microwave sintering temperature than the sintering duration, similar to the case of conventional furnace method.
- The microwave method obtains the same dense LSGM with different doping rate in much shorter sintering time (~1hr).

Deposition of Thin Films of $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ on Alumina Substrates Using Centrifugation Technique

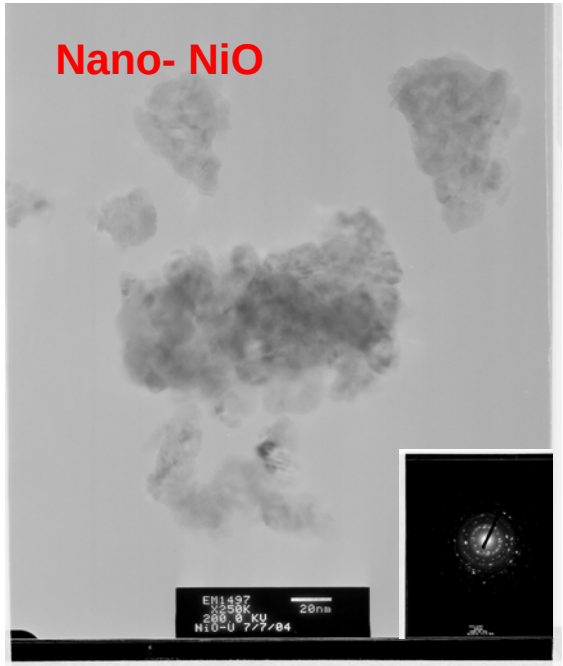


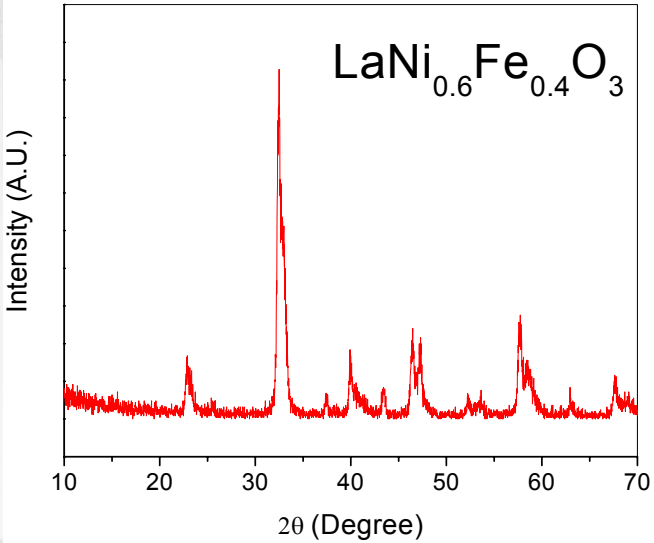
SEM micrographs of conventionally sintered LSGM film on alumina substrate

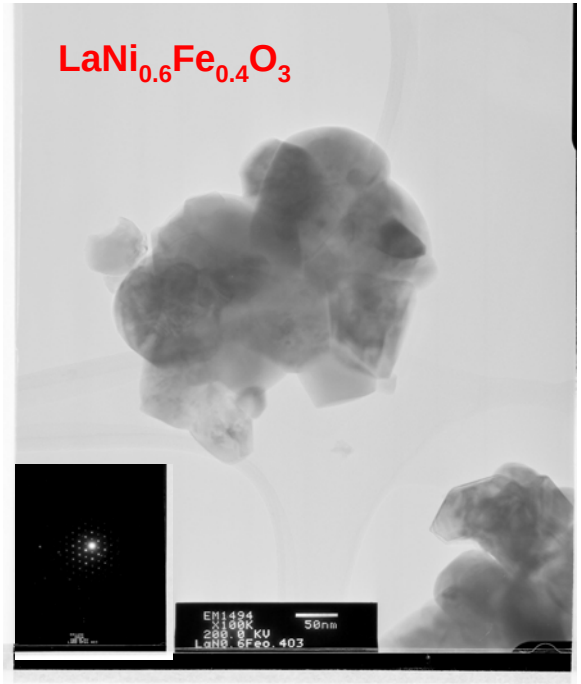


SEM micrographs of microwave sintered LSGM films on alumina substrate

Nanocrystalline NiO, and Porus $LaNi_{0.6}Fe_{0.4}O_3$ Anodes Synthesized Using Dimethyl Urea (DMU)

