

The High Pressure Synthesis of Single Crystal Ruddlesden-Popper Nickelates

$R_{n+1}Ni_nO_{3n+1}$ ($R=La,Pr,Nd,Sm$)

Shreenithi Katta

School of Physics, Georgia Institute of Technology

(Dated: August 20, 2024)

Room-temperature superconductivity is a prominent area of today's research. In recent years, the spotlight has shifted to layered nickelate materials as candidates for high temperature superconductivity. In this report, we attempt to grow single crystals of Ruddlesden-Popper nickelates $R_{n+1}Ni_nO_{3n+1}$ ($R=La,Pr,Nd,Sm$) using a high pressure optical floating zone. Specifically, we were able to stabilize $Nd_3Ni_2O_7$ and $Nd_4Ni_3O_{10}$ phases under pressures of 110-120 bar and 180-250 bar respectively. Though we are not able to exclusively isolate each phase at specific pressures, the signature of the $Nd_3Ni_2O_7$ phase is a promising step in the right direction. Future work should be done to further optimize and isolate single crystals of each Nd phase for resistivity measurements and potential device applications.

I. INTRODUCTION

The search for room-temperature superconductors has been at the forefront of research for over a century. The most prominent family of superconductors has been the copper based materials or the cuprates. Though the mechanism behind superconductivity is not fully realized, it is believed to lie in the copper-oxide planes. In more recent years, the focus has shifted to mimicking the superconductivity of the cuprates in a similar material, the nickelates. In theory, nickelates should have the same electronic properties since nickel is right next to copper in the periodic table. Specifically, there has been evidence of trace superconductivity found at 80 K in $La_3Ni_2O_7$, a Ruddlesden-Popper nickelate [1]. Therefore, the goal of this summer was to stabilize any Ruddlesden-Popper nickelate of Pr, Nd, and Sm in single crystal form. To do this, high pressure is needed, therefore, we used the 300 bar high pressure optical floating zone furnace in PARADIM.

II. METHODS

High pressure synthesis of the various nickelates was conducting using the PARADIM 300 bar high pressure optical floating zone (HPFZ). Specifically, growths were attempted to stabilize the following phases: $La_3Ni_2O_7$, $La_4Ni_3O_{10}$, $Pr_3Ni_2O_7$, $Pr_4Ni_3O_{10}$, $Nd_3Ni_2O_7$, $Nd_4Ni_3O_{10}$, $Sm_3Ni_2O_7$, $La_{0.9}Sr_{0.1}NiO_3$, $La_{0.85}Sr_{0.15}NiO_3$. Polycrystalline powder samples were made using solid state synthesis in a box furnace. Rare-earth oxides (La_2O_3 , Pr_6O_{11} , Nd_2O_3) and nickel oxide (NiO) were stoichiometrically combined and held at 1100 C for 12 hours. $SrCO_3$ was used to introduce strontium as a doping agent. Because the rare-earth oxides interact with air to form hydroxides, they were dried at 1100 C for 12 hours and held in a desiccator before making any powder samples.

The polycrystalline powder samples were then pressed into dense rods by hand before using the vacuum pump and isostatic press. The resulting rods were sintered for >30 hours at temperatures between 1100 and 1400 C depending on their composition. Rods sintered at 1400 C

did not crack during growths and gave the best results. Typical HPFZ growths, once stabilized, were very slow. The translation of the seed rod was typically between 2-5 mm/h while the feed was between 5-15 mm/h. Resulting crystals were cut in different places using the diamond saw to find any signature of single crystals. Each crystal slice was observed under the microscope to visually confirm any traces of crystallinity before an x-ray diffraction scan. Depending on the quality of the x-ray profile, either Laue was conducted on the crystal slice or a different part of the crystal was scanned. Due to equipment malfunctions, Laue was not performed extensively enough for any analysis purposes. No resistivity measurements were conducted due to time constraints and poor crystal quality.

III. RESULTS AND DISCUSSION

Lanthanum and Strontium Doped Series As a tutorial of the new system, we attempted growths of $La_3Ni_2O_7$ and $La_4Ni_3O_{10}$. Two growths of $La_3Ni_2O_7$ were done at 15 bar as established by previous literature [1]. However, due to inexperience with the system, no viable crystals were obtained from either attempts. The $La_4Ni_3O_{10}$ was later abandoned due to time constraints.

Strontium doped growths shared the same level of disaster. $La_{0.85}Sr_{0.15}NiO_3$ rods were grown under 200 bars of oxygen pressure. The seed rod melted very inconsistently and the resulting melt had traces of $LaNiO_3$ and heavily Sr doped La_2NiO_4 . To avoid the formation of the heavily doped La_2NiO_4 , $La_{0.9}Sr_{0.1}NiO_3$ was attempted at 200 bar. However, we were met with the same issue of inconsistent melting and were unable to get any significant zone stabilization or growth.

Praseodymium and Samarium Series Growth of $Pr_3Ni_2O_7$ was done at 80 bars of oxygen pressure. During the growth, severe cracking formed throughout both the seed and feed rod. The resulting crystal indicated residual Pr_6O_{11} and trace amounts of Pr_2NiO_4 in the x-ray diffraction profile. Upon further discussion, the difficulty in stabilizing the $Pr_3Ni_2O_7$ phase could be a result of praseodymium's oxidation state of either 3+ or 4+. Coupled with the various oxidation states of Ni,

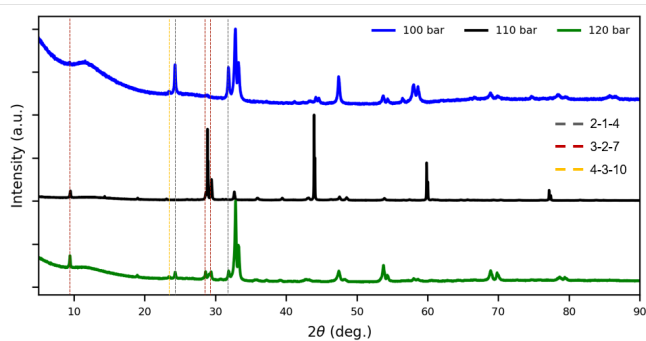


FIG. 1. X-ray diffraction profiles of the $\text{Nd}_3\text{Ni}_2\text{O}_7$ growths at 100, 110, and 120 bar oxygen pressure. The dashed lines correspond to unique peaks of each Ruddlesden-Popper phase.

