Magnetic Order and Superconductivity in Perovskites

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Chapter 2

Sample preparation and characterization

2.1 Introduction

As mentioned in the introductory chapter, the Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ system has a large composition range of antiferromagnetism and a narrow range of superconductivity. This combination is a unique feature in the copper-oxide superconductors. It has resulted in a large number of experimental and theoretical works that discuss the intrinsic properties both in the superconducting and in the normal state [1]. For these studies, a well defined chemically and crystallographically single-crystalline sample is mandatory in order to avoid the complications from impurity effects. Several methods, such as the top seeded solution [2], the flux [3] and the traveling solvent floating zone (TSFZ) techniques [4] have been reported for the single-crystal growth. Not all techniques lead to the required quality of the sample due to inhomogeneous distributions of Ce and to the presence of impurities. Both can form a serious obstacle for the study of the intrinsic properties as they give rise to extrinsic effects such as a broad resistive transition to the superconducting state.

In this chapter, the preparation and characterization of single crystals of Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ with $x = 0, 0.08, 0.13, 0.15,$ and $0.20$ are presented in the subsequent sections. This includes a description of the TSFZ technique, of the preparation of polycrystalline ceramic material and of the growth conditions. The samples are characterized by Laue back scattering X-Ray Diffraction and by Electron Probe Micro Analyzer (EPMA). In addition to that, the structural properties of these crystals in the as-grown and in the reduced-oxygen cases are characterized by XRD powder diffraction, which analysis is based on the Rietveld refinement method. Finally, the characterization of superconducting Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ is discussed.
Figure 2.1: Crystallographic structures of the 214-type of compounds; (a) T has two apical oxygen, (b) T* has one apical oxygen, and (c) T' has none apical oxygen.

Figure 2.2: Phase diagram of \((Nd, Ce)_{2}CuO_{4}\) [5].

### 2.2 Traveling solvent floating zone technique

The 214 family has three kinds of structures, known as T, T* and T' structures with two, one and none apical oxygen atoms, respectively, as depicted in Fig. 2.1. Although they are different in structure, successful experiments to grow single-crystalline ingots of the three different phases have been reported using the same phase diagram displayed in Fig. 2.2 [5]. This phase diagram contains an incongruently melting 214 phase. Following this diagram, the expected composition can not be obtained directly from the melt. Solidification of the liquid will lead to the formation of different phases with compositions that differ from the initial composition. In order to get the desired compound from the incongruently melted phase, the solvent composition must appropriately be chosen to allow the growth process to proceed peritectically into the phase region in which the desired composition co-exists with the solvent in the liquid state.
For incongruently melting compounds, the solvent composition must change to keep the growth process along the peritectic line but not to fall into the eutectic point. This can be insured by adjusting the growth rate or the cooling speed. Maintaining the equilibrium liquid state for an excessively long time in the crucible could induce impurities from the crucible material. Therefore, a crucible-free method such as the traveling solvent floating zone (TSFZ) technique is the best choice to grow sufficient-quality and large single crystals.

The materials employed in the TSFZ technique consist of feed material (polycrystalline or densified rod), solvent and seed material (crystalline material). All these components are placed vertically at the center of the mirror furnace and enclosed in a quartz tube with a well-controlled atmosphere. Soon after the solvent is melted and the feed is connected to the solvent (in the liquid phase), the solvent floating zone configuration can be formed. In order to keep the growth stability, a homogenous temperature distribution and a mixture of the feed material in the solvent must be maintained by rotating the feed and seed rod in the opposite directions at proper speeds. Depending on the behavior of the liquid, the stability of the floating zone is obtained by controlling the size of the gap between feed and seed either by changing the power of the heating lamps or by moving the shaft. Details of all the possible processes in this configuration have been reviewed by Emmen [7].

In this thesis, the TSFZ technique is reported for a four-mirrors furnace of Crystal System Inc. The mirror has an ellipsoidal shape and is made from a high quality glass with high reflectivity and long operating life. Each mirror in this furnace has its own halogen lamp which is cooled by compressed air. The power of the lamp is controlled by a programmable controller Euroterm 903P. The maximum power of 1500
Watt for each lamp can reach a temperature of about 2000 °C. The configuration of this mirror furnace is displayed in Fig. 2.3. In this furnace, the growth can be performed in vacuum, air, pure gases of H₂, Ar, and O₂ or their mixtures (H₂ + Ar and O₂ + Ar). Those atmospheres can be applied in either a static or flowing mode at pressures ranging from 1 to 10 bar. During the growth process, the mirrors are moved in the upward direction while the shaft holding the feed and the seed remains fixed. Adjustment of the gap can be done by moving the upper shaft.

