

Copyright

by

Ao Shi

2018

**The Thesis Committee for Ao Shi
Certifies that this is the approved version of the following Thesis:**

**Crystal growth of the cuprate superconductor $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ by
the traveling solvent floating zone method**

**APPROVED BY
SUPERVISING COMMITTEE:**

Xiaoqin Li, Supervisor

Jianshi Zhou

**Crystal growth of the cuprate superconductor $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ by
the traveling solvent floating zone method**

by

Ao Shi

Thesis

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Master of Arts

The University of Texas at Austin

August 2018

Acknowledgements

First I want to begin by thanking my thesis committee members, Prof. Li and Prof. Zhou, for taking the time in reading and providing valuable suggestions and comments, for detailedly checking the errors, grammars, problems in my thesis writing. Some of them are even painfully frank, but they will push me to go beyond what I have and can currently achieve. Thank you for your time!

I am very grateful to Prof. Zhou for giving me this opportunity to conduct this interesting thesis project of growing high temperature cuprate superconductors in the lab, and almost always being available for help and discussions. Besides, I have been lucky to participate in some other interesting projects during my time in lab, and I get to broaden my views and delve deeper into the field of condensed matter physics due to these interesting experiences. Development and growth of new materials always lies at the core of condensed matter physics, and I am very grateful that I have had these experiences to learn more about them, and I cherish every moment of my time. Thanks Prof. Zhou!

Finally, I want to thank my lab mates, Dr. Xiang Li, Dr. Xi Chen, and Zongyao Li for always being there for help, discussions, and offering many useful guidance and suggestions. Particularly I want to thank Zongyao, for guiding me almost step by step from basic lab fundamentals, solid state synthesis, to operating the more advanced image furnace and finally conducting single crystal growth myself. I have almost learned all of my lab skills from him, and we have built up a good friendship outside the lab. The lab work has truly become more fun and interesting due to this. Thank you!

Abstract

Crystal growth of the cuprate superconductor $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ by the traveling solvent floating zone method

Ao Shi, M.A.

The University of Texas at Austin, 2018

Supervisor: Xiaoqin Li

In this thesis, my efforts of the single crystal growth of a cuprate series $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ by the travelling solvent floating zone method will be described. The availability of high quality single crystals is essential to facilitate experimental studies of high temperature superconductivity in the cuprates. Repeated attempts gradually lead to crystals with the improved qualities. A single pattern well indexed via the X-ray powder diffraction suggests that the crystals were grown with the correct chemistry and single phase. Laue back reflection, on the other hand, indicates that domains with different orientations in the same crystals still exist, and crystal growth processes can be further optimized. Discussions, and possible routes of further optimization of the growth process are suggested at the end of the thesis based on the principles of the travelling solvent growth. A continuous supply of large and better quality crystals would help offer more insight into this challenging strongly correlated system.

Table of Contents

List of Tables	vii
List of Figures	viii
Chapter 1: Introduction	1
Chapter 2: Experimental methods.....	8
The material characterizations	13
X-ray powder diffraction	13
Laue back reflection.....	13
Chapter 3: Results and discussions	15
Chapter 4: Summary	30
References.....	31

List of Tables

Table 1: Summary of the previous crystal growths.	17
--	----

List of Figures

Figure 1:	Universal phase diagram of hope doped cuprates[2].	2
Figure 2:	Examples of structural models for several cuprate superconductors.	4
Figure 3:	Schematic of the image furnace set-up.	9
Figure 4:	Thermodynamic phase diagram of the La_2O_3 - CuO system.	12
Figure 5:	Photograph of an example of the grown crystal with Sr doping $x=0.1$.	20
Figure 6:	The pattern from X-ray Powder diffraction of a LNSCO sample with Sr $x=0.19$.	21
Figure 7:	Same pattern, compared with the pre-saved LNSCO ($x=0.15$) data in the PDF database.	22
Figure 8:	Laue Back reflection patterns checked at two different locations on the same grown crystal LNSCO with $x=0.1$.	23
Figure 9:	Shapes of the molten zones for growths of $\text{Dy}_2\text{Ti}_2\text{O}_7$. Taken from Ref. [17]. (a) Good conditions; (b) Zone overheated; growth too slow or not enough feeding; (c) Too much feeding; temperature not high enough; (d) Power not enough, growth too fast.	26

Chapter 1: Introduction

Cuprates refer to a transition oxide family containing copper ions. This family of ceramic materials has attracted considerable attention in the last few decades because of the superconductivity discovered in them with surprisingly high transition temperature[1]. The high transition temperature, together with the proximity of the superconducting phase to a magnetic instability suggests that the mechanism be different from the conventional Bardeen-Cooper-Schrieffer (BCS) superconductivity in which electron-phonon interactions mediate Cooper pairs. Currently, there is no consensus on the origin of this superconductivity.

Most superconductivity phases have been observed in simple metallic systems, where a well-defined Fermi surface and quasi-particles could be observed above the transition temperature. However, the superconductivity in cuprates takes place at the crossover from an insulator-to-metal transition. Figure 1 shows the updated phase diagram of a cuprate system [2]: the parent compound of all hole-doped cuprates (which means that no dopants are substituted) is an antiferromagnetic insulator where Coulomb repulsions split the narrow band originated from the Cu $d_{x^2-y^2}$ electrons. Superconductivity is achieved by doping holes into this insulating parent compound, where doping from alkaline-earth elements quickly suppresses the static antiferromagnetic order. Superconductivity emerges at the crossover of localized and itinerant electronic behavior; the critical temperature follows a dome-like behavior where optimal superconductivity with maximum transition temperature usually takes place at a doping concentration of around 0.15. Added to the complexity is the various abnormal phases discovered above the superconducting transition temperature T_c . A strange metallic behavior is observed above T_c where the resistivity follows the linear temperature dependence, which strongly

denies a simple quasi-particle picture. Spectroscopy measurements also suggest a partial gap in momentum space has already opened at a temperature well above T_c (which is termed the “pseudo-gap”) in the underdoped regime[3]. Therefore, the challenge to understand superconductivity in cuprates is to explain not only the superconductivity transition in the crossover itself, but also the unconventional normal state and doping-induced evolution of physical properties out of which the superconductivity was born within the entire doping range.

