

Preface

The key point in condensed matter science is the discovery of new class of compounds with interesting features in physics and chemistry, such as structure, electronic properties, magnetization and superconductivity. The first superconductor of mercury was discovered dropping to zero resistance at liquid helium temperature of 4.2 K by Heike Kammerlingh Onnes, a Dutch physicist from Leiden University in 1908. After half a century, Bernd Matthias et al. found superconductivity at 23.3 K in Nb_3Ge with the cubic A15 structure in 1967. Almost no one, least of all Bernd Matthias who discovered more than a thousand superconductors, imagined superconductivity in such materials at that time.

About 80 years passed, superconductivity remained a property of metals at very low temperatures. A breakthrough in the history of materials science came in the 1980s, the $T_c \sim 30$ K in $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$ ceramics was discovered by Bednorz and Muller. Sleight and co-workers found $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (1989) at 34 K. This remarkable discovery has renewed the interest in superconductive research. One major point to superconductivity in these materials is the mixed valence of Bi and Cu. These compounds are structurally derived from the perovskite type, and only shortly later materials with so far unimaginable critical temperatures were discovered. The most prominent is $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) with a critical temperature of 92 K, well above the boiling point of liquid nitrogen. The up-to-date highest transition temperature close to 135 K was observed in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ ceramics in 1990s.

In spite of the immense scientific efforts on the cuprate-based materials with more than one hundred thousand publications till now, the detailed physical mechanism still remains uncertain. Hence, the late discovery of superconductivity in non-cuprate compounds is paid a great attention: The rare earth transition metal borocarbides (1994), the unusual features in conventional superconductors; high transition temperature $T_c \sim 40$ K in MgB_2 (2001), an ordinary s-p metal; sodium cobaltate Na_xCoO_2 (2003), a strongly correlated electron system. Apart from the high transition temperature of 40 K, two-band superconductivity was the other

unexpected phenomenon in MgB_2 which is the only superconductor with substantiated theoretical and experimental evidence for two-band superconductivity.

An “iron age” came in 2008. The discovery of a new family of high critical temperature iron and arsenic superconductors (FeAs) marked a new major revolution in the world of superconductivity. The new compounds, which do not contain copper (Cu) but have iron (Fe), arsenic (As), oxygen (O), and fluorine (F) will help scientists to solve some of the mysteries in the area of solid-state physics. These compounds reveal many properties similar to high- T_c cuprates, and at the same time superconducting state has multiband character. The experimental investigations revealed a great variety of “exotic” physical properties in the above-presented compounds such as multiband and anisotropic effects in the superconducting state. Detailed comparison of the available data for new class of superconductors, especially with the high- T_c cuprates, might be helpful to improve our present incompetent understanding of challenging novel members of the rich and rapidly growing family of superconductors.

This book deals with the new class of materials of unconventional superconductors—cuprate compounds, