Chapter 6

Floating zone crystal growth of CTMO

6.1 Overview

Since single crystals maintain translational symmetry over macroscopic distances, in contrast with polycrystals, they can give us more reliable information of the structures and intrinsic properties. Therefore, many research scientists starve for a wide variety of single crystals, e.g. CTMO, high T_c superconductors, giant magnetoresistance materials, etc, in order to investigate the fundamental intriguing physics by employing the most advanced synchrotron x-ray and neutron scattering techniques, and so forth. The requirement of these techniques for the quality of single crystals (e.g. size, purity, etc.) is quite rigorous. The lack of large single crystals of CTMO has been a longstanding obstacle in the study of their fascinating physical properties.

A number of single crystal growth techniques have been used for years, e.g. floating zone (FZ), Czochralski, Bridgman, top seeded solution and gas-phase growth, etc. Table 6.1 compares two often used methods: Czochralski and FZ growth. Compared to others, the FZ method with infrared image furnace is a particularly useful one for laboratory crystal growth for preparing research samples because it is crucible-free and thus the grown crystals show the highest purity (the property of single crystals is very sensitive to the purity). The FZ method is thus widely used to grow a wide range of refractory single crystals of CTMO.

Under ideal external physical conditions, the biggest grain inside one polycrystal spontaneously grows on the expense of the smaller ones around it if the active energy is enough. In this way, it gets larger and larger. The amount of grain boundaries becomes smaller and smaller as the gradual increase in the grain size. The final state, single crystal, keeps the lowest energy. Thus it is the stablest state.

Not every compound can be formed easily. It strongly depends on the change of the Gibbs free energy of the reaction ($\Delta G < 0$, favorable; $\Delta G > 0$, unfavorable). In the earlier stages of crystal growth for a new system, it is absolutely necessary to know or to explore the phase diagram for assessing the feasibility of single crystal formation and choosing the appropriate growth parameters. Most of the CTMO have high melting points [141]. The valence state and the degree of stoichiometry of CTMO are very sensitive to the synthesis conditions [142]. Especially, they may decompose near their melting temperatures. Thus they have to be grown under controlled atmospheres with a high

Table 6.1: Comparison of two single crystal growth methods: Czochralski and Floating-zone.

Features \ Methods	Czochralski	Floating-zone
Purity	Poor	Highest
Crystal size	Large diameters easy; Large weights	Large diameters possible; Reasonable weights
Mechanical conditions	Gravity stabilizes melt and crystal	Gravity destabilizes melt and crystal; Rotation speed is critical
Thermal condition	Small gradients	Large gradients

enough pressure [143]. To grow large high-quality single crystals of CTMO continuous to be a real challenge for material scientists.

The multidisciplinary nature of single crystal growth makes it lack of scientific understanding [144], though some simulations have been performed [145]. It is thus regarded as more of a craft, or even an art than a science. This chapter is dedicated to this art.

6.2 Preparation of longer and stronger rods

To grow high-quality single crystals, the first and the most important step is to prepare the feed and seed rods. The length of ~2-3 cm for a seed rod is enough, while the longer the better for a feed rod within the limitations of apparatus.

Figure 6.1 schematically shows the process of rod preparation using the usual lopsided pressurizer. First, one has to put the powder material (black) into the mold B, and then increases the pressure N to 30-70 KN using the pressurizer A. After about ten minutes, the powder material will be pressed into a rod with the shape of the mold. The rod prepared in this way has the length of at most ~6 cm (C). With more powder, i.e. a longer rod, it will crack easily (D) due to the inhomogeneously pressed state. Having been sintered, the density of the rod is about 60-75% of the theoretical one, depending on the pressure and the sintering temperature. This method can be manipulated easily and is actually feasible to optimize the powder preparation. However, the rod prepared by this method is not the ideal one for single crystal growth.