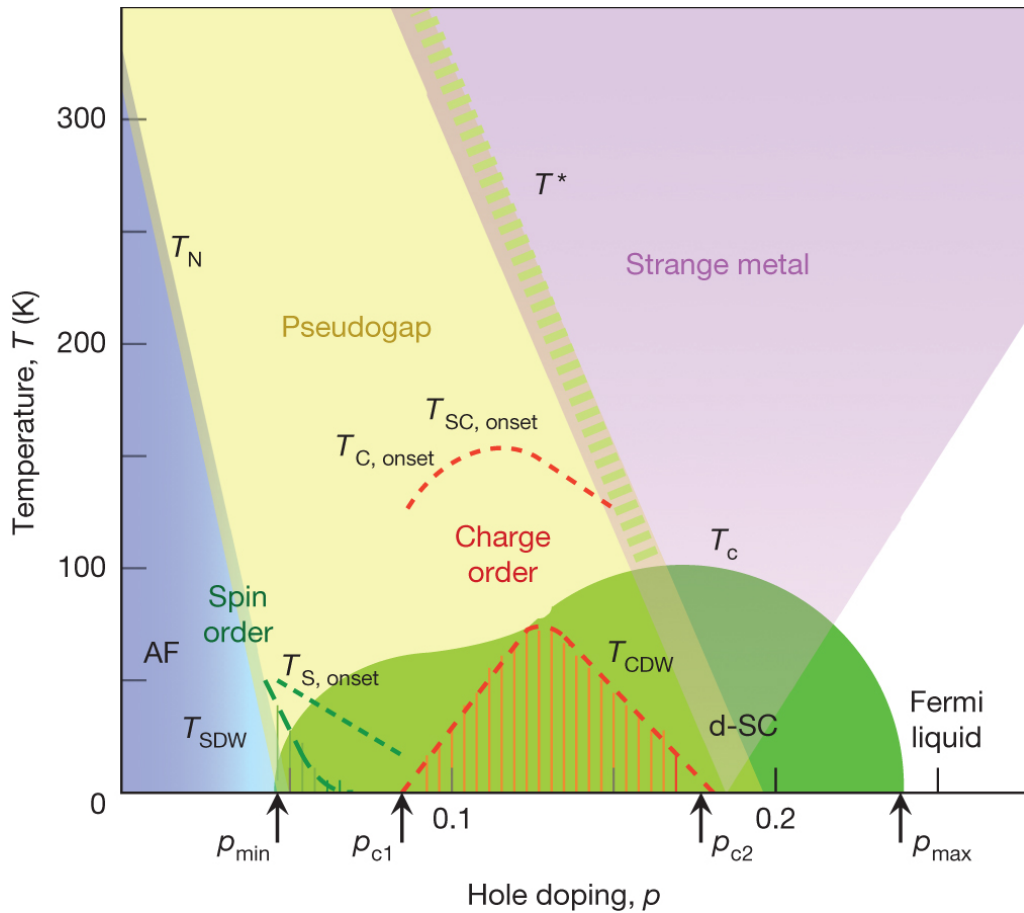


Figure 1: Universal phase diagram of hole doped cuprates[2].

Experimental advancement in understanding superconductivity in cuprates relies on continuous development in physical measurement techniques and higher qualities of materials. Most cuprates are complex inter-growth layered materials. A few examples of the structures of cuprates have been shown in Figure 2. As can be seen, the structures of cuprates are perovskite-related as they consist of the blocks of corner-shared CuO_6 octahedra; however, periodic layers formed by rare or alkaline earth metal blocks disrupt the connection of CuO_2 layers in the 001 direction. This weaker interaction from Cu-O-O-Cu in the vertical direction to the CuO_2 planes results in strongly anisotropic properties in most cuprates. Superconductivity in cuprates has been believed to take place in copper oxide planes, and T_c has been found to be correlated with the number of CuO_2 layers in the unit cell[4].

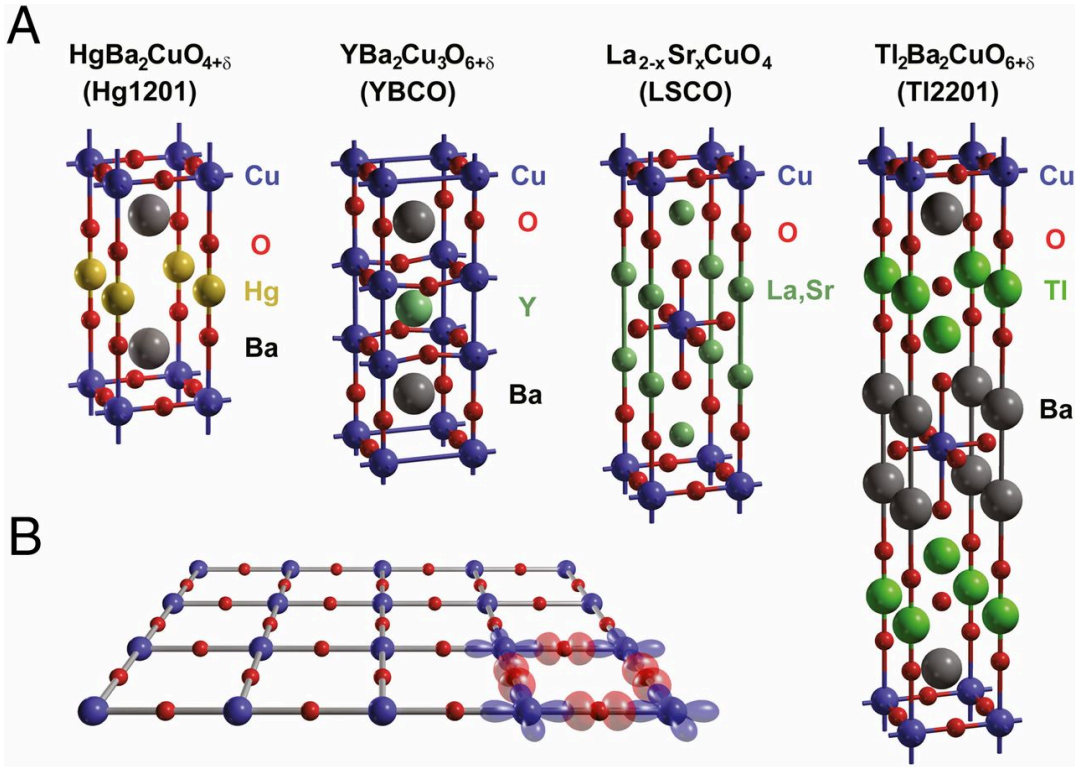


Figure 2: Examples of structural models for several cuprate superconductors.

The strong anisotropic properties of cuprates make single crystal samples a necessary step to study the intrinsic properties of these compounds. Indeed superconductivity in cuprates has been discovered to be sensitive to sample processing procedures, and intensive early studies have been focused on how superconductivity can be correlated with chemical homogeneity and oxygen stoichiometry in the samples[5-7]. Growing high quality single crystals would allow properties to be investigated without influence coming from possible local grain boundaries or random distributions. Moreover, suitable sizes and good quality surfaces of crystals are also essential to the experiments with scattering techniques.

This thesis describes my efforts of growth of a particular cuprate compound $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ by the travelling solvent floating zone method. Generally speaking, the

choice of the method for crystal growth depends on material systems. The flux-growth method remains the most popular and economic one. The materials of interest are dissolved in specifically chosen solvent “flux” and placed in the chemically stable crucible. Crystal formation is possible by carefully controlling the cooling temperature of the crucible and spontaneous precipitation is formed out of the solution. While relatively convenient and applicable to a wide range of materials, this growth method suffers from small yield and sizes of grown crystals and the possible contamination with flux or crucible materials. Also, the growth process is usually conducted in a furnace and the direct observation of the process is not possible. The thesis introduces my efforts of using a different method, called the traveling floating zone growth method with an image furnace, to grow single crystals of cuprates. Compared with the conventional flux growth method, the sizes of the grown crystals are relatively larger, the crystals having a higher purity, making them suitable for further measurements of physical properties.

The specific cuprate compound to be grown is $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ (LNSCO). Containing only one CuO_2 layer in the unit cell, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) is one of the simpler structures in the cuprate families. While the transition temperature relatively low compared with other cuprates, the LSCO system has an advantage of possible doping through the entire doping range, allowing the phase diagram to be carefully studied. It has been shown that when suitable concentrations of Nd ions are substituted into La (~ 0.4), the low-temperature tetragonal phase (LTT) structurally different from the high-temperature tetragonal phase (HTT) of LSCO can be stabilized. Due to the commensuration between spin/charge order (stripes) and the lattice distortion at $x=1/8$, static stripes have been identified via various diffraction techniques[8-10], and how the dynamics of stripes is related to superconductivity is currently under debate. Superconductivity transition temperature has also been suppressed for $x=1/8$.

The relatively low critical temperature of LNSCO allows its superconductivity to be completely suppressed with high magnetic fields. Especially recent work of low temperature study of cuprates under high magnetic fields has provided new insight into the nature of the pseudogap phase where a metal-metal transition has been identified[11], and how the critical point of the pseudogap has affected a wide range of transport properties[12]. The growth of high quality single crystals, therefore, will allow further studies for revealing more insight into this system.

In Prof. Zhou's lab, previous studies of single crystals LNSCO via thermal conductivity measurement have been conducted with dopings $x=0.12$, 0.15 and 0.20 . The thermal conductivity measurement has provided insight into how bond length fluctuations are intertwined with superconductivity and stripe order. It has been surprisingly found out that the strong thermal conductivity peak has been recovered in the LTT superconducting phase, suggesting that the fluctuations may have little to do with this superconducting phase[13]. It has now been established that the stripe order may take place in a doping range around $x=1/8$, and the critical point of this stripe/charge order may be distinct from the pseudo-gap critical point[14]. Additional insight may be further gained by continuing the transport studies on samples with other dopings.

In this thesis I will describe my efforts of using the travelling solvent floating zone method to grow large single crystals of LNSCO with dopings $x=0.1$, $x=0.17$, $x=0.19$. Optimization of the growth requires careful observation of the growth process and control of the relevant parameters. In the next chapter, I will introduce the method of the floating zone growth of large crystals, and how it can be modified into the travelling solvent zone method for cuprates for the incongruent melting phase diagrams, and relevant characterization techniques in characterizing the quality of the crystals. And the third chapter will describe my procedures of growing LNSCO crystals with these

dopings. Currently, large crystals with single domains are not achieved; however, trials of the crystal growths lead to some insight into possible improvement of the growth process. Some of the discussions are based on them, hoping to facilitate future growths of this important cuprate superconducting system.

Chapter 2: Experimental methods

The key instrument set-up for the floating zone growth is an image furnace, as is depicted below. The two-mirror image furnace to be used is NEC SC-M35HD. To enable the crystal growth, an extremely large temperature gradient is established along the vertical direction. This is achieved by using two highly reflective ellipsoidal reflectors sharing a same focal point at the center of the furnace. Two halogen lamps, which are able to provide high power infrared radiation, are placed at each of the other focal points of the reflectors. By absorbing the intense infrared light coming from the halogen lamps at the focal point, the materials at the center can be melt, forming a “molten zone”, reaching a temperature of more than 2000°C. The real crystal growth process takes place by simultaneously moving the two materials rods, one hanging above the molten zone, and one as the seed below, downwards at a very slow rate controlled by the two rotating shafts of the furnace; in this way, a continuous supply of materials into the molten zone and recrystallization out of it will result in large single crystals continuously grown onto the lower rod ideally forming a large single domain. The entire stable growth of the crystals, can therefore, be sustained with a stable molten zone formed at the center of the rods. A long quartz tube is mounted around to seal the whole rods and the molten zone, and supply or maintain a controlled pressure of different types of atmosphere. Because the entire growth is essentially sustained by the surface tension of the liquid phase in the molten zone, no crucible is needed, which eliminates any possible contaminations.

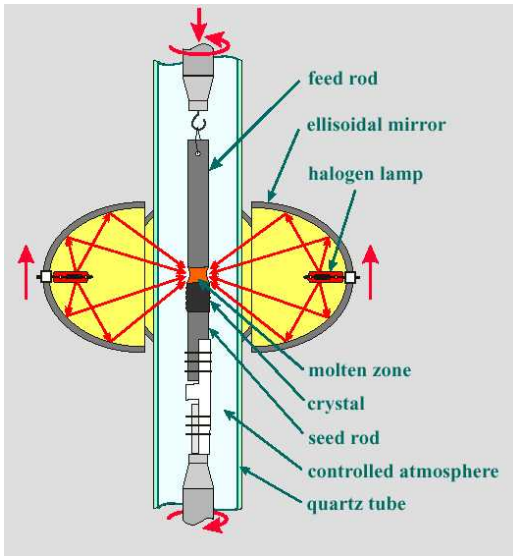


Figure 3: Schematic of the image furnace set-up.

One important feature about the image furnace set-up is that, the hot zone can be visually accessed through an optical window in front of the furnace. When crystal growth is conducted, the temperature of the molten zone is extremely high, and most of the visible light coming from the lamp is focused around it, therefore the entire growth process can be visually monitored through the lens and the screen configured on the image furnace. This offers another advantage of the optical floating zone crystal growth method: the molten zone formation and crystal growth can be directly visualized, which establishes an important first step to evaluate or inspect the status of crystal growth directly.

To start the growth process, the power of the lamps is first increased, either computer controlled or manually, until the solvent attached to the bottom of the feed rod is melted. Then the position of the rods is carefully tuned (by adjusting the heights of the shafts with the system) to connect the two rods forming a stable molten zone at the center. The crystal growth can be directly initiated by setting a proper growth rate and

feed rate independently and stabilize all the systems parameters thereof; however, a “necking” process conducted at the beginning would be helpful in establishing single domain growth as fast as possible. In this situation, the feed rate is first set-up much slower than the growth rate at the very beginning, then gradually increased so that the width of the resulting crystal will form a thin neck at the beginning before the final single domain growth continues. After that, all growth parameters would maintain the same; however, due to the possible inhomogeneity of the rods, occasional manual adjustments may be required. The process can be directly monitored through the optical system of the furnace. Usually a single crystal with a new domain will start after the adjustment.