2.3 Preparation of starting polycrystalline powder and crystal growth of Nd₂₋ₓCeₓCuO₄

Polycrystalline powder with a molar ratio of 49% (Nd₁₋ₓCeₓ)₂O₃ : 51% Cu is prepared according to the phase diagram in Fig. 2.2, for feed and seed. The slightly Cu-rich composition is chosen to compensate the evaporation of Cu during the growth while a molar ratio of 15% (Nd₁₋ₓCeₓ)₂O₃ : 85% Cu is adopted for the solvent. The starting materials used in this reaction are the oxides Nd₂O₃ 99.9%, CeO₂ 99.9% and metallic Cu 99.99%. The reason of using metallic Cu is to avoid the formation of an off-stoichiometry due to the possible presence of the Cu₂O and CuO phase which may exist in CuO [6].

In the wet mixing reaction, the starting materials which are weighted according to the molar composition are dissolved into HNO₃. In our experiments, 100 ml of HNO₃ (analytic purity) is used for about 25 to 30 g of starting materials. The solution is then heated at 250 °C in order to dry with continuous stirring to attain a homogeneous mixture. The powder obtained in this process is heated at 400 °C for about 10 h to remove all the residual nitrates. Subsequently, the powder is heated at 600 °C for about 10 h to allow the formation of the reacted precursor. The calcination is performed at 900 °C for about 20 h. Finally the calcinated powder is sintered at 1100 °C for about 40 h. For each of the steps, the powder is grounded by ball milling with a few drops of ethanol as a milling agent. The powder is used to fill a rubber tube of 8 mm in diameter and 120 mm in length. This tube is then pressed by hydrostatic pressure (6 kbar) into a dense rod. This rod is zoned in a furnace with an up-down translation of 10-20 mm/h and a rotation of 5 rpm at 1100 °C for 40 h. Using this procedure, dense and homogeneously reacted materials can be obtained.

The growth of Nd₂₋ₓCeₓCuO₄ with x=0, 0.08, 0.13, 0.15 and 0.20 was performed in the four-mirror furnace using a 300 Watt halogen lamp at each mirror. For the single crystal growth of this system, the density of the feed is a very important factor. Unfortunately, rods obtained from the process described above still do not meet the
requirements due to the penetration of the liquid/solvent into the feed rod by means of capillary forces. This results in an irregular shape at the interface between the feed rod and the liquid. In order to avoid this penetration, the densified sintered rod has to be transferred through the floating zone with a high speed (40-50 cm/h) in order to assure a fast solidification process. This procedure is called the fast-scanning process. In this work, the fast-scanning process is carried out in the two-mirror NEC furnace at using either a 400 W or a 1500 W halogen lamp at each mirror. This rapid process is performed not only to get a dense feed but also to avoid inhomogeneities in the stoichiometry composition of the feed. A successful growth of Nd$_{2-x}$Ce$_x$CuO$_4$ is further obtained by using an atmosphere of mixed gases of Ar and O$_2$ with a partial pressure ratio of 8:1 and a total pressure of 2.5 bar in combination with a growth speed between 0.25 and 0.35 mm/h and a rotation speed between 25-30 rpm. By using these parameters, a stable floating zone, as shown in Fig. 2.4, can be achieved.

### 2.4 Characterization of the Nd$_{2-x}$Ce$_x$CuO$_4$ single crystals

In this work, the typical length of the as grown crystal obtained by the TSFZ technique is about 60 to 80 mm. The segment located at about 30 to 40 mm from the end is cut for characterization. The remaining part of the crystal rod, connected to the seed, normally contains small grains and deviations from the stoichiometric composition. At cutting the crystal (close to the end), sometimes a visible grain boundary becomes evident. In that case it is possible to select one grain by cleaving the sample. Typical examples of a cut crystal and a cleaved crystal are shown in Fig. 2.5. The crystallinity of the crystal is checked by Laue X-ray diffraction. The Laue X-ray diffraction pattern...
is found to be in very good agreement with the simulated pattern of the tetragonal structure (I4/mmm) with a lattice parameter obtained from a refinement of the XRD spectrum as displayed in Fig. 2.6.