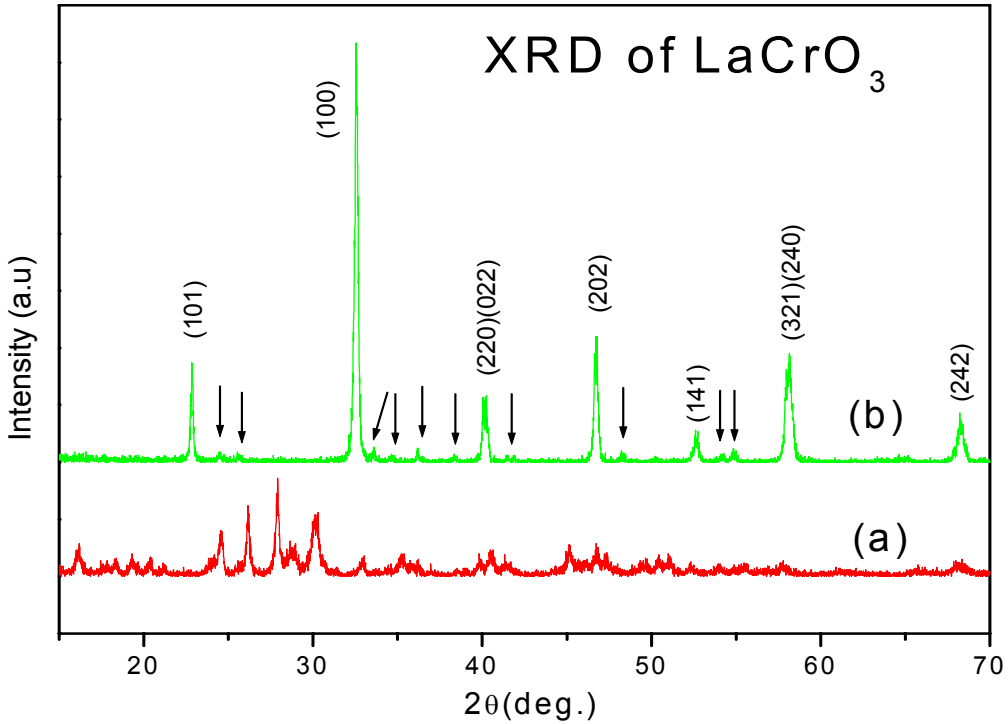






$LaCrO_3$ as an Interconnect Material

For efficient performance of $LaCrO_3$ interconnector, it's sintered density should be close to its theoretical density (≥ 96% TD) or the porosity should be negligible to avoid inter-diffusion of H_2 and O_2. High sintered density is usually achieved by high temperature treatment (≥ 1200 °C) for prolonged duration.

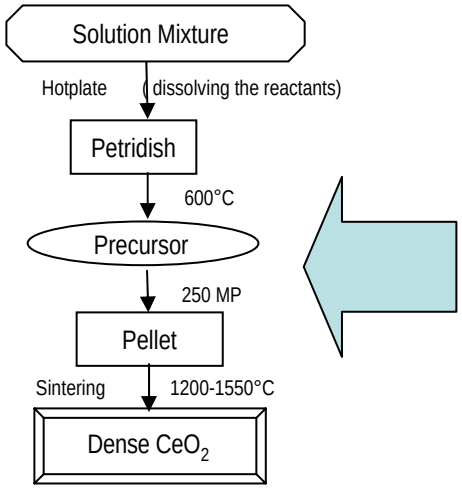


(a) before and (b) after microwave heating using graphite as microwave susceptors

Gadolinia Doped Ceria (GDC)

- In our effort to produce sintered targets for pulsed laser ablation, a series of doped ceria pellets were studied.
- Gadolinia doped cerium oxide with varying contents of 5, 10, 15 mole% of Gd_2O_3 were prepared by solid-state reaction from high purity powders of Gd_2O_3 and CeO_2. The mixed powders were pressed into pellets uniaxially at 4 tons of pressure and the pellets were sintered at 1550°C for 6 h with a heating and cooling rate of about 10oC/min. The sintered pellets were found to have density in the range 85-92%. X-ray diffraction indicated that the pellets were single phasic and the lattice parameters were found to increase with increasing doping concentration from 0.5407 nm to 0. 5419 nm. AC impedance spectroscopy was used to calculate the ionic conductivities of these pellets in the temperature range 400-800°C and the 10 mole% of Gd_2O_3 doped CeO_2 was found to have the best conductivity of 0.49 S/cm at 1073 K
- Prepared fine polycrystalline ceria powders at temperature of 200°C by hydrothermal treatment of microwave precipitated precursor from aqueous solution of $(NH_4)_2Ce(NO_3)_6$ and urea.