Historically, the optical floating zone technique has been developed mostly for growing large crystals of semiconductor and metal oxides, particularly, the growth of various transition metal oxides which would be difficult by using other crystal growth techniques because of their relatively high melting temperatures, is made possible by the floating zone technique because of their high optical absorption coefficient[15]. A particular example is the yttrium iron garnet ($Y_3Fe_5O_{12}$)[16], which has found applications in various industrial applications including optical rotators, transmitters, and non-linear crystals, etc. due to their ideal magnetic and magneto-optic properties, has now been industrialized using the optical floating zone method achieving larger pure high quality single crystals. However, it should be noted that because of the drastically different thermodynamic characteristics of different materials, suitable growth parameters have to be worked out individually for each specific materials. For most congruent materials where the liquid melting phase has the same composition as the feed rod, the growth can be directly initiated by gradually increasing the power melting the tip of the rod. However, a modified travelling floating zone method must be developed to grow the

incongruent melting materials where the compound decomposed before reaching to the liquid phase.

As all cuprates are all incongruent melting materials, crystal growth using the traveling solvent floating zone method is essential for achieving high quality single crystals. The principle of the method can be best illustrated considering the phase diagram of the cuprates. Here the phase diagram is shown in Figure 4 for the La_2CuO_4 ; while the partial substitution of Nd and Sr ions is expected to change the melting points and phase boundaries of different compositions, the phase diagram should be more or less the same. It can be seen that, if starting materials of the exact same composition of the crystal to be grown, La_2CuO_4 , is heated up in the center zone, the materials will decompose into La_2O_3 and a liquid phase before entering into a complete liquid state. Gradually lowering the temperature, therefore, will result in La_2O_3 first precipitated out, while leaving the liquid zone CuO rich; continuous growth will result in gradual accumulation of CuO in the molten zone, essentially moving the solid-liquid interface toward a point which essentially connects with higher CuO percentage on the phase diagram. This process will continue until a stable growth of crystal with the same composition LSCO can be reached on the phase diagram: this corresponds to the liquid phase line spanning the CuO composition from around 75% to 90% on the phase diagram.

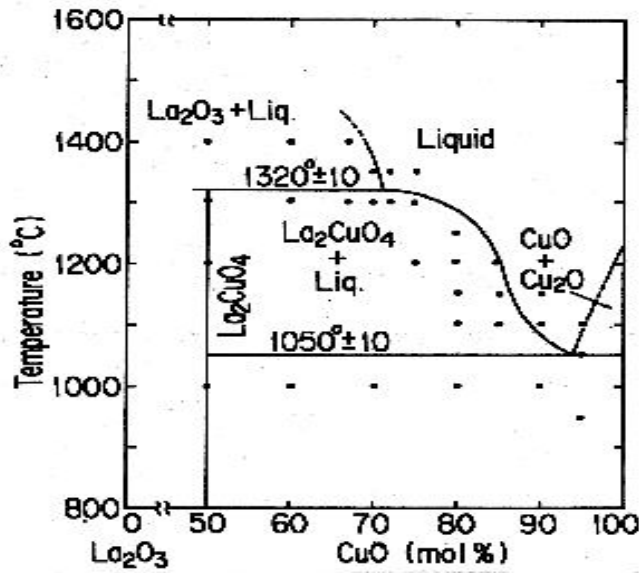


Figure 4: Thermodynamic phase diagram of the La₂O₃ - CuO system.

A continuous growth, therefore, will result in La₂O₃ from the molten zone first precipitated out; only until the liquid zone has CuO accumulated to a certain percentage portion, the stable growth of stoichiometry compound can be allowed. The gradual change of composition in the melt, on the other hand, also suggests a continuous change of the temperature and growth parameters to maintain a stable equilibrium of the crystal growth.

To help facilitate fast establishment of a stable growth, a solvent disk therefore can be directly placed between the feed and seed rod choosing a composition directly corresponds the stable liquid phase spanning the crystal compound of stoichiometry composition and liquid state, in the LSCO case, corresponding to a rich CuO composition of around 75% - 90%. The solvent melts at a temperature below the decomposition temperature for La₂CuO₄; therefore a stable growth can be resulted by continuously

precipitating out the stoichiometric compound along the same critical point on the phase diagram.

The material characterizations

X-ray powder diffraction

X-ray powder diffraction is frequently applied to characterize the phase purity of the crystal. A monochromatic X-ray is sent to the sample powder, diffracted by the crystal planes, therefore forming unique patterns collected by the detectors. The powder samples are placed on a glass plate and the angle with respect to the X-ray beam are varied. Only when the Bragg condition $2d\sin\theta=l$ is satisfied a peak can be formed. Because of the different lattice structures of compounds, unique positions of the peaks can be indexed to identify and characterize these different phases. If impurity phases do show up, additional peaks with different positions will appear. A bench-top MiniFlex diffractometer was used in the experiment. The angle 2θ varies between 20 – 70 degrees at 0.04 intervals at 10s/step. The data can be analyzed with the software JADE.

Laue back reflection

To check the crystallinities of the crystals, Laue Back reflection can be performed. A white X-ray beam with continuous wavelengths is shined onto the crystal, while back reflections are collected on the image plate. Bragg planes each with different orientations will generate spots and zones in the Laue pattern. Therefore, a pattern of round spots, with each corresponding to a certain set of planes, can be collected on the plate, and a pattern with undistorted spots (the image of collimator) indicates a good single domain of the crystal, while the distributions of zones in the pattern tells information about the orientation of that domain. For this reason, Laue Back Diffraction

is a powerful technique to check the quality of the grown crystal. In the lab a Fuji Image Plate (IP) is used to collect the diffraction pattern, and after that the image plate is then inserted, and the pattern is read through the FUJIFILM Bio-imaging Analyzer BAS-1800II. The digital image can be saved on the computer and edited via Image Gauge. And crystal orientation is then performed with the software OrientExpress.

The unique superconducting property like the Meissner effect makes a direct physical property measurement a suitable method to characterize the quality and dopings of the crystal, for example, the magnetic susceptibility. A sharp superconducting transition at the critical temperature is expected for a crystal of good quality, and the transition temperature for a particular composition can be traced then to suggest whether a suitable amount of doping was correctly achieved. In addition, other microscope-based techniques can give important information on the local structure/grains and the elemental distribution of the crystal, which further provides deeper insight into the crystal growth process. These methods include, for example, SEM, which will be able to characterize the local boundary or the solvent penetration at the interface between the rods and the molten zone, and EDX, which can be applied to trace the elemental profiling.

Chapter 3: Results and discussions

In this chapter, the procedures of single crystal growths of $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ will be described. Based on currently the preliminary growth experiments, the results and possible future improvements in the growth process will be discussed.

Singles crystals of $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ with doping concentrations $x=0.1, 0.17, 0.19$ are grown by the travelling solvent floating zone methods using the rod made with carefully reacted stoichiometric compounds. The starting materials consist of La_2O_3 , Nd_2O_3 , SrCO_3 , CuO mixed with appropriate mole ratios according to the expected dopings. Material powders are carefully weighed before mixing into the mortar thoroughly stirred with the pestle. It should be noted that La_2O_3 are susceptible to water absorption in air, so the original chemical powder is put into an alumina crucible and heated in an electrical furnace overnight at about 1000°C to remove excess water and possible impurities. After that, the La_2O_3 powder is quickly fetched and weighed on the electronic balance. Usually an approximate mass of around 6g is sufficient to make long rods used for the floating zone growth. It can be observed that the mass of powder is gradually increasing on the balance because of the quick absorption of water. In this case, the actual amount can be taken to be slightly less than the reading as suggested to compensate for the additional water being absorbed. Additional 3% mole of CuO is also added and mixed at this stage into the starting powder. Since CuO is easily evaporated at high temperatures, this has been proved to be in an important step to ensure the stable composition of the molten zone during the growth and drastically improved the stability of the entire growth.

The mixture of powder is then carefully transferred into the alumina crucible and goes through the conventional solid-state reaction steps to synthesize starting materials used in making seed and feed rods. The mixture is heated at about 900°C for 12h for pre-fires and then 950°C for 60h with four intermediate re-grindings to ensure maximum reaction and homogeneities.

X-ray diffraction is done between and after intermediate steps to check the phase purity and the completeness of the reactions. Fully reacted powders as determined are then packed into a balloon tube and applied hydrostatic pressure of about 4000 atm with a hydrostatics pressure kit. Rods pressured this way are partially hardened and will then be carefully taken out from the balloon tube and further sent to the furnace to be heated at 1200°C for 20 hours under oxygen flow to increase the hardness and the density. A high density of rods is important to sustain a stable molten zone during the growth, to decrease the possible permeation of solvent into the rods due to the composition gradient. It has been found out that part of the rod was melted and re-solidified at this stage, perhaps due to the slightly higher concentration of CuO mixed into the powder.

As was previously described, applying the travelling solvent growth methods requires a separate solvent disk prepared according to the range of the phase diagram suggesting stable solidification of stoichiometric pure phase. Based on the diagram for La_2O_3 - CuO, solvent disks rich in CuO of about 78% mol percentage were chosen to facilitate stable travelling growth. Powder mixed via such proportions was heated at 920°C for 15h before taken out similarly pressured and sintered into the rod shape. Disks of about 100-200 mg were cut attached to the rods for crystal growth.

The sintered and densified rods can then be hung and fixed in the image furnace to start the crystal growth as described previously in Chapter 2. Note that at especially the beginning stage of the growth process, because the equilibrium state of the molten zone

may not be quickly established, manual adjustment of the power lamp and feed or seed rates may be necessary to facilitate the continuous growth. However, once the stable growth is managed to result, any adjustment of growth parameters is not recommended at this time to disrupt the continuous growth of single domains. For the specific cuprate compound LNSCO grown in the thesis, heating of the molten zone will result in La_2O_3 as inclusions in the grown crystals. In this case, the grown crystals may break into pieces due to the moisture absorption from these secondary phases.

A total of four growths were conducted during the time for the thesis research, covering the whole range of the expected dopings $x=0.1$, $x=0.17$, $x=0.19$ planned at the beginning. The attempts have been focused on the careful tuning of the furnace parameters to help growth reach steady state as quickly as possible, and it has been observed that some may be critical for stable crystal growth. Some of the key parameters and issues for each growth have been summarized in the table below:

Trial	Rod preparation	Solvent	Growth issues
#1: Composition with $x=0.1$	Solid-state reaction as described. Rods sintered at 1100°C due to their lower melting point.	78% CuO. Nd was not substituted into the solvent.	0.5mm/h growth rate maintained. The feed rate was increased to about 0.2-0.3mm/h in 5 hours. However, -

Table 1: Summary of the previous crystal growths.

			-the growth could not continue. Large solvent boules were seen to solidify onto the seed.
#2: Composition with $x=0.19$	Rods sintered at 1200°C.	78% CuO. Nd of mole ratio $x=0.4$ was substituted into the solvent.	0.5 mm/h growth rate. It has been found out that feed rate had to be adjusted very slowly. Maintained at 0.2 mm/h in the end, however, with multiple adjustments in between. Crystal broken into pieces after exposed in air for several days.
#3: Composition with $x=0.17$	Rods sintered at 1200°C.	78% CuO, without any Nd substituted into the solvent.	Necking was performed by increasing the feed rate very slowly-

Table 1 (continued)

			-from 0.0 mm/h to 0.2 mm/h in about two days. While crystal growth can continue, slight instability within the molten zone was observed throughout the entire growth.
#4: Composition with $x=0.1$	Rods sintered at 1200°C.	78% CuO. Nd was not substituted into the solvent.	The feed rate was directly set at 0.2 mm/h and kept constant. However, the power was adjusted to keep the molten zone stable. Slight instability was still observed after that, while the growth can -

Table 1 (continued)

			-continue relatively smoothly.
--	--	--	--------------------------------

Table 1 (continued)

Longer and higher quality crystals were generally observed for the later growths. An example of a crystal with composition Sr $x=0.1$ grown in 2017 summer was shown in the photograph below:

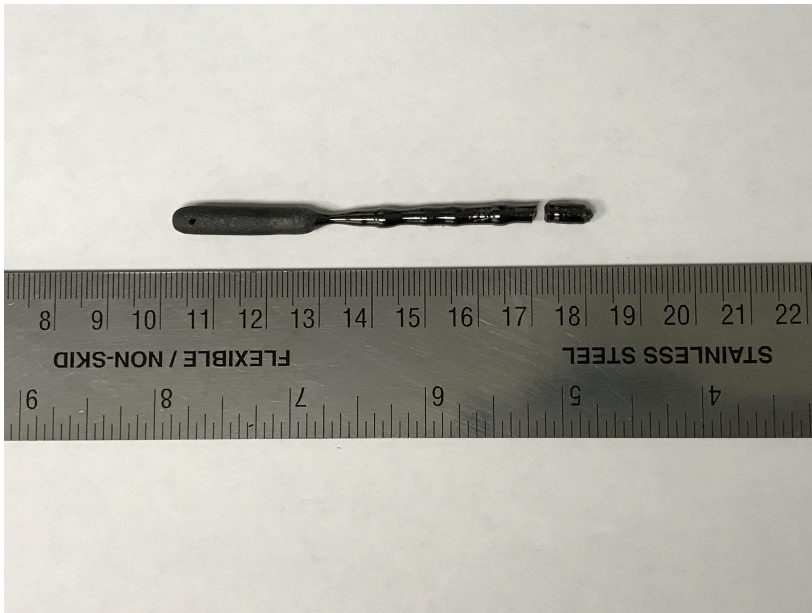


Figure 5: Photograph of an example of the grown crystal with Sr doping $x=0.1$.

It can be seen that the as-grown crystal is cylindrical shaped and show shiny and textured surfaces, which usually indicates a good quality of the crystal. Occasional break-ups may result from possible inclusions of La_2O_3 due to any power change of the lamp. The grown crystal has a diameter of about 5mm and is 5 cm long. Stable growth can continue until the entire feed rod has been dissolved, resulting in long size of the crystal.

Changes of the size of the crystal, as can be seen in the photograph, are usually due to the power changes. Any change of the power results in re-establishment of the molten zone, and crystal size changes accordingly. Note that for this crystal growth, lamp power was changed multiple times during the process.