All crystals produced by the different starting compositions of feed and solvent, as described above, are relatively rich in Nd or short in Cu. However, the Ce concentration is very close to the nominal value, so that the intrinsic physical properties of these Ce doped samples can reliably be investigated from these single crystals. The deficiency of Cu can be due to its extensive evaporation during the fast-scanning process, and to a difference between the concentrations of elements in the solvent and the crystal.

The composition of the crystals is checked by EPMA JEOL JXA8621. The resolution of EPMA is determined by the excitation volume of the X-rays which is approximately 1 μm in diameter and 0.5 to 1 μm in depth. Within this volume the absolute accuracy in determining the composition is about 3%, and the relative accuracy over the sample is better than 1%. The composition of the Nd$_{2-x}$Ce$_x$CuO$_4$ single crystals
Table 2.1: The nominal and the as-grown composition of the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$.

<table>
<thead>
<tr>
<th>The nominal composition</th>
<th>The as-grown composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Nd}_2\text{CuO}_4$</td>
<td>$\text{Nd}_{2.33}\text{CuO}_x$</td>
</tr>
<tr>
<td>$\text{Nd}<em>{1.92}\text{Ce}</em>{0.08}\text{CuO}_4$</td>
<td>$\text{Nd}<em>{2.29}\text{Ce}</em>{0.08}\text{CuO}_x$</td>
</tr>
<tr>
<td>$\text{Nd}<em>{1.87}\text{Ce}</em>{0.13}\text{CuO}_4$</td>
<td>$\text{Nd}<em>{1.93}\text{Ce}</em>{0.13}\text{CuO}_x$</td>
</tr>
<tr>
<td>$\text{Nd}<em>{1.85}\text{Ce}</em>{0.15}\text{CuO}_4$</td>
<td>$\text{Nd}<em>{1.98}\text{Ce}</em>{0.15}\text{CuO}_x$</td>
</tr>
<tr>
<td>$\text{Nd}<em>{1.80}\text{Ce}</em>{0.2}\text{CuO}_4$</td>
<td>$\text{Nd}<em>{1.89}\text{Ce}</em>{0.20}\text{CuO}_x$</td>
</tr>
</tbody>
</table>

Figure 2.7: A typical SEM photograph for the single-crystalline $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$.

was measured at random positions near the growth end of the crystal. The average composition was normalized to a Cu stoichiometry of one. The variation in composition for the different positions of the cut crystals is very small, indicating that the crystals are quite homogeneous. The results are listed in Table 2.1. Moreover, no second phase was observed in the sample. A typical Scanning Electron Microscope (SEM) photograph is displayed in Fig. 2.7.

2.5 The effect of Ce doping and O reduction on the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4-\delta$ structure

It is generally accepted that superconductivity in the electron-type superconductor depends on: (1) the concentration of Ce, and (2) the reduction of the oxygen content. In the presence of the Ce dopant, the lattice constant $c$ becomes smaller and the lattice constant $a$ slightly larger, without any sign of a structural transition. These properties, however, were also found in the case of oxygen reduction. In this work, a
structural refinement of XRD powder diffraction data has been carried out by means of the Rietveld method for the as-grown single crystals of NCCO with variations of Ce doping as well as oxygen reduction. In contrast to the results reported by Hor et al. [8], a difference between the lattice parameter changes in the case of Ce doping and the case of oxygen reduction is observed. The change in lattice parameters in these two cases are related to the occurrence of superconductivity.

![Crystal Structure of Nd$_{2-x}$Ce$_x$CuO$_4$.](image)

**Figure 2.8: Crystal Structure of Nd$_{2-x}$Ce$_x$CuO$_4$.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd/Ce</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>z</td>
</tr>
<tr>
<td>Cu</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(1)</td>
<td>4c</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>O(2)</td>
<td>4d</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 2.2: Atomic positions of Nd$_{2-x}$Ce$_x$CuO$_4$ in the tetragonal I4/mmm space group.

