Thermal Properties of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$

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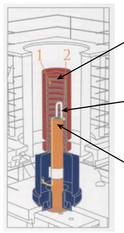
1. Introduction

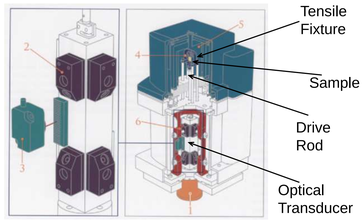
- $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ is strontium and magnesium doped $LaGaO_3$. It is a strong ionic conductor, but a weak electronic conductor, which lends itself for use as an electrolyte in SOFCs.
- A benefit of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ is that it has a higher ionic conductivity at low temperatures (~600 ºC) than other materials used as electrolytes. SOFCs that operate at lower temperatures have higher reliability, broader materials choices, and an extended lifetime.
- The goal of this research is to study the thermal expansion behavior of both pure and Sr-and-Mg doped $LaGaO_3$ perovskites and determine their phase stability in reducing and oxidizing atmospheres.

2. TMA



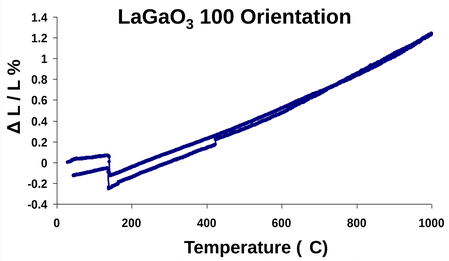
The Thermal Mechanical Analyzer (TMA) is used to discern the thermal properties of materials, notably the coefficient of thermal expansion (α). The TMA rests a probe on the upper surface of the sample (<40mm tall sample), and the probe is supported on an air bearing. As the furnace heats the sample, the sample expands, lifting the probe and the air bearing. An optical transducer measures the distance that the air bearing moves, and saves the data to a computer.

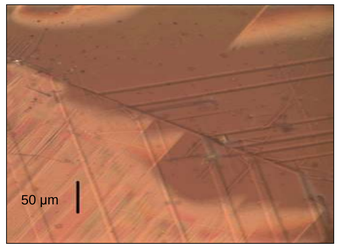
3.DMA



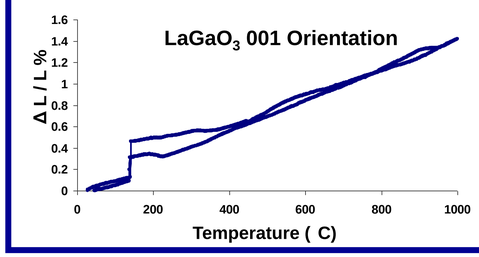
The Dynamic Mechanical Analyzer (DMA) is used to determine elastic properties of materials at different temperatures. Different fixtures can be used to test different properties, such as elastic modulus and tensile strength. The single cantilever fixture, used for experiments shown on this poster, clamps a beam at both ends and applies a force with adjustable frequency to measure the properties of the sample. The DMA, like the TMA, uses an optical transducer for accurate measurements.

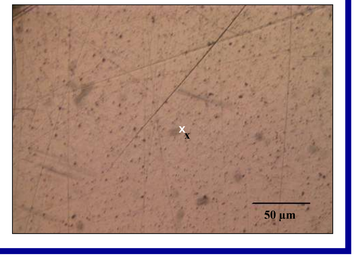
4. Single Crystal $LaGaO_3$



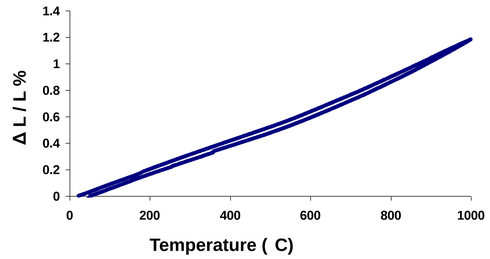


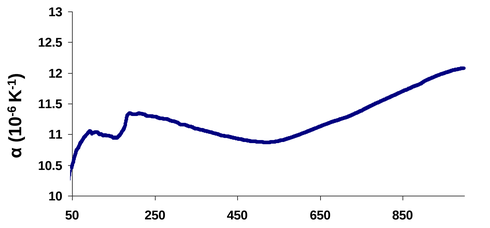
Pure $LaGaO_3$ perovskites are orthorhombic in space group *Pb nm* at ambient temperature, but they undergo a first-order transition to a rhombohedral space group *R3C* at 145 C. While significant changes have been observed in the lattice parameters of orthorhombic and rhombohedral phases, volume change during the phase transition has not been determined. This was explained because while $LaGaO_3$ expands in one crystallographic direction, it contracts in the perpendicular direction. Our measurments of $LaGaO_3$ single crystals confirm this. A strong shrinkage in the [100] direction and a strong expansion in the [001] direction occur during heating, which correspond to the orthorhombic to rhombohedral phase transition. This transition is reversible because [100] expands and [001] contracts during cooling. After the heating/cooling experiments, the $LaGaO_3$ had changed in color from a transparent orange to a much darker orange brown.

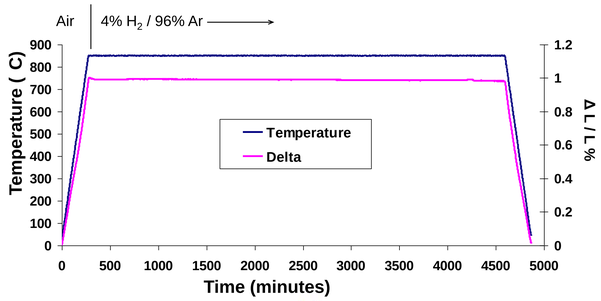




5. Properties in 4% H_2 96% Ar







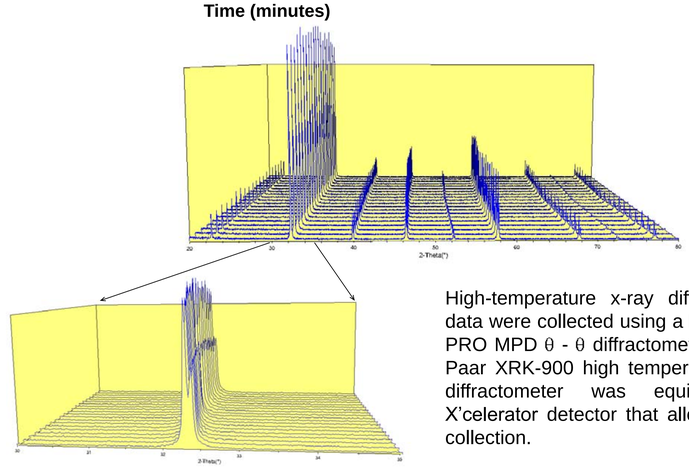
$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ perovskite was heated in 4% H_2 / 96% Ar gas up to 1000 C in order to study its expansion/contraction behavior in reducing atmospheres, which exist on the anode of a SOFC. The stability of the structure is a required parameter under operational SOFC conditions.

The CTE of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ in 4% H_2 / 96% Ar matches closely with its α in air. Both are about 11 x 10^{-6} K^{-1} until about 550 ºC and then they each rise. In air the CTE reaches about 13 x 10^{-6} K^{-1} while in 4% H_2 / 96% Ar the α reaches only 12 x 10^{-6} K^1.

This graph of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ heated to 1000 ºC and then cooled, in 4% H_2 / 96% Ar, shows stability equal to that when heated in air.

It should be noted that before heating in 4% H_2 / 96% Ar the sample was dark brown in color throughout, but afterwards it was light grey, almost white, uniformly throughout the sample.

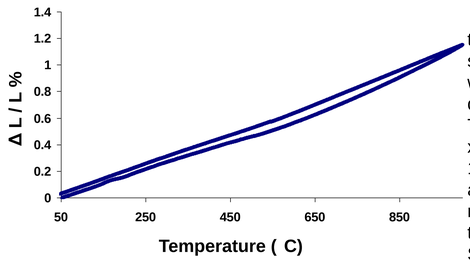
When $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ was heated to 850 C in air and allowed to soak in 4% H_2 / 96% Ar for 72 hours no instability was detected. The sample showed a CTE between 11 and 12 (x 10^{-6} K^{-1}) during the entire test.