Pieces of the crystal can be cut from the ingot and ground into powder, and then characterized via X-ray powder diffraction. An example of the diffraction patterns is shown in Figure 6:

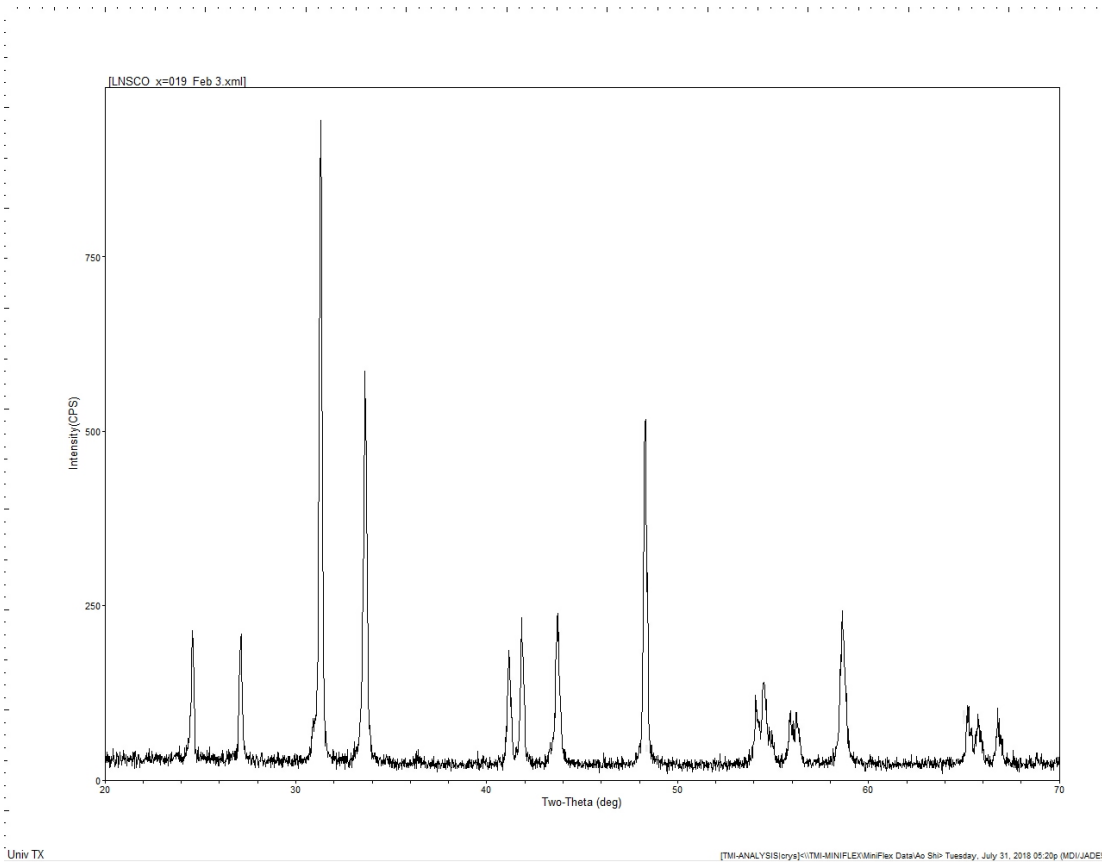


Figure 6: The pattern from X-ray Powder diffraction of a LNSCO sample with Sr $x=0.19$.

Compared with the patterns of the polycrystalline sample prepared by the standard solid state reaction, the grown crystals usually show higher and sharper peaks in XRD patterns, indicating the higher purity of the sample. To check the phase purity of the crystal, existing patterns can be read from the PDF database in the Jade software and be directly compared with the measured pattern:

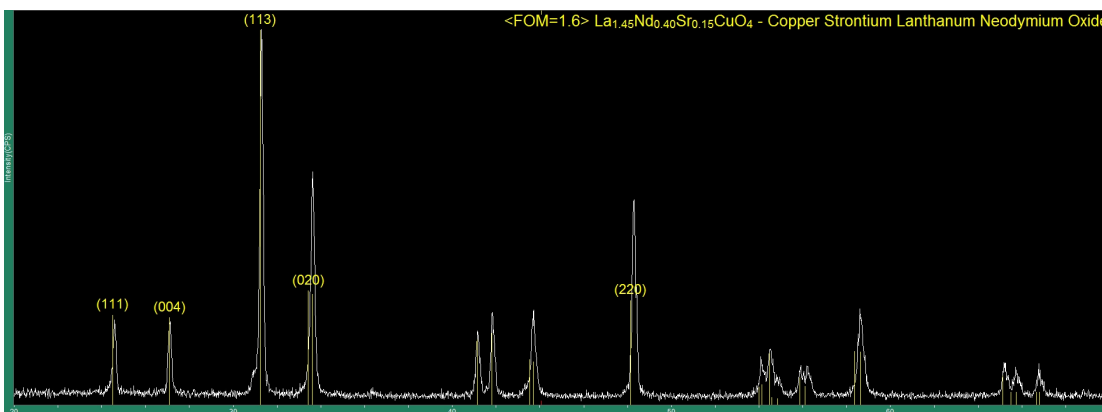


Figure 7: Same pattern, compared with the pre-saved LNSCO ($x=0.15$) data in the PDF database.

Clearly, all of the peaks can be labeled and match well with the existing pattern of the LNSCO phase. No other peaks are found indicating the crystal was grown as a pure phase. It should be mentioned that the positions of the peaks are slightly shifted compared with the pattern for Sr $x=0.15$. This should be due to the slight difference of the doping in the grown crystal. The powder showing this pattern comes from the piece of the crystal coming from the LNSCO with Sr doping of $x=0.19$. For all other trials of growth, results indicate that crystals were also grown as pure phases. This clearly indicates the equilibrium dynamics were established at the correct temperature and composition in the phase diagram and solvent has the appropriate proportion of CuO, therefore with only one pure phase of LNSCO grown. But it should be mentioned X-ray

powder diffraction has a detection limit and slight possible inclusions, for example, La_2O_3 and CuO , will not be detected in this case. This can be also confirmed by part of the crystals broken into pieces. These crystals have La_2O_3 included while not detected by XRD. Generally, these possible impurity phases should be kept in mind as all of them may influence the stability of the crystal growth, lowering the possible quality of the resulting crystals, and may show up as possible features applied with other characterization techniques.

The crystals were checked by Laue back reflection at several locations along the crystal growth direction. The diffraction patterns for the last crystal grown with Sr $x=0.1$ are shown in Figure 8:

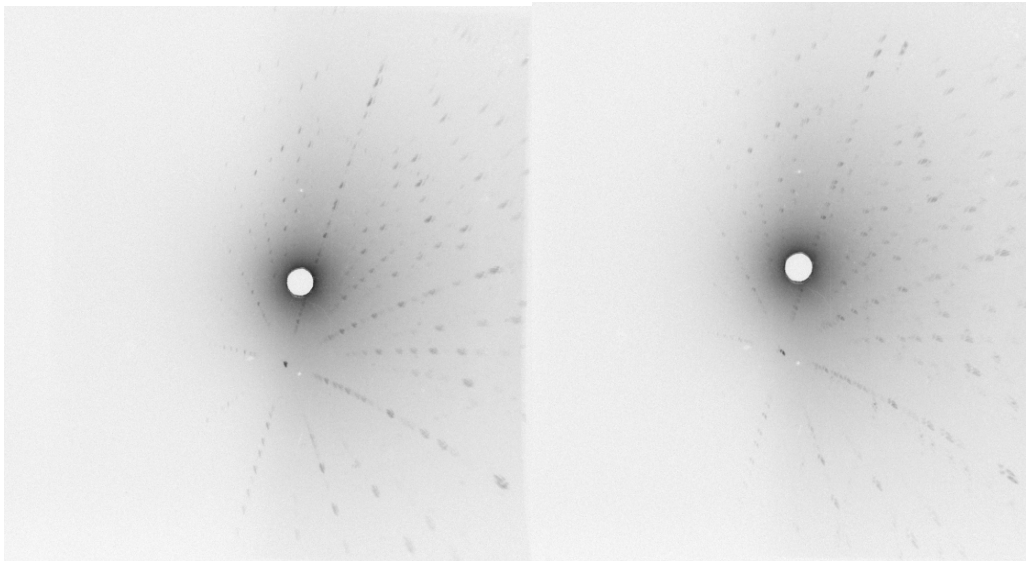


Figure 8: Laue Back reflection patterns checked at two different locations on the same grown crystal LNSCO with $x=0.1$.

Clear, round spots coming from a main single pattern, along the 001 direction, can be identified, which therefore suggests that the crystal grown is of good quality.

Moreover, the pattern has been made with the beam along the crystal growth direction, which indicates the crystal orientation along the direction. However, occasional, minor patterns blurring the overall diffraction patterns can be also observed especially noticed at the second position, indicating that the overall crystal is still not entirely of single domain. Therefore, to achieve the single domain crystal necessary for the further intrinsic property investigation of cuprate superconductivity, either: the crystal needs to be further polished and cut until a single domain piece can be identified; or: continuous improvement and optimization of the crystal growth process needs to be performed to achieve large, continuous single domain growth.

Important insights can be drawn from the previous trials of crystal growths. While due to the time scale further characterizations for example using EDX checking the detailed compositions of the crystals or the molten zone were not conducted, however as can be seen directly from the summary in Table 1: the biggest issue of the crystal growths comes from the slight instability of the molten zone. As has been observed by the author during all the crystal growth trials, even after several possible adjustments of other growth parameters, a slight excess of solids not completely dissolved in the molten zone was always observed at the interface between the feed rod and the molten zone. This always caused slight shaking of the feed rod as observed visually and suggested that the complete melting point has not been achieved. The increase of the lamp power may result in enlarging of the molten zone; however, the issue remained during all the trials of the growths.

Considering that different sintering temperatures of the rods and the compositions of the solvent tried, it can be tentatively concluded that for this cuprate compound, the preparation of the starting materials may not be the key issue to the stability of the crystal growth. Moreover, both growths with/without “necking” and no significant difference of

crystal quality were observed. Therefore, the necking process may not be particularly important the travelling solvent growth of this cuprate system. This may be attributed to the fact that for the travelling solvent growth, initial growth usually takes place by rebuilding the equilibrium in molten zone constantly adjusting the composition both in the solvent zone itself and the crystal grown, and therefore, particular change of the width of the crystal may not be directly correlated to the assistance of the single domain growth. However, it can be learnt from these trials that since the effect of any change of the growth parameters usually takes place in an extremely delayed manner, any operation or tuning of image furnace must be done carefully correspondingly for this incongruent melting compound.

Stability of the molten zone is a key factor controlling the crystal growth process, and is usually the main reason why crystal growth of a specific compound may fail with the floating zone method. While the instability after careful control of the furnace may not be severe for the later trials of the growths, ideally a large single domain can only be achieved with a completely smooth growth with the molten zone at its perfectly stable state. Reference [17] suggests several usually encountered issues for the instability of the possible molten zone:

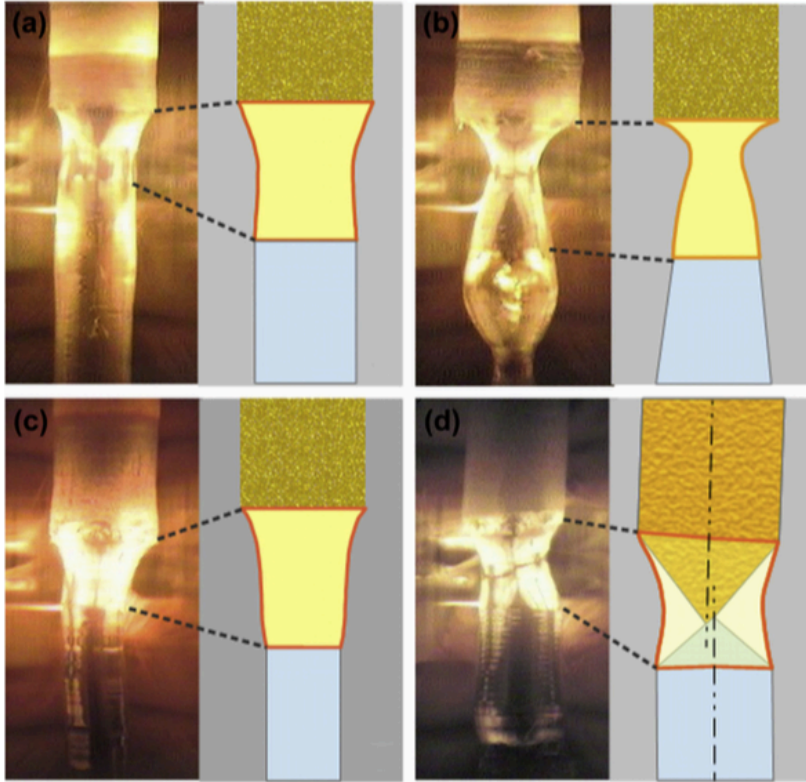


Figure 9: Shapes of the molten zones for growths of $\text{Dy}_2\text{Ti}_2\text{O}_7$. Taken from Ref. [17].
 (a) Good conditions; (b) Zone overheated; growth too slow or not enough feeding; (c) Too much feeding; temperature not high enough; (d) Power not enough, growth too fast.

These issues, frequently encountered in growths of different materials systems, can usually be directly visualized through the shape and stability of the molten zone, and results from not controlling feed and growth rate appropriately enough, or the power is not correspondingly selected carefully to ensure good thermal stability in the molten zone. During the travelling growths of this cuprate, however, the problem of (c) and (d) seems to be most frequently observed, which generally shows by slight rubbing of the two rods in the molten zone, or instability at the molten zone interface with excess solids precipitated there. These issues are usually correlated with an incorrect feed rod rate

(often by sending them too fast), or too low of the lamp power so that the complete melting point of the molten zone is not achieved. However, it should be kept in mind that the essence of the incongruent melting behavior of this cuprate compound and the place of a travelling solvent during the growths may make its dynamics completely different from the usual congruent melting oxides, as $\text{Dy}_2\text{Ti}_2\text{O}_7$ described in the reference [17].