The X-ray measurements were performed on a series of single-crystalline samples of Nd$_{2-x}$Ce$_x$CuO$_4$ with $x=0$, 0.08, 0.13, 0.15 and 0.20, grown by the method mentioned in the previous section. The crystals were ground and referred as the as-grown powder, while the as-reduced powder is obtained after the as-grown powder was annealed in a flow of N$_2$ gas at 900 °C for 20 h. The X-ray diffraction is carried out by means of the Phillips diffractometer with a detector of type the PW1050, and a goniometer of the type PW1752. The measurements were performed by using a current of 40 mA and a voltage of 40 kV with 5 sec/step. The structural model for Nd$_{2-x}$Ce$_x$CuO$_4$ was refined using the Rietveld refinement code GSAS [9]. The initial values for the
lattice constants and the atomic positions were taken from Kwei et al. [10], while the anisotropic thermal parameters which describe the displacement of the atoms along the crystallographic direction were taken from Izumi et al. [11]. The structures were refined with the space group I4/mmm, yielding values for the refined lattice parameters and the atomic coordinate z for Nd/Ce.

<table>
<thead>
<tr>
<th>Ce</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>z (Å)</th>
<th>CuO-M1M1 (Å)</th>
<th>MM-M1M1 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.9404</td>
<td>12.1480</td>
<td>0.3501</td>
<td>1.8209</td>
<td>2.4322</td>
</tr>
<tr>
<td>0.08</td>
<td>3.9429</td>
<td>12.1114</td>
<td>0.3524</td>
<td>1.7872</td>
<td>2.4812</td>
</tr>
<tr>
<td>0.13</td>
<td>2.9456</td>
<td>12.0885</td>
<td>0.3521</td>
<td>1.7876</td>
<td>2.6913</td>
</tr>
<tr>
<td>0.15</td>
<td>3.9465</td>
<td>12.0743</td>
<td>0.3496</td>
<td>1.8157</td>
<td>2.4058</td>
</tr>
<tr>
<td>0.20</td>
<td>3.9467</td>
<td>12.0575</td>
<td>0.3530</td>
<td>1.7722</td>
<td>2.4844</td>
</tr>
</tbody>
</table>

Table 2.3: Structural parameters for the as-grown Nd$_{2-x}$Ce$_x$CuO$_4$.

<table>
<thead>
<tr>
<th>Ce</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>z (Å)</th>
<th>CuO-M1M1 (Å)</th>
<th>MM-M1M1 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.9435</td>
<td>12.1678</td>
<td>0.3524</td>
<td>1.7964</td>
<td>2.4912</td>
</tr>
<tr>
<td>0.08</td>
<td>3.9439</td>
<td>12.1142</td>
<td>0.3502</td>
<td>1.8142</td>
<td>2.4287</td>
</tr>
<tr>
<td>0.13</td>
<td>3.9449</td>
<td>12.0895</td>
<td>0.3529</td>
<td>1.7786</td>
<td>2.4876</td>
</tr>
<tr>
<td>0.15</td>
<td>3.9454</td>
<td>12.0825</td>
<td>0.3537</td>
<td>1.7673</td>
<td>2.5066</td>
</tr>
<tr>
<td>0.20</td>
<td>3.9463</td>
<td>12.0775</td>
<td>0.3520</td>
<td>1.7880</td>
<td>2.4628</td>
</tr>
</tbody>
</table>

Table 2.4: Structural parameters for the as-reduced Nd$_{2-x}$Ce$_x$CuO$_4$.

The refinement analysis assumes that the NCCO compound crystallizes in the T' structure with the space group of I4/mmm. The crystal structure is shown in Fig. 2.8. The atomic positions are listed in Table 2.2. The resulting structural parameters obtained for various Ce doping and oxygen reduction levels are given in Tables 2.3-2.4. The agreement factors Rwp (between 5 and 8) and Rp (around 5) obtained from the refinement are reasonably good for the spectra obtained by the conventional method described above. For the as-grown samples, a increases by 0.16 % and c decreases by 0.745 % with respect to the undoped composition while for the as-reduced samples, a increases by 0.071 % and c decreases by 0.742 % with respect to the undoped composition and as-reduced. In this system, the Nd/Ce - O(2) - Nd/Ce layers are considered as reservoir blocks. Since the fractional occupancy at the O(2) site is less than that at the O(1) sites, the change of oxygen in the reduced sample will most likely
affect the occupancy of the reservoir layer. On the other hand, the decrease in c implies a smaller radius r for the Ce ion. This leads to the valence state Ce$^{4+}$ as $r$ Ce$^{4+} < r$ Nd$^{3+} < r$ Ce$^{3+}$ [12]. The interlayer spacing within the reservoir block (2 CuOM1M1) increases as x is increased from 0.08 to 0.15 in the as-grown samples, whereas it decreases in the as-reduced samples. The shorter the interlayer spacing within the reservoir block the larger becomes the chemical pressure applied to the CuO$_2$ plane.