Synthesis Route of Ceria by Solution Combustion Technique



A. Mixture of cerric ammonium nitrate (CAN) and maleic acid:

$$(NH_4)_2Ce(NO_3)_6 + 2(HOOC\text{-}CH{=}CH\text{-}COOH) \rightarrow \underline{CeO_2} + 4N_2 + 8CO_2 + 8H_2O$$

B. Mixture of cerrium nitrate and maleic acid:

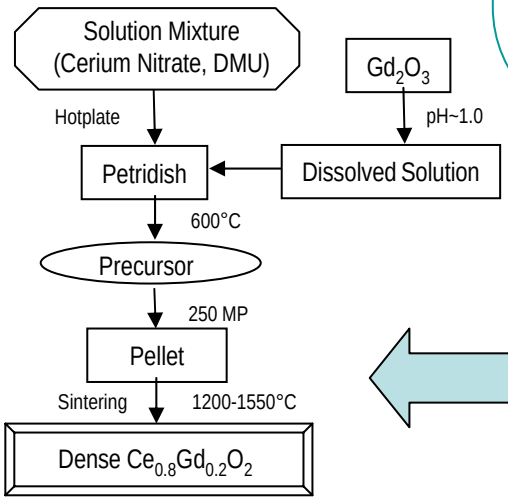
$$4Ce(NO_3)_3 + 5(HOOC\text{-}CH{=}CH\text{-}COOH) + O_2 \rightarrow 4\underline{CeO_2} + 6N_2 + 20CO_2 + 10H_2O$$

C. Mixture of cerric ammonium nitrate (CAN) and 1,3-dimethylurea (DMU) :

$$3(NH_4)_2Ce(NO_3)_6 + 4(H_3C\text{-}NH\text{-}CO\text{-}NH\text{-}CH_3) \rightarrow 3\underline{CeO_2} + 4N_2 + 12CO_2 + 28H_2O$$

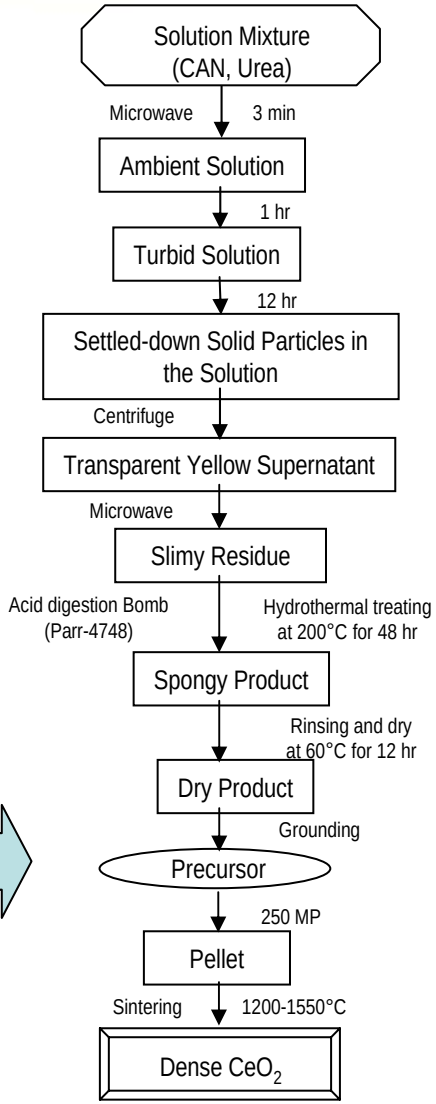
D. Mixture of cerium nitrate and 1,3-dimethylurea (DMU) :

$$6Ce(NO_3)_3 + 5(H_3C\text{-}NH\text{-}CO\text{-}NH\text{-}CH_3) + 3/2O_2 \rightarrow 6\underline{CeO_2} + 14N_2 + 15CO_2 + 20H_2O$$