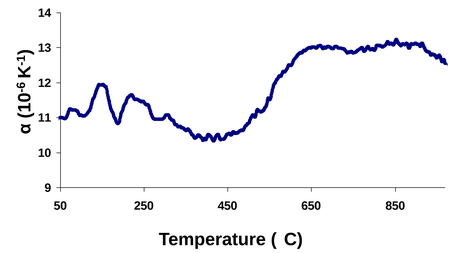


High-temperature x-ray diffraction (HTXRD) data were collected using a PANalytical X'Pert PRO MPD θ - θ diffractometer with an Anton-Paar XRK-900 high temperature stage. The diffractometer was equipped with an X'celerator detector that allows ultrafast data collection.

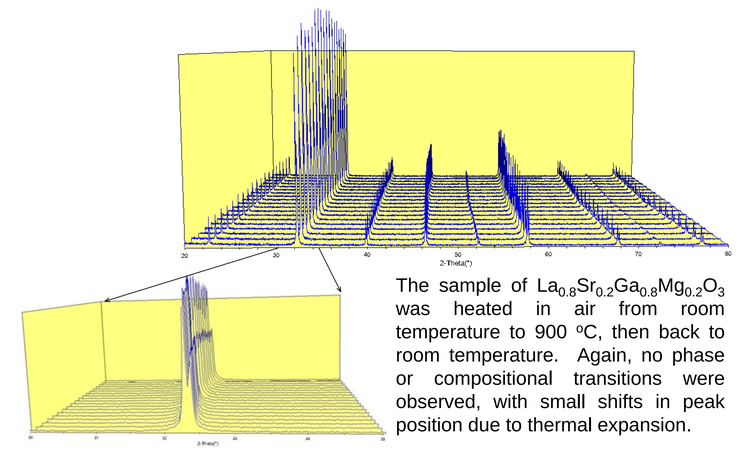
The data were collected using Cu Ka radiation at 45 kV and 40 mA. The sample of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ was heated from room temperature to 900°C, and then back to room temperature, heating at 5 C per minute. Scans were performed every 25 °C using the Anton-Paar XRK 900 linear accelerator, from 10 to 80° 2*θ*, on a scan step of 15 seconds in continuous scan mode. As is seen in the graph, no phase or compositional transitions were detected. A small shift in peak position occurred due to thermal expansion.

6. Properties in Air





The expansion/contraction of the $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ sample has been almost linear with no significant "pop-in" during heating/cooling in air. The α chaned from 11 to 10 x10^{-6} K^{-1} at lower temperatures 100 °C -500 C to ~13 x10^{-6} K^{-1} at higher temperatures. It remained almost the same in the range of 600 °C -1000 C. Such α changes can occur due to orthorhombic to cubic phase transitions, which were reported to occur at 500 C. It was reported ["Metastable Crystal Structure of Strontium- and Magnesium- substituted $LaGaO_3$", M. Rozumek, P. Majewski, F. Aldinger, J. Ann. Ceramic Society, 87, 4, 656-61, 2004] that for orthorhombic modification αs were determined to be $\alpha_{a,ortho}$=10.81 x 10^{-6} K^{-1}, $\alpha_{b,ortho}$=9.77 x 10^{-6} K^{-1}, and $\alpha_{c,ortho}$=9.83 x 10^{-6} K^{-1} (25-400 C), and for the cubic modification to be α_{cubic}=13.67 x 10^{-6} K^{-1}.



The sample of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ was heated in air from room temperature to 900 ºC, then back to room temperature. Again, no phase or compositional transitions were observed, with small shifts in peak position due to thermal expansion.

7. Conclusions

- A reversible expansion/contraction due to a first order phase transformation during heating/cooling experiments has been observed in pure $LaGaO_3$ perovskite at 145 C.
- $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ perovskite has shown no significant expansion or contraction after heating/cooling experiments in air or hydrogen.
- Doping of $LaGaO_3$ with Sr and Mg on A and B sites has led to the formation of a lattice with cubic symmetry which is stable upon heating both in oxidizing and reducing environments.

8. Acknowledgements

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