Experimental report

02/11/2024

Proposal: 5-25-288 **Council:** 4/2023

Title: Charge Compensation Mechanism and the Role of Oxygen Vacancies in Ca-doped La2Ni0.75Cu0.25O4+/-d Oxygen Transport Membranes

Research area: Materials

This proposal is a new proposal

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Samples: La1.8Ca0.2Ni0.75Cu0.25O4

Instrument	Requested days	Allocated days	From	To
D20	1	1	06/11/2023	07/11/2023

Abstract:

Predicting proper amount and type of dopants and the required materials processing conditions in electroceramic materials is an intriguing and complex challenge, so far based on intensive trial-&-error experimental studies. For semiconductor materials first concepts and tools have evolved. We have recently started the Collaborative Research Center FLAIR in order to develop a similar predictive tool using the concept of Fermi level engineering. The idea behind is that the charge compensation mechanisms activated by the respective doping are all linked to the formation of defined defects in the material. The available compensation mechanisms are electronic, ionic, and mixed electronic-ionic charge compensation (important for oxygen transport membrane (OTM) materials), valence changes, and phase segregation. The presence of defects affects the electronic band structure and the Fermi energy. Hence, a Fermi energy-based model aligns all defects/charge compensation mechanisms on a common energy scale, which eventually allows for a predictive selection of dopants, when understanding these interrelationships. Neutrons are needed to track the oxygen content and distribution during T change.

Charge Compensation Mechanism and the Role of Oxygen Vacancies in Ca-doped $La_2Ni_{0.75}Cu_{0.25}O_{4\pm d}$ Oxygen Transport Membranes (5-25-288)

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A sample with the nominal composition $(La_{0.9}Ca_{0.1})_2Ni_{0.75}Cu_{0.25}O_{4\pm d}$ (LCNC) was measured at RT and 1273 K on D20 with an incident wavelength of 1.87 Å at 120° take-off angle for a determination of oxygen content in flowing CO_2 gas atmosphere at a flow rate of 100 sccm. After an initial measurement at RT, the D20 furnace was switched on in stage leading to an immediate raise of the temperature to about 500 K. Then the sample was heated with 1 K/min to 1273 K was constantly collecting diffraction data. The observed data were analyzed via Rietveld refinements. FullProf (version: 7.70) was used for the refinements applying pseudo-Voigt functions to describe the reflection profile and *I*4/*mmm* as space group type.

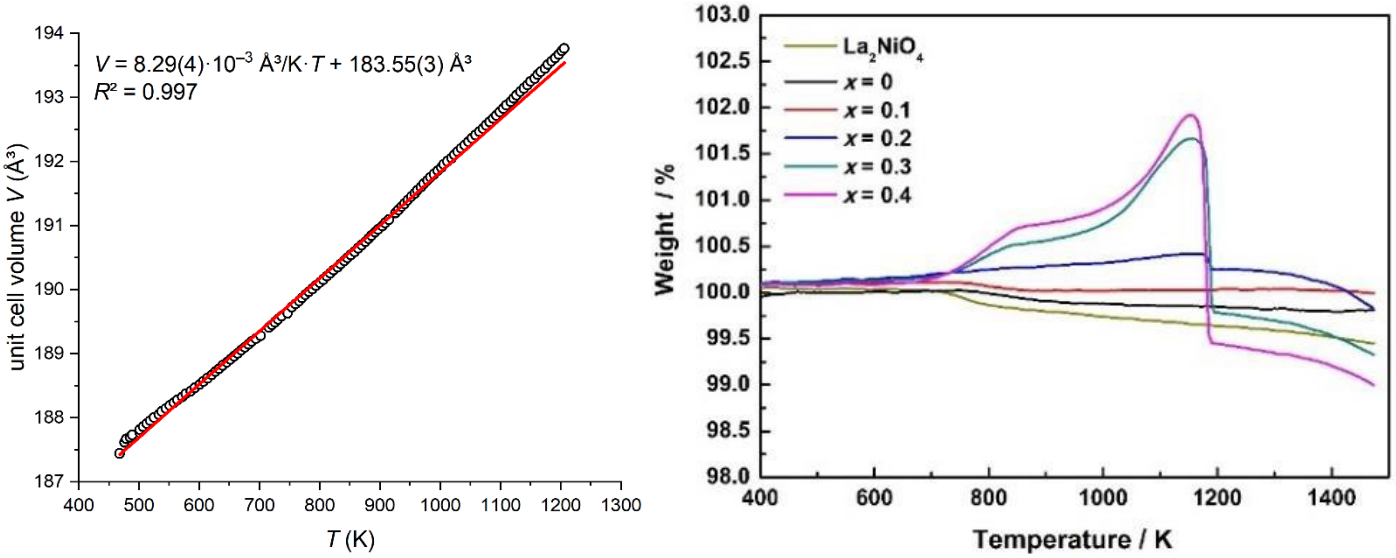

Fig. 1. Left. Refined unit cell volume from variable temperature powder neutron diffraction data collected at D20. Right. Thermogravimetric analysis (TGA) of different Ca-doped $La_2Ni_{0.75}Cu_{0.25}O_{4\pm d}$ in flowing CO_2 atmosphere.

The refined unit cell volumes follow after temperature stabilization of the furnace at around 500 K until nearly 1100 K a perfect linear change with raising temperature indicating the absence of phase transitions and absorption of CO_2. In agreement with the beforehand collected TGA data [1] at temperatures higher than 1100 K a slight deviation towards higher unit cell volumes was recognized potentially indicating a starting reaction with the CO_2. However, the amount was so small that no reflections of $CaCO_3$ were observed. Besides, the pretty linear increase of the unit cell volume is also indicating that the oxygen content staid more or less constant over the entire investigated temperature range. A specific emphasis was laid on this aspect in order to extract more information about the charge compensation mechanism in LCNC. The refinements showed a significant difference of the Biso values (nearly a factor 2) between O(1) on 4*e* and O(2) on 4*c*. Additionally, refinements of the occupation factor of the 4*e* site delivered in accordance an over-occupation resulting in an oxygen excess of about 0.04, hence $d = 0.04$, which staid within error bars constant throughout the measurement. It is well-known that La_2NiO_4-based Ruddlesden-Popper phases tend to be

overstochiometric [2] due to the ability of Ni to be partially present as Ni^{3+}. Further attempts localizing the excess oxygen have failed so far and are under further investigation.

References

[1] G. Chen et al., *Front. Chem. Sci. Eng.* **2020**, *14*, 405–414.
[2] O. Ravkina et al., *J. Eur. Ceram. Soc.* **2015**, *35*, 2833–2843.