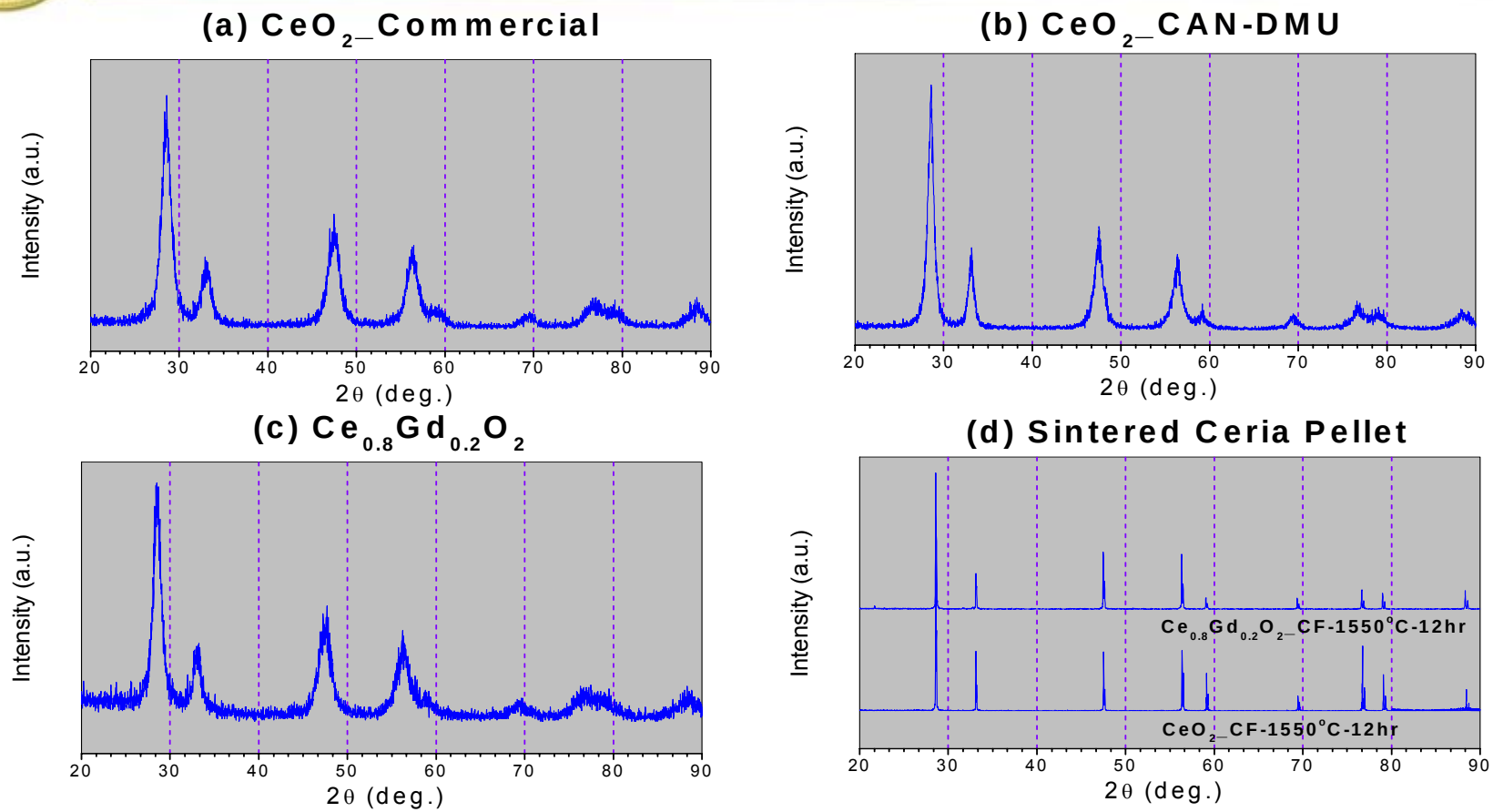


E. Hydrothermal synthesis: mixture of cerric ammonium nitrate (CAN) and urea :

F. Mixture of cerium nitrate, 1,3-dimethylurea (DMU) and Gd_2O_3:



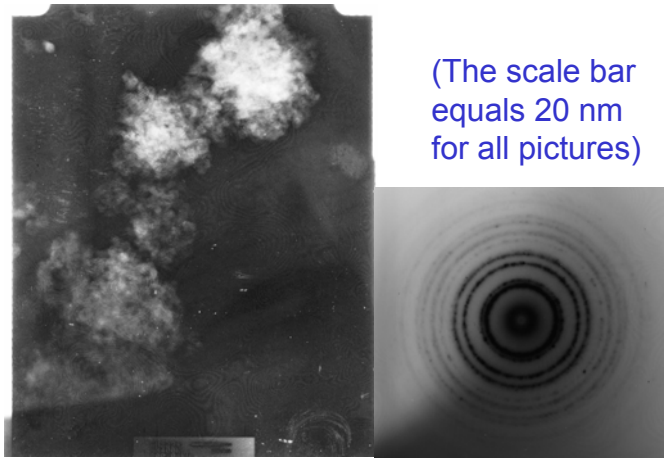
XRD of Nano-CeO_2 and $Ce_{0.8}Gd_{0.2}O_2$



- Pure phase Gd-doped and pure ceria were obtained by solution combustion technique.
- The widened XRD peaks indicate the obtained ceria precursors in (b) and (c) have similar nano-grain sizes as the commercial nano-ceria in (a).
- The nano-ceria in (b) and (c) form pure phase ceria pellet after sintering, ref. (d).