In crystal growth via the traveling solvent floating zone method, instead of the relatively simpler dynamics of melting and re-solidifying as applicable in the congruent melting system, the growth is essentially driven by a composition gradient at the interface of the molten zone, which helps keep the rods continuously dissolved. In this case, therefore, any tuning of the growth parameters will result in new equilibrium dynamics, and thus composition difference re-established. This problem usually cannot be resolved easily, due to the change of the melting point, or the size of the crystals, as for most congruent melting systems. The increase of the lamp power, for example, may change the composition within the molten zone so as by pushing more of La_2O_3 out into the crystal grown so that the entire composition will be changed. This was frequently observed in the previously grown crystals where parts of them may break due to this same reason. On the other hand, any change of the growth or feed rate may not be simply considered as resulting in tuning the size of the molten zone or the crystal grown, but is also crucial to establishing a suitable dissolving rate appropriately matching this composition difference. In all these growths, it was observed that the feed rate must not exceed a certain limit once a fixed growth rate has been set-up; otherwise the entire molten zone would be unstable and crystal growth could not continue.

With these considerations in mind, several new growths are proposed below to explore whether some of these factors can help improve the growth condition so that a large single domain could eventually result:

- The impact of the feeding rate of the feed rod on the stability of molten zone. Apparently, for this incongruent melting system, a too fast feeding rate may result in sending the materials that may not be dissolved in the molten zone quickly enough; this may lead to the increase of the melting point at the interface of the molten zone, which created the phenomena of the feed “shaking” as observed in previous growths. To compensate for this, it may be good to explore whether the slight decrease of the feed rate in future growths may help fuller dissolving of the rods in the solvent zone. If the stability increases, higher quality of the crystals could also be expected. Previous growths all set the feed rate to be 0.2 mm/h while maintaining the growth of about 0.5 mm/h. Another strategy is to simultaneously increase the growing rate and the feeding rate, while keeping the relative ratio the same, so that the crystal size could maintain. Any decrease of the feed rod rate may unavoidably decrease the size of the as-grown crystal accordingly.
- Slight change of the amount of CuO added to the feed rod. Since the essential driving force to send the feed rod materials into the molten zone for the traveling solvent growth method is the composition gradient at the interface, any change of the feed rod compositions will have a drastic effect on the stability of the growth. It has been previously tested that adding a certain amount of excess CuO can greatly improve the stability of the molten zone, and therefore a ubiquitous 3% mole percentage amount was chosen for all growths. However, whether this amount still remains ideal for this new LNSCO system using our image furnace for growth is still to be tested. Slight increase of CuO, for example, to about 4%, may help decrease the compositional difference at the interface, which may expect to increase the dissolving rate and lower the melting point of the molten

zone, but it should also be kept in mind that excess CuO may also be embedded in the crystal grown lowering the overall quality of the as-grown crystals.

- Finally, whether the further increase of the power (even higher than the limit that has been explored in previous growths) may help increase the stability of the molten zone can be checked also. However, the result may also lead to additional La_2O_3 precipitated into the crystal as can be observed in the phase diagram with the system going into a higher melting phase. Previous growth already showed that parts of the crystals would therefore break out.

Based on the above proposed methods and continuous exploration of the new growth experiments, improvement of the stability of the molten zone, and therefore the crystallinity of the resulting crystals, would be expected.

Chapter 4: Summary

In this thesis, I showed my efforts of growing a particular cuprate superconductor $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ with dopings Sr $x=0.1, 0.17, 0.19$. In total four growths performed, the stable molten zone of and crystals of better quality have been obtained in some cases. X-ray powder diffraction indicated that the grown crystals are of pure and correct phase. Though based on the Laue-reflection technique, multiple domain patterns can still be observed, suggesting that the quality of the crystals can be further improved. The main issue is the slight instability of the molten zone, which prevents complete smooth growth. Based on the detailed observation of the situations of the molten zone, taking into consideration of the principles of the traveling solvent growth, two important issues are suggested, i.e. the rate of the feed rod, and the slight mole ratio of excess CuO added to the feed rod. Further explorations and tuning of these parameters in the new growth experiments would hopefully lead to better qualities of larger single crystals. With the continuous growth of higher quality large single crystals, further experimental studies can be conducted to provide more insight into this interesting and challenging cuprate superconductor systems showing inter-twinned phenomena between unconventional superconductivity, stipe order and quantum criticality phases.

References

- [1] Bednorz J.G., Muller K.A., *Zeitschrift für Physik B* 64, 2, 189(1986)
- [2] B. Keimer, S.A. Kivelson, M.R. Norman, S.Uchida, J.Zaanen, *Nature* 518, 179(2015)
- [3] Ch. Renner, B. Revaz, J.-Y. Genoud, K. Kadowaki, and Ø. Fischer, *Phys. Rev. Lett.* 80, 149(1998)
- [4] A.Iyo, Y. Tanaka, H. Kito *et al.*, *J. Phys. Soc. Jpn.* 76, 094711(2007)
- [5] M.R. Presland, J.L.Tallon, R.G. Buckley *et al.*, *Physica C: Superconductivity* 176, 1-3, 95(1991)
- [6] H. Eisaki, N. Kaneko, D. L. Feng *et al.*, *Phys. Rev. B* 69, 064512(2004)
- [7] O. Matsumoto, A. Utsuki, A. Tsukada *et al.*, *Physica C: Superconductivity* 469, 15-20, 924(2009)
- [8] J. M. Tranquada, J. D. Axe, N. Ichikawa *et al.*, *Phys. Rev. Lett.* 78, 338(1997)
- [9] T. Wu, H. Mayaffre, S. Kramer *et al.*, *Nature* 477, 191(2011)
- [10] R. Comin, R. Sutarto, F. He *et al.*, *Nature Materials* 14, 796(2015)
- [11] S. Badoux, W. Tabis, F. Laliberté *et al.*, *Nature* 531, 210(2016)
- [12] Olivier Cyr-Choinière, R. Daou, J. Chang *et al.*, *Physica C* 470, S12(2010)
- [13] J.-Q. Yan, J.-S. Zhou, and J. B. Goodenough, *Phys. Rev. B* 68, 104520(2003)
- [14] S. Badoux, W. Tabis, F. Laliberte *et al.*, *Nature* 531, 210(2016)
- [15] S. M. Koohpayeh, D. Fort, J. S. Abell, *Progress in Crystal Growth and Characterization of Materials* 54, 3-4, 121(2008)
- [16] S. Kimura, I. Shindo, *Journal of Crystal Growth* 41, 2, 192(1977)
- [17] H. A. Dabkowska, A. B. Dabkowski, *Springer Handbook of Crystal Growth*, 367-391.