

Phase separation in oxygen doped $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($0 \leq x \leq 0.12$).M. Hücker (BNL), M. Chand, and D. Buttrey (U. of Delaware), J. Tranquada, T. Vogt (BNL)
Beamline: X7A

Introduction: Stoichiometric La_2NiO_4 is an antiferromagnetic insulator with orthorhombic (LTO) structure at RT. To dope the NiO_2 planes with charge carriers, La_2NiO_4 can be doped by Sr (x) and/or excess oxygen (δ). While Sr replaces La, excess oxygen occupies interstitial lattice sites. It is well known that in $\text{La}_2\text{NiO}_{4+\delta}$ oxygen intercalation causes phase separation, staging and ordering of the interstitial oxygen ions [1,2]. With increasing δ the orthorhombic LTO ($Abma$) phase transforms into the tetragonal LTT ($P4_2/ncm$) phase and finally into the tetragonal HTT ($F4/mmm$) phase. At intermediate δ values one can find mixed structural phases of LTO/LTT and LTT/HTT which are the consequence of a phase separation into oxygen poor and oxygen rich phases [2]. In the HTT phase eventually different types of oxygen staging are observed upon slow cooling below room temperature [2]. The starting point of our investigation was the question whether Sr doping causes similar electronic and structural effects as excess oxygen, and how these effects evolve in systems doped by both excess oxygen and Sr.

Experiment and Results: Several series of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ samples with fixed Sr content $x=0.02, 0.04, 0.06, 0.08, 0.12$ and variable excess oxygen content δ have been studied. Synchrotron x-ray powder diffraction patterns were collected at beamline X7A at a wavelength of $\lambda=0.7\text{\AA}$ and temperatures between 20K and RT. We find that the miscibility gaps observed in $\text{La}_2\text{NiO}_{4+\delta}$ exist also in the Sr co-doped compounds. On studying the phase boundaries at RT up to a Sr content of $x=0.08$, we observe that with increasing x all phase boundaries systematically shift to higher $2c/(a+b)$ values. Moreover, we find that compared to $x=0$ the LTO phase expands significantly. The chemical analysis of δ is in process and first results show at least no strong shift of the miscibility gaps (compared to $x=0$) when plotted versus δ . In the figure we present room temperature lattice parameters a, b, c , the volume V of the unit cell, and the orthorhombic strain $2(b-a)/(a+b)$ plotted versus $2c/(a+b)$. For a, b as well as the strain we observe almost an universal dependence as a function of Sr and O doping. Just for large $2(b-a)/(a+b)$ values the lattice parameters for high and low x start to deviate, as the highly Sr doped samples contain less excess oxygen. For $x=0.12$ all samples are tetragonal at RT and measurements at low temperatures are required. Temperature dependent measurements were performed for $x \leq 0.06$ and the most important result here is that staging is suppressed by small amounts of Sr. The Coulomb interactions with the Sr ions obviously prevent the interstitial oxygen ions from segregating into every third layer (stage 3), as is the case in $\text{La}_2\text{NiO}_{4+\delta}$ [2].

Future plans: Further experiments at X7A are necessary to complete the low temperature phase diagrams and to gain a better insight in the suppression of oxygen staging. Single crystal diffraction experiments at X7B are planned to study super lattice reflections which is of great help to distinguish between the different phases.

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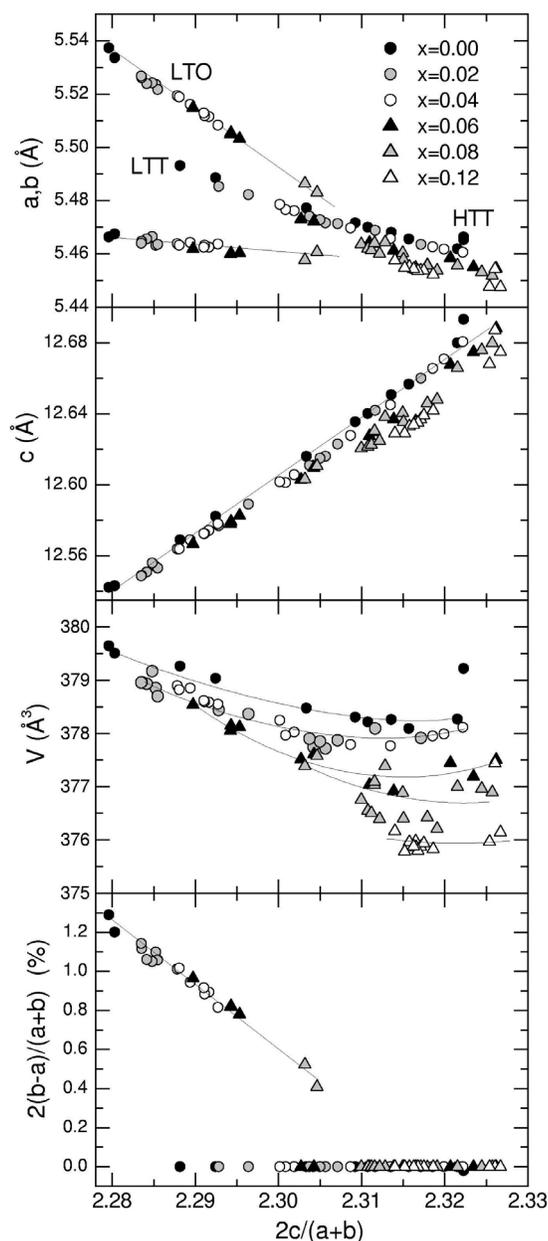


Fig. 1: Room temperature lattice parameters a, b, c , unit cell volume V and orthorhombic strain $2(b-a)/(a+b)$ of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ for fixed Sr content $x=0.02, 0.04, 0.06, 0.08, 0.12$ and variable excess oxygen content δ , with δ increases with increasing $2c/(a+b)$.

References: [1] J. M. Tranquada et al., Phys. Rev. B 50, 6340 (1994), [2] D. E. Rice and D. Buttrey, J. Solid State Chem. 105, 197(1993)