Another apparatus for preparing rods is the isostatic pressurizer (A′) as shown in figure 6.2. One plastic cylindrical balloon (B′) is filled with ~15 g powder material (with fine particle size). One has to remove the air in the filled balloon and then squeeze it with a hydrostatic pressure of 50-70 MPa for about twenty minutes. It is hard to control the initial shape of the evacuated balloon (C′), e.g. the vertical homogeneity, especially at the two ends where the shape is usually irregular and the length perpendicular to the long direction is smaller than the averaged diameter of the rod (the corresponding circle area is decreased). That often results in the crack of the pressed rod (D′). The reason could be

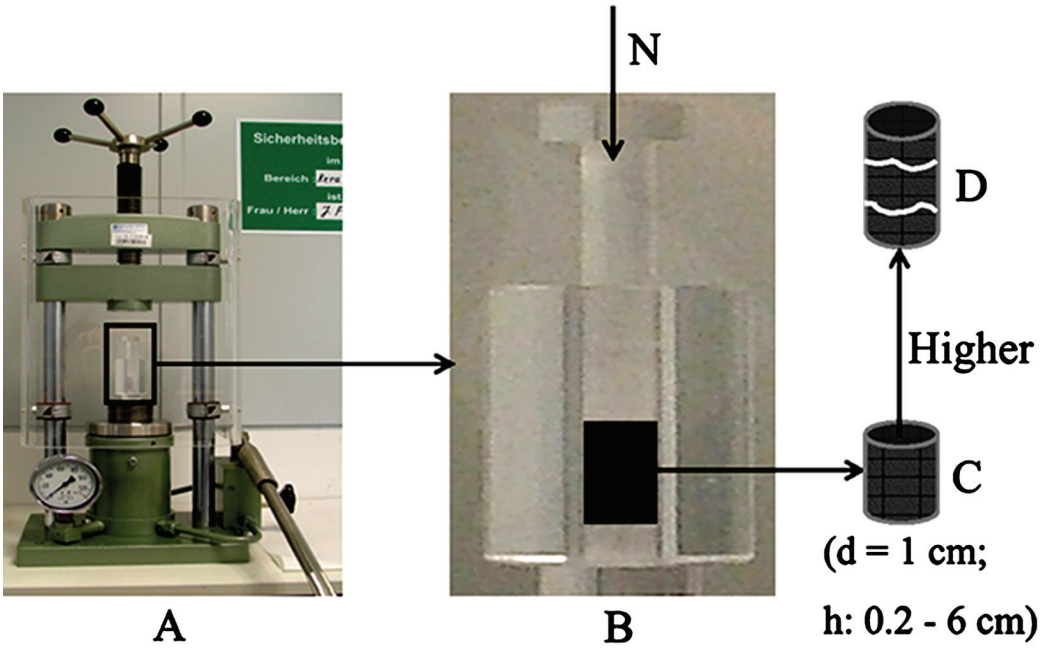

Figure 6.1: Schematic of the short rod preparation using the usual pressurizer.

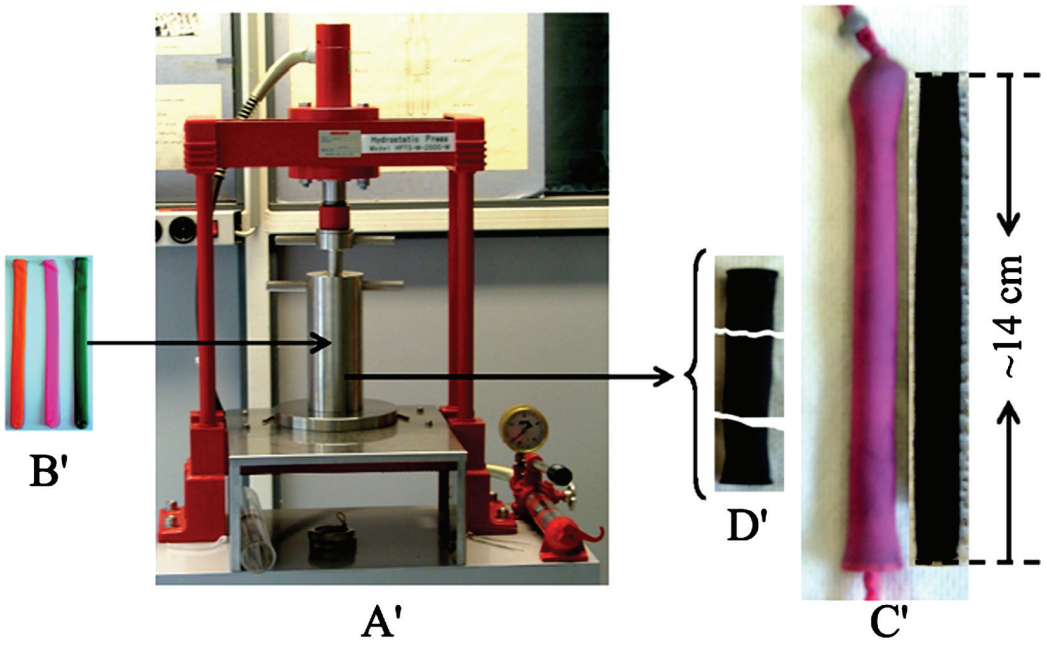

Figure 6.2: Schematic of the long rod preparation using the isostatic pressurizer.