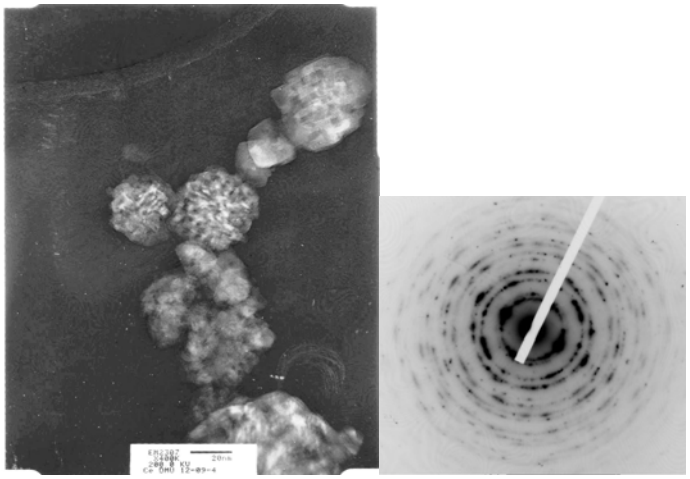
TEM of CeO_2 and $Ce_{0.8}Gd_{0.2}O_2$ Precursor Nano- Powders

CeO_2_Commercial

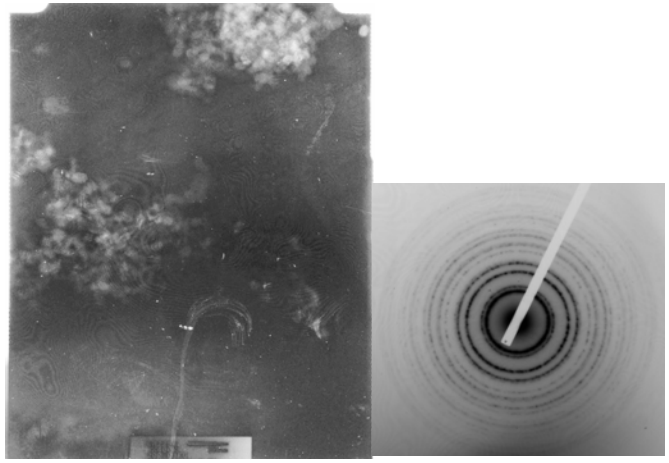


(The scale bar equals 20 nm for all pictures)