It can be observed from Tables 2.3-2.4 that the thickness of the reservoir block (MM-M1M1) changes drastically over the range $x=0.13$ to 0.20 in the case of the as-grown samples. This indicates that there is a competition between Nd and Ce in occupying sites within the reservoir block. In this experiment, Ce doping appears most effective in compressing the reservoir at $x=0.15$ where there is a pronounced compression effect of the reservoir block with respect to the case with $x=0$. This situation will increase the charge density in the reservoir layers. This effect disappears at $x=0.20$ where the reservoir layers recover their initial value. This expansion effect due to the larger x can be explained by the large number of lattice sites occupied by Ce atoms which are more highly charged. The saturation of the reservoir layer expansion is related to the maximum number of Nd sites that can be replaced by Ce. It is also clear from the Tables 2.3-2.4 that oxygen reduction generally has a reverse effect with respect to the Ce doping in the as-grown samples in the range from $x=0.08$ to 0.20.

In connection to the optimal value of the superconducting transition temperature at Ce=0.15, the analysis of the interlayer data shows that at this level of Ce doping, the interlayer spacing within the reservoir block reaches its minimum value, leading to a correspondingly higher charge density which is expected to facilitate the charge transport to the conduction layer. However, it is also found in this experiment that by controlling the amount of oxygen reduction at the Ce doping of $x=0.13$, the same $T_c$ can also be achieved.

In summary, the structural refinement of Nd$_{2-x}$Ce$_x$CuO$_4$ at various levels of Ce doping in the as-grown as well as the as-reduced samples will reduce the lattice constant c and increase the lattice constant a, in both cases, upon increasing the Ce doping level. The effect of Ce in the as-grown sample becomes most effective in the compression of the reservoir block, at $x=0.15$, resulting in the highest critical temperature, $T_c$, of the compound. The oxygen reduction in this material is shown to reverse the effects of Ce doping, and can be controlled to optimize the superconductivity at $x=0.15$ and 0.13 as well. This suggests that the reservoir compression may well be a key factor in understanding the mechanism of superconductivity in the electron-type superconductors.
2.6 Characterization of the superconducting \(\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4-\delta\) single crystal

It is known that the superconductivity in the \(T'\) structure is found only in the concentration between 13% up 18% doping of Ce or Th with a maximum \(T_c\) value of about 25 K after reduction of the oxygen content. In this work, the reduction of oxygen was performed on an as-grown single crystal of \(\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4\). The superconducting transition at \(T_c \sim 21\) K (with \(\Delta T_c \sim 1\) K ) as shown in Fig. 2.9 is obtained by annealing at 900 °C in a flow of \(\text{N}_2\) for about 30 h and, subsequently by quenching to room temperature. The superconducting sample remains stable after the annealing treatment. The superconductivity can be easily removed by annealing the superconducting crystal at 900 °C in air.

The temperature dependence of structural properties of the as-reduced \(\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4-\delta\) is carried out by the XRD powder diffraction from 300 K down to 5 K. The results from the Rietveld refinement are displayed in Fig. 2.10. It is clear from the
Figure 2.10: The temperature dependence of the lattice parameters $a$ and $c$, the volume ($V$), and the atomic position of Nd/Ce ($z$) for an as-reduced $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ sample. The lines are guides to the eyes. The error bars on the curve indicate the standard deviations from the corresponding average values of $a$, $c$, $V$, and $z$.

figures that the lattice parameters $a$ and $c$ as well as the volume is changed abruptly at $T_c$, and nearly constant in the superconducting state. However the positions of the Nd/Ce atom only slightly change.
References