that the added force along the long direction is not enough ($\underline{F} = \underline{P}S$, where $\underline{F}$ is the force, $\underline{P}$ is the isostatic intensity of pressure and S is the area perpendicular to the added force). In addition, the longer the rod, the more difficult the force transfers along the long direction. Sometimes, the rod is well pressed along the diameter direction, while in the long direction it is badly done. Before pressing, if we put two suitable flat plates on the

two ends of the quasi rod, the shape of its two ends can be well controlled and thus the force along the long direction can be increased largely and transferred easily. As a consequence, we can prepare the longer (up to ~14 cm) and stronger (the density of the sintered rod is up to 92% of the theoretical one) feed rods with any diameter needed.

A straight and very uniformly densified feed rod [146] with a homogenous composition distribution is absolutely necessary to achieve and keep a perfectly stable melting zone, preventing it from collapse and providing regular melting when the steady-state growth conditions of the FZ are reached.

6.3 Floating zone furnace and crystal growth

The FZ method grows single crystals by holding the melting zone through obtaining a balance between the surface tension and the hydrostatic pressure. The competing of both forces determines the shape of the melting zone. The obtained crystals are free standing and without contamination by crucible material, which compared to other methods ensures the highest purity of the grown crystals.

A new FZ furnace (figure 6.3, Crystal Systems Inc. Model FZ-T-10000-H-VI-VPO) with four IR-heating halogen lamps as the heat source and four ellipsoidal mirrors as the reflectors has been available at FZJ GmbH, Germany, since 2006 and is fully operational for the growth of CTMO. A similar furnace is also available at the Institute for Crystallography of the RWTH Aachen. Four ellipsoidal mirrors focus the infrared radiation on the focal point to result in a localized high-temperature point in the middle of the cavity, achieving crystal growth temperatures up to ~2000℃ with a homogenous temperature distribution. Attaining the maximum temperature takes about thirty minutes. The growth environment is either in vacuum or employing three different kinds of working gases (Ar, N_2 and O_2) individually or simultaneously at pressures up to 8.5 bar.

The FZ furnace is schematically shown in detail in figure 6.4, which also involves the special growth steps: (1) cleaning the whole furnace, especially around the upper shaft 1 because most of the evaporated material adheres there; (2) placing the upper shaft 1 and the bottom shaft 2 to the right positions; (3) fixing the feed rod 3 and the seed rod 4 using upper shaft 1 and bottom shaft 2, respectively, after which the two rods must be coaxial; (4) mounting the quartz tube 5 (the thickness of it is different for one-atmosphere and high-pressure growths), inside which the controlled atmosphere 6 for different growths can be used; (5) placing the two rods very close together so that the point of contact is at the center of the maximum temperature point; (6) gradually increasing the power of the halogen lamp 7 and individually rotating the two shafts oppositely (rotation speed: ~20-40 rpm, which can lead to a uniform composition distribution during growth and guarantee a homogenous temperature distribution in the melting-zone, producing a straight cylindrical crystal); (7) the focused radiation heat by the ellipsoidal mirror 8 will develop a liquid solvent phase called melting zone 9 which is suspended between two rods; (8) moving the two shafts with respect to the mirrors (the speeds are particularly important and different for various compounds) slowly down, the feed rod will be dissolved little by little while the material will solidify on the top of the seed rod; (9) hopefully, after long-time growth, the crystal 10 grown will become single crystalline; (10) after growth, normally some of the evaporated material 11 has sublimated on the wall of the quartz tube.