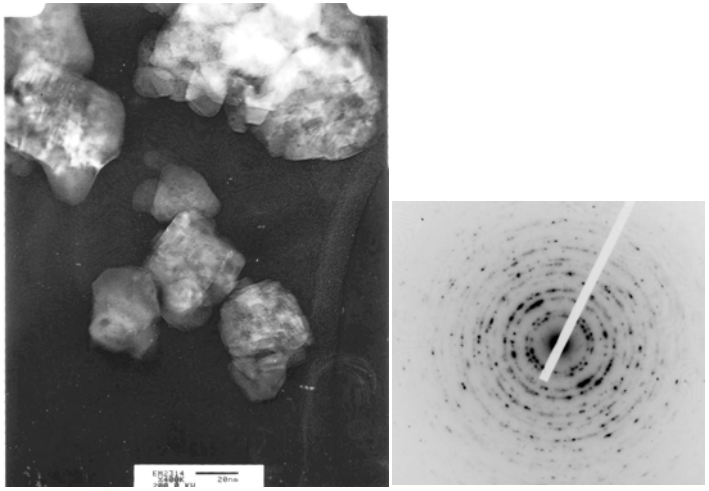
CeO_2_ Cerium nitrate and DMU



CeO_2_ Microwave and hydrothermal synthesis

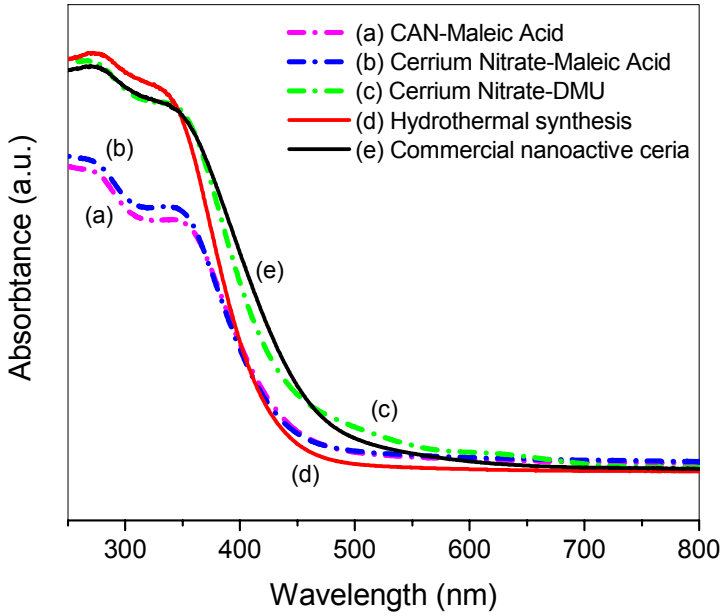


$Ce_{0.8}Gd_{0.2}O_2$

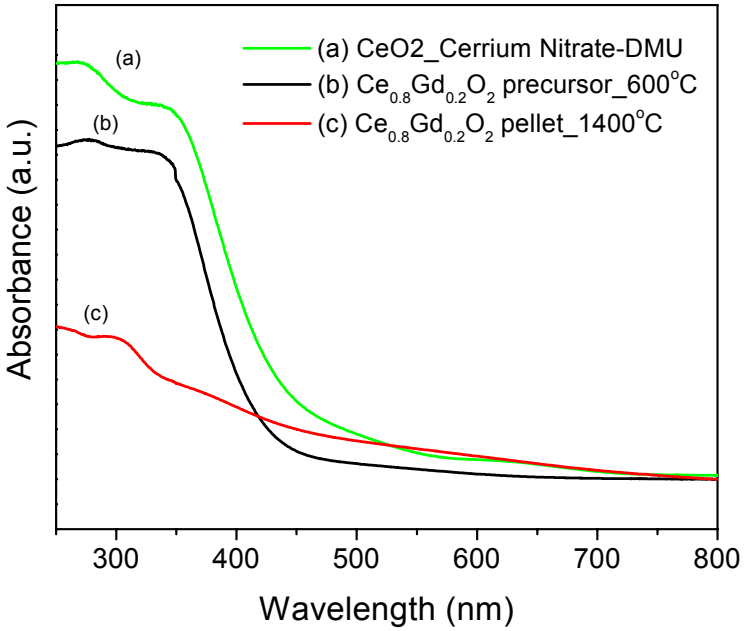


Diffuse Reflectance Spectra (DRS) of ***Nano-CeO_2 and $Ce_{0.8}Gd_{0.2}O_2$***

(A) DRS of CeO_2 Precursors (powder)

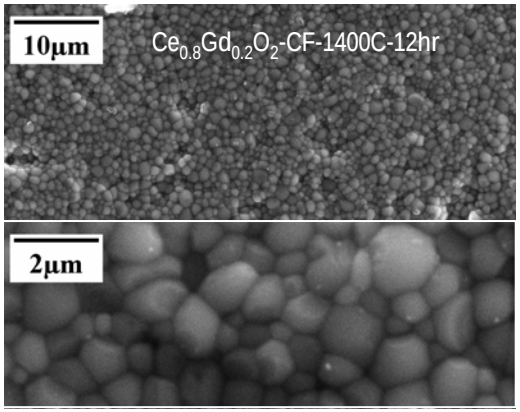


(B) DRS of $Ce_{0.8}Gd_{0.2}O_2$



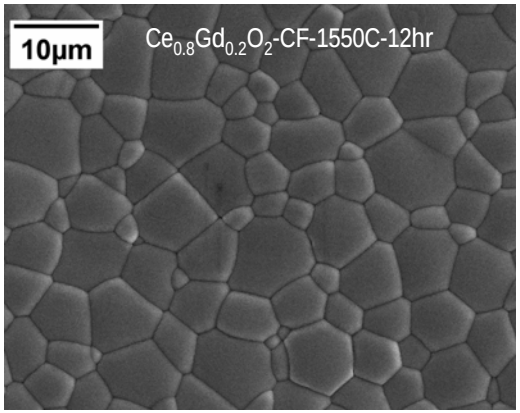
The ceria obtained by the hydrothermal synthesis route (Fig. A-(d)) is more blue shifted compared to the commercial nano-ceria (Fig. A-(e)), which suggests smaller nano-grain size than the commercial nano-ceria.