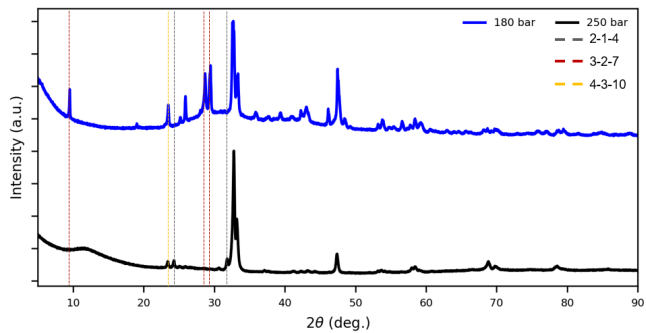


FIG. 2. X-ray diffraction profiles of the $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ growths done at 180 and 250 bar oxygen pressure. The dashed lines correspond to unique peaks of each Ruddlesden-Popper phase.

praseodymium's variability could narrow the pressure region where $\text{Pr}_3\text{Ni}_2\text{O}_7$ is stabilized. Therefore, further exploration of the Pr series was abandoned and the focus was switched to samarium, another rare-earth that only has the 3+ oxidation state.

$\text{Sm}_3\text{Ni}_2\text{O}_7$ rods were sintered at 1100 C for 42 hours to avoid cracking and growth was attempted at 150 bar. To further avoid cracking during the growth, the feed rod was passed through the molten zone at lower power for a densification round. However, during this pass, the rod cracked and growth was subsequently aborted. Due these results and time constraints, this portion of the project was abandoned.

Neodymium Series The most notable growths of the summer were attempts to stabilize $\text{Nd}_3\text{Ni}_2\text{O}_7$ and $\text{Nd}_4\text{Ni}_3\text{O}_{10}$. The first attempt of $\text{Nd}_3\text{Ni}_2\text{O}_7$ was done at 120 bar with the rods sintered at 1100 C for 46 hours. The feed rod indicated some cracking therefore a densification round was conducted from the tip to the end. The growth was done with the seed rod translating around 5

mm/h and the feed rod around 10 mm/h. The diffraction profile from the best part of the resulting crystal showed a new peak around 10 degrees in 2θ as seen in Figure 1. We believe the newer peaks can be attributed to the new $\text{Nd}_3\text{Ni}_2\text{O}_7$ phase as similar peak locations can be found in $\text{La}_3\text{Ni}_2\text{O}_7$. However, there are also trace amounts of other phases in the crystal, therefore we continued exploring the phase space of the Nd series.

Two growths were attempted of the $\text{Nd}_3\text{Ni}_2\text{O}_7$ phase at 100 and 110 bar oxygen pressure. Rods for both growths were sintered at 1400 C which severely reduced cracking issues. Both growths were also done with very slow translation with the seed rod around 2-4 mm/h and the feed rod around 5-7 mm/h. As seen in Figure 1, the 100 bar growth has no signature of the $\text{Nd}_3\text{Ni}_2\text{O}_7$ phase. On the other hand, the 110 bar growth has very sharp and ordered peaks indicative of something very crystalline. It also has very little phase impurities which is promising. Further analysis is needed to refine the profiles and extract the crystal structure.

$\text{Nd}_4\text{Ni}_3\text{O}_{10}$ growths were attempted at 180 bar and 250 bar of oxygen pressure. The rods used were sintered at 1100 C and 1400 C for >30 hours for the 180 and 250 bar respectively. Because of the low sintering temperature, there was severe cracking in the 180 bar growth compared to the 250 bar growth. The x-ray diffraction profiles of the crystals show similar results. As seen in Figure 2, the 180 bar growth has a lot more signatures of the other Ruddlesden-Popper phases than the 250 bar growth. Though strong conclusions cannot be made from the diffraction profiles, we can still predict that higher pressure is ideal for stabilizing the $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ crystal. Further exploration of the pressure space is needed to completely stabilize the $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ phase here as well.

IV. CONCLUSIONS

In this report, we attempted the high pressure synthesis of single crystal Ruddlesden-Popper nickelates $\text{R}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ ($\text{R}=\text{La},\text{Pr},\text{Nd},\text{Sm}$). Of the many growths attempted, we were able to stabilize $\text{Nd}_3\text{Ni}_2\text{O}_7$ and $\text{Nd}_4\text{Ni}_3\text{O}_{10}$ phases under pressures of 110-120 bar and 180-250 bar respectively. Though we are not able to exclusively isolate each phase at specific pressures, their existence in the x-ray diffraction profiles is a promising step in the right direction. Future work will be done to further isolate single crystals and stabilize the failed growths attempted.

V. ACKNOWLEDGEMENTS

This work would not have been possible without the help and guidance of my mentor Thomas Whoriskey, the input of Dr. Tyrel McQueen and Dr. Satya Kushwaha, and funding and opportunity from PARADIM and the NSF.

[1] H. Sun, M. Huo, and X. H. et. al., Signatures of superconductivity near 80 K in a nickelate under high pressure,