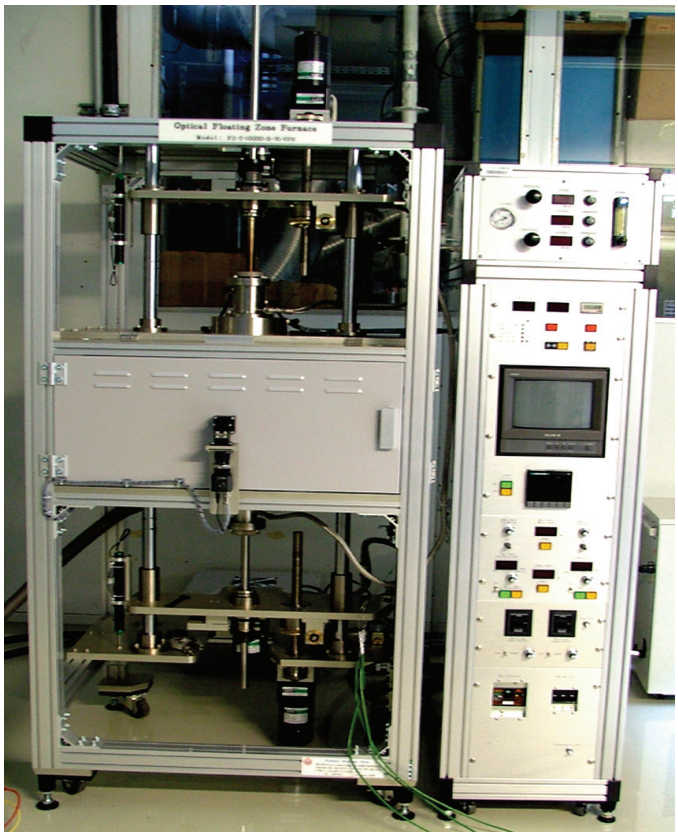

Figure 6.3: FZ furnace operated at FZJ GmbH, Germany.

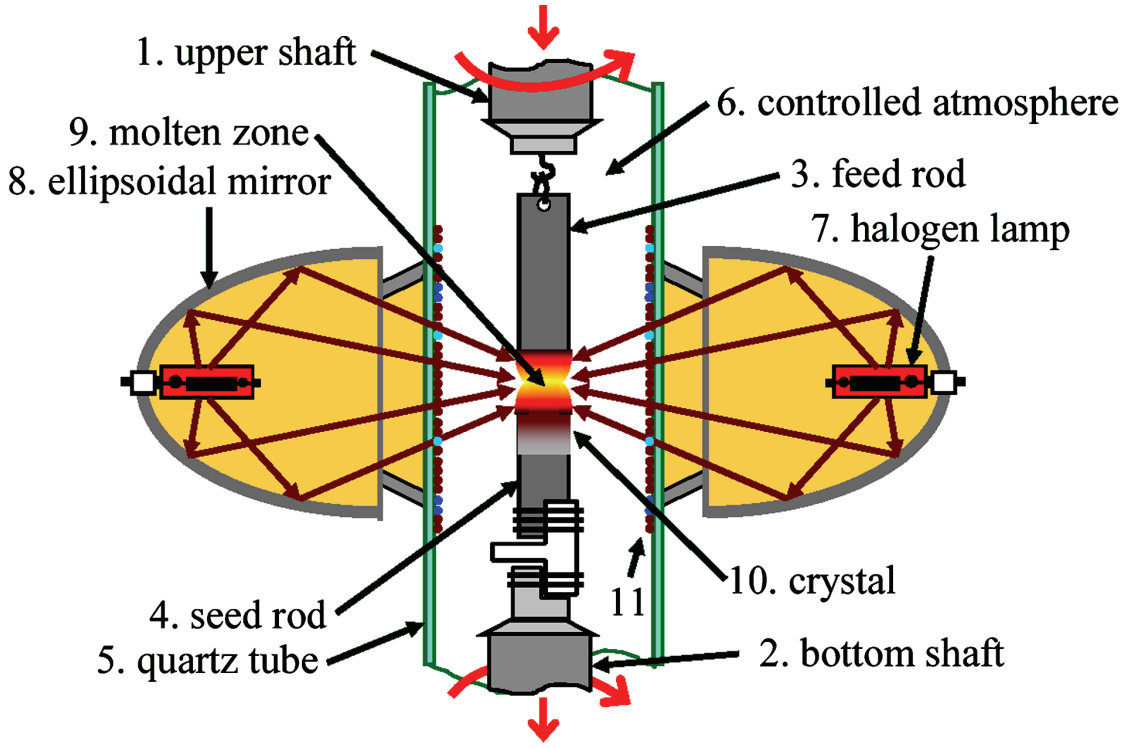

Figure 6.4: Schematic sketch of the FZ furnace and the growth process.

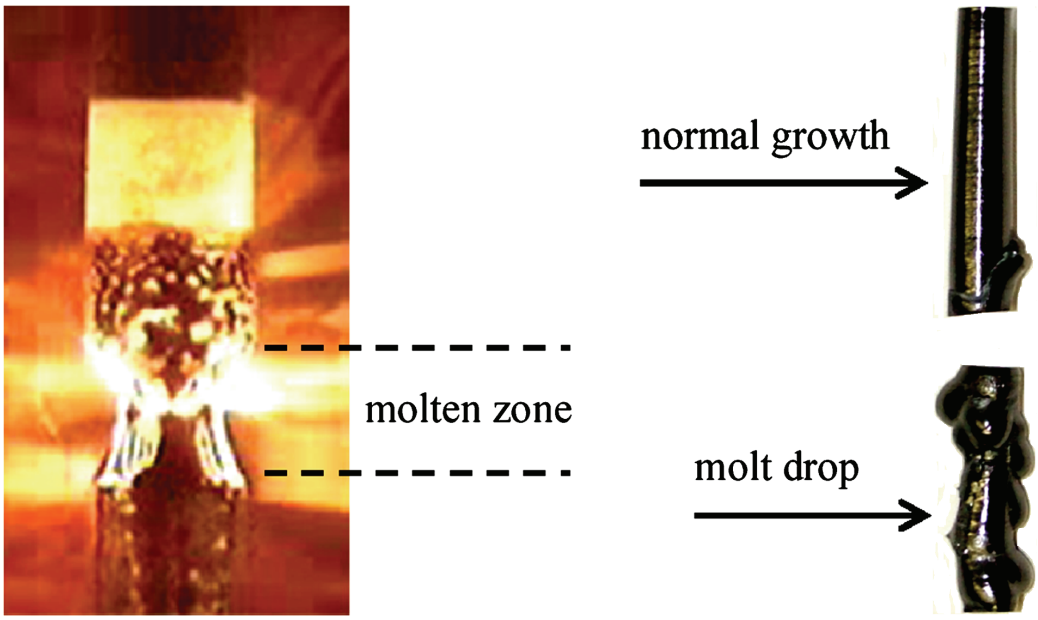

Figure 6.5: (left) An image of a stable melting zone [147]. (right) The crystals grown under a stable state (normal growth) and an unstable state (molt drop).

To form and maintain a stable melting zone between feed and seed rods is the prerequisite for normal single crystal growth. The diameter of the crystal grown is usually larger than that of the feed rod due to the pear shaped melting-zone volume. In order to keep a melting zone stable, the mass of the material melted from the feed rod must be equal to the mass sum of the crystalloid material on the seed rod and the evaporated material [148]. The length of a melting zone has a maximum [149], above which the melting zone will collapse. The shape of the liquid solid interface near the seed rod is a good indicator to direct the crystal growth [150]. When temperature is right at the melting point of a sample, it is isothermal. If it is concave to the melting zone, the crystal growth can be developed. To achieve this, the speeds of lowering the feed and seed rods should be controlled independently. Decreasing the temperature fluctuation on the melting zone is critical.

An actual picture of a good growth state is shown in the left of figure 6.5. With this normal growth state, we can keep the melting zone quite stable for long time and get a good result of growth (right-top). Otherwise, e.g. the temperature is too high, some big blobs will spill over from the melting zone sometimes, just sticking on the surface or directly resulting in the separation of feed and seed rods (right-bottom). Carefully controlling the temperature (even only several Kelvin) is absolutely important to avoid this problem. Furthermore, there are another two big problems appearing in the crystal growth with FZ method: (i) The evaporation of some elements or their compounds, e.g. manganese, especially when the temperature of a melting zone is close to their boiling temperatures. Some of the evaporated material deposits on the cold wall of the quartz tube. After growth, it can be collected and identified (XRPD) if enough amount is available. This is the important information to optimize the crystal growth. This problem can be diminished by using a high-pressure atmosphere or arbitrarily adding somewhat excess raw material to compensate for the mass loss by evaporation during melt growth. (ii) The

formation of cracks in crystals grown. This can be diminished by choosing an appropriate growth speed [151] and prolonging the process of cooling to room temperature after growth.