SEM of CeO_2 and $Ce_{0.8}Gd_{0.2}O_2$ Pellets



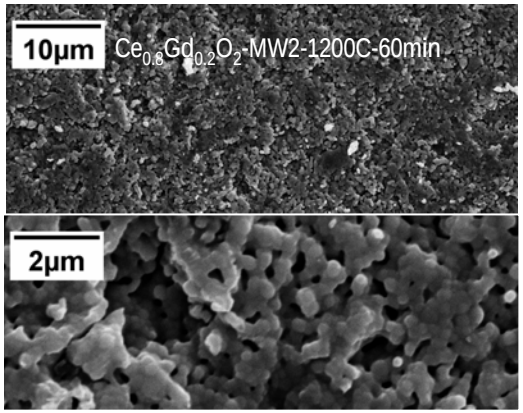
Higher Firing-T

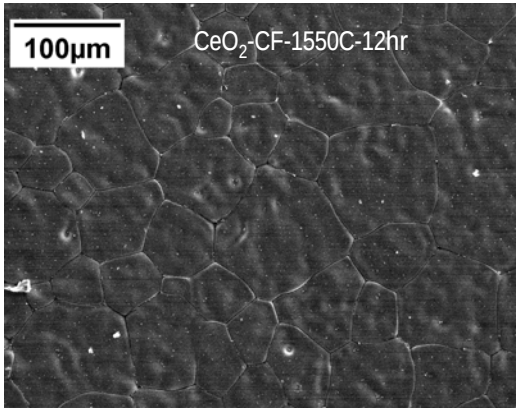
Higher Density



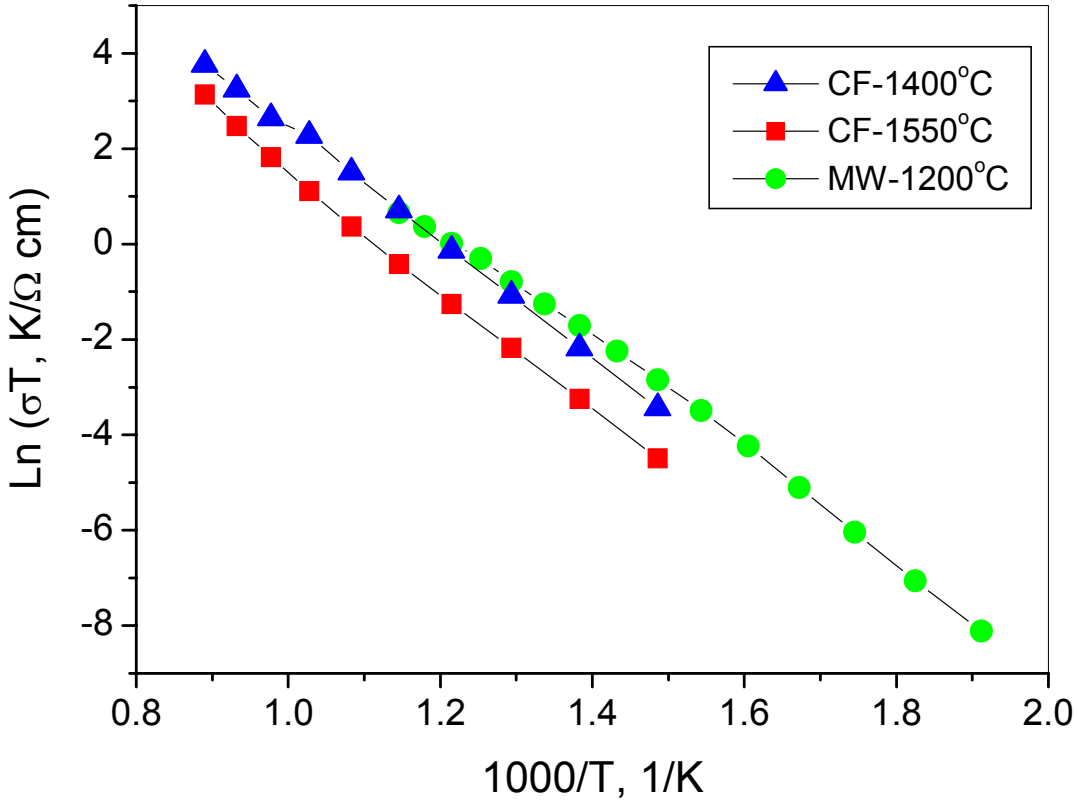
Bigger Grains

Bigger Diffusion Coefficient





Conductivity Measurement of $Ce_{0.8}Gd_{0.2}O_2$ Sintered by Conventional Furnace and Microwave Furnace



Summary of the Work Done During 12/01/2003- Present

- Regenerative Sol Gel (RSG), Microwave Assisted Synthesis, and Solid State Conventional Synthetic techniques have been employed to prepare:

  1) several compositions $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ as an electrolyte,
  2) synthesized porus $LaNi_{0.6}Fe_{0.4}O_3$, and deposited LSGM electrolyte on $LaNi_{0.6}Fe_{0.4}O_3$ as anode
  3) synthesized porus $LaSrCrMnO_3$ to be used as cathode
  4) synthesized $LaCrO_3$ to be used as an interconnector

  It is demonstrated for the first time the Sr- and Mg-doped $LaGaO_3$ solid-state precursors can be regenerated to aqueous solution precursors, a cost-effective way for lab or industry use of large amount expansive gallium containing precursors. Dense, pure-phase and small-grain-sized $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ pellets starting from the regenerative sol-gel precursors have been prepared.

- Pulsed laser deposition (PLD) and centrifugation techniques were to deposit thin layers of oxides of various substrates using above powders as targets

- Synthesized 1,3-dimethyl urea (DMU) to be used as a new fuel in the combustion synthesis of nano oxides. We have developed a combustion synthesis method using a cheap, safe, dimethyl urea (DMU) which is ignited at a temperature much lower than the actual phase formation temperature. This fuel is new and has not reported earlier. We have demonstrated the utility of this fuel and successfully prepared nanocrystalline NiO, Fe_2O_3, CeO_2, TiO_2.

- Nanocrystalline pure CeO_2 and Gadolinium doped CeO_2 were prepared, characterized and compared with commercial CeO_2.

- Supported three African American undergraduate and three graduate (one African American) students

Students and Staff Supported with this Project

1. Jason Winfrey [EE major, 3.7 GPA]
2. Carahma Quiett [Science Education major (1/12/04-6/15/2004)
3. Kourtney L. Jackson [EE major, 3.9 GPA]
4. Vinay B Venktasivareddy [EE graduate student]
5. Yenfeng Li [Physics graduate student]
6. Samarat Ghosh [Research Associate on J1, 4/01/2005-1/15/2005]
7. Weichang Zhao [Research Associate 10/01/2005-8/05/2005]
8. Marcus Lemond [summer 2004]

Conference Presentations and Publications during the year 2004-2005 from our Solid State Ionics Laboratory

Abstracts Accepted for Oral Presentation [2005]

- Innovative processing of dense LSGM based electrolytes/LSCM electrodes for all perovskite based IT-SOFCs, H. Jena, S. Ghosh, Weichang Zhao, B. Rambabu, accepted for oral presentation at ICMAT-2005 conference, July 3-8, 2005, Singapore.
- Nanocrystalline CeO_2 based electrolytes on porous LNF electrode for IT-SOFCs, S. Ghosh, Weichang Zhao, J.C. Jiang*, and B. Rambabu*, accepted for oral presentation in the XIV International Materials Research Congress, Marriot Cosa Magna, Cancun, August 21-25, 2005.
- Nano Fe_2O_3: a promising anode material for Li-ion Batteries, V. Subramanian, Carahma J. Quiett, and B. Rambabu, accepted for oral presentation in the XIV International Materials Research Congress, Marriot Cosa Magna, Cancun, August 21-25, 2005.
- Regenerative solution synthesis of $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ as an electrolyte for IT-SOFC by microwave and conventional sintering, Weichang Zhao, S. Ghosh, and B. Rambabu, submitted for publication in the Journal of New Materials for Electrochemical Systems 2005.
- NANO-IONIC HYBRID POWER SOURCES FOR MICROSYSTEM TECHNOLOGY AND WIRELESS MICROSENSOR NETWORKS, A.L. Despotuli, A.V. Andreeva, B. Rambabu*), accepted for oral presentation at ICMAT-2005 conference, July 3-8, 2005, Singapore.
- CRYSTAL INTERFACE ENGINEERING IN NANOSYSTEMS OF ADVANCED SUPERIONIC CONDUCTORS, A.V. Andreeva, A.L. Despotuli, B. Rambabu*), accepted for oral presentation at ICMAT-2005 conference, July 3-8, 2005, Singapore.
- Mesoprous Oxides for Li-based Energy Storage Devices, accepted for oral presentation at ICMAT-2005 conference, July 3-8, 2005, Singapore.
- *[The following papers were published during the Year 2004-2005 from our SSI laboratory]*
- 1. Mesoporus RuO_2 as supercpacitor electrode material, V. Subramanain, Sean C. Hall, Patricia H. Smith, B. Rambabu, Solid State Ionics, 175 (2004), 511-515
- 2. Nanocrystalline TiO_2: a promising anode for Li-ion batteries, V. Subramanian, Amar Karki, and B. Rambabu, accepted for publication in the Journal of Material Science, 2004
- 3. Nanocrystalline SnO_2 and In-doped SnO_2 as anode materials for lithium batteries , V. Subramanian, K.I. Gnanasekar and B. Rambabu, Solid State Ionics 175 (2004) 615-621
- 4. Synthesis and electrochemical properties of submicron $LiNi_{0.5}Co_{0.5}O_2$ V. Subramanian, Kishor Karki and B. Rambabu, Solid State Ionics 175 (2004) 809-813
- 5. Influence of metal–support interaction in Pt/C on CO and methanol oxidation reactions , Sean C. Halla, V. Subramaniana, Glenn Teeterb and B. Rambabu, Solid State Ionics 175 (2004) 315-318
- 6. Cycling behavior of $LiNi_xCo_yMn_{2-x-y}O_4$ prepared by sol–gel route A. Manuel Stephana, N.G. Renganathana, S. Gopukumara, , , V. Subramanianb and B. Rambabu, Solid State Ionics, 175 (2004) 291-295.

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- Ms. Jodi Collins, U.S-DOE-NETL, Contract Officer
- Ms. Paula Flenory B and Dr. Kamalendu Das, the organizers of this review meeting
- Ms. Cherryl Hall, Office of Sponsored Programs at SUBR