6.4 Necking technique

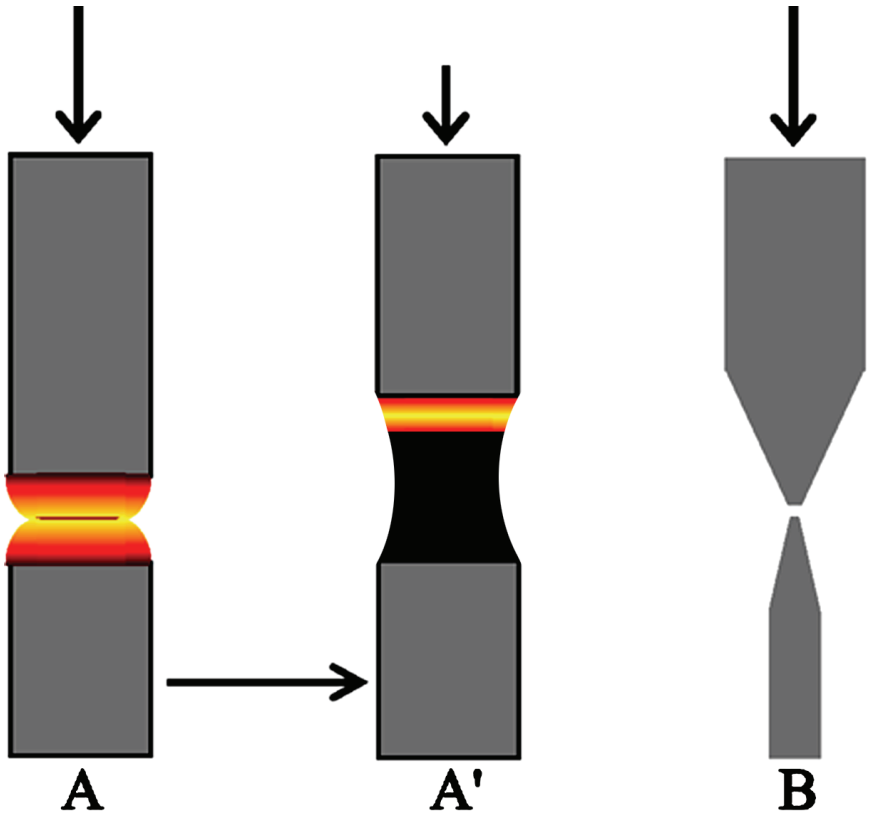

Figure 6.6: Schematics of the necking technique (A and A′) and the initial shape of feed and seed rods (B).

For a new compound, the initial crystal growth has to be performed on the polycrystalline seed rod. This makes the crystal growth much more difficult because a polycrystal has too many spontaneous nucleation sites.

Figure 6.6 (A and A′) shows one method named necking technique used to select one seed grain. After forming a stable saturated liquid FZ between feed and seed rods (A), we reduce the lowering speed of feed rod whilst keeping that of the seed rod higher. This step makes the crystallization export from the melting zone to the seed rod larger than the solvent import from the feed rod to the melting zone. Thus, the diameter of the grown part will become smaller and smaller. This process is continued until the diameter is ~2-3 mm. Then we can recover the lowering speed of feed rod little by little (A′). The purpose of this technique is to grow a small perfect single crystal (during the process of decreasing diameter) around which we can later grow a larger one. However, this technique is very hard to manipulate. It entails slow and painstaking work. Practice makes perfect.

Only experienced crystal grower can do it.

An alternative method is shown in figure 6.6 B, i.e. arbitrarily reducing the contact area between feed and seed rods through designing proper end shapes. The shape designed here for feed and seed rods (already tested in our growths) can not only decrease the dislocation density, improving the crystal perfection, but also decrease the axial temperature gradient for seed rod, especially in the top part.

Both methods have a similar effect on improving crystal quality. For growing a larger single crystal, it is essential that the seed rod used for growth should be single crystalline [152]. In this case, a good single crystal growth mode can be developed. Such a kind of seed crystal can be obtained from the single crystal grown previously.

6.5 Characterizations

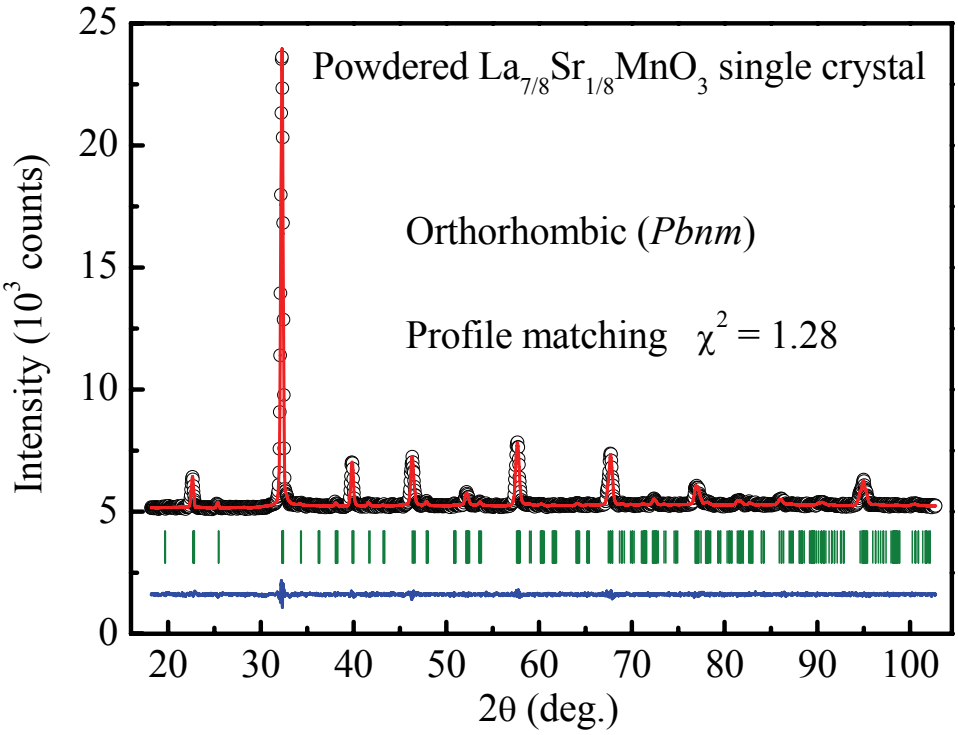

Figure 6.7: Profile matching of the XRPD data of a powdered $La_{7/8}Sr_{1/8}MnO_3$ single crystal at room temperature shows no appearance of impurity phase within the detection accuracy.

Accurate characterization is quite indispensable to optimize the crystal growth, e.g. crystal composition, especially the oxygen content measured by iodometric titration method, high sensitivity TGA or ICP-OES and infrared detection methods, phase purity and structures determined by XRPD (figure 6.7), SQUID (figure 6.8) and physical property measurements (PPMS), etc.

According to the feedback of characterizations on the properties of crystals, we can improve the quality and size of the crystals by adjusting and changing the growing parameters. For example, from the measurement of oxygen content in grown crystals we

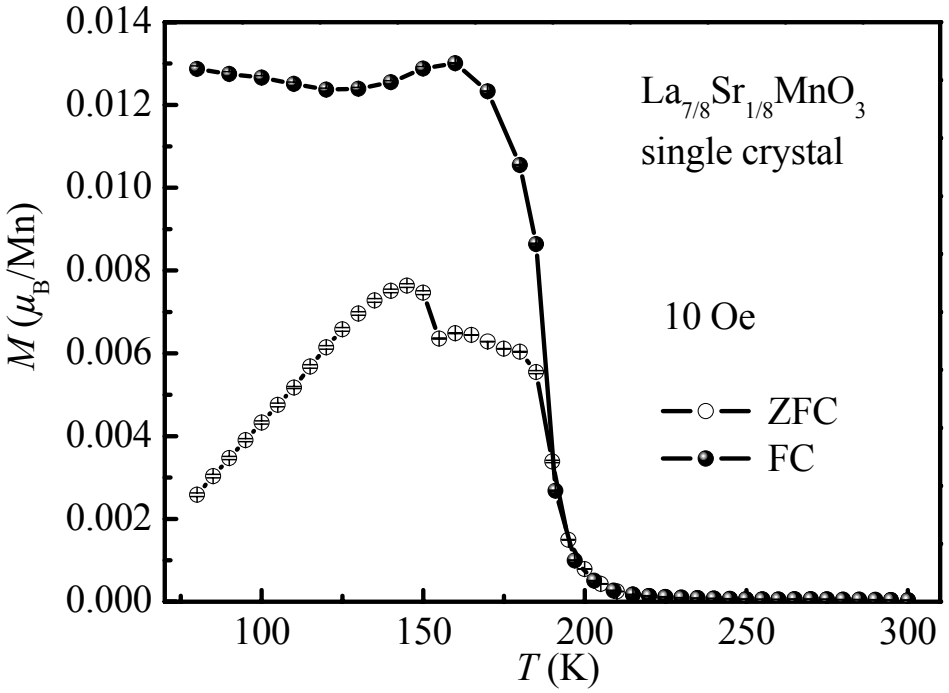

Figure 6.8: Magnetization *M* measurement with SQUID shows that there are the expected and sharp phase transitions, indicating a good quality of the single crystal.

can adjust the concentration of oxygen gas in the growing environment; from the observation of the crack degree we can change the growth speed and so on.

After obtaining a single crystal, it can be oriented to a particular crystal direction by Laue camera, cut into desired shapes by diamond cutter and polished in the determined orientation by a polishing machine for various subsequent measurements. Different studying techniques demand different single crystals, e.g. the measurements of magnetic and transport properties by PPMS require a high-purity small single crystal, the structure determination by powder diffraction needs a powdered single-crystalline sample, resonant x-ray diffraction demands the single crystals with good surface quality and a large volume (~cm^3) is the prerequisite for neutron scattering in order to get a good experimental signal.

6.6 Summary

The procedure of single crystal growth by FZ method is summarized as follows:

(1) Weighing, ball mixing and milling and calcining the raw powder materials using the method described in detail in chapter 5.
(2) Isostatic pressing the precursor powder materials into desired feed and seed rods and sintering them.
(3) Carefully mounting and pre-melting the sintered rods.
(4) Choosing the suitable growth parameters and forming a stable melting-zone.
(5) Crystal growth by lowering the feed rod and the seed rod independently.

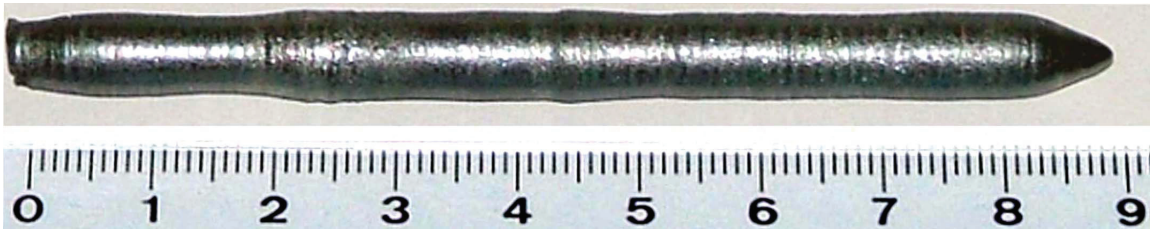

Figure 6.9: One manganite crystal grown at Institut für Festkörperforschung, FZJ GmbH, Germany.

To explore and optimize the growth parameters for a special kind of material usually takes a long time. This process strongly depends on your experience. Thus single crystal growth is a time-consuming and labor-intensive project. However, once you acquire the optimal conditions, it can be grown as a batch production.

Utilizing the FZ method, so far series of single crystals of $La_{1-x}Sr_xMnO_3$, $La_{1-x}Ca_xMnO_3$, $TbMnO_3$ and $GdMnO_3$ have been grown successfully with good quality at FZJ GmbH, Germany [153]. Figure 6.9 shows one representative single crystal (manganite). We will continue to focus on the growth of large, high-quality single crystals of CTMO, metals and alloys and to explore some new interesting compounds by the FZ and CZ techniques. With them, the electronic and magnetic properties have been investigating by complementary neutron and synchrotron radiation x-ray scattering methods at the instruments of the neutron source at FRJ-II in Jülich (substitution is the JCNS-Jülich Center for Neutron Science in Munich), at the Institute Laue-Langevin (ILL) in Grenoble, at the Synchrotron Radiation Sources in Berlin (BESSY), Grenoble (ESRF) and Argonne, USA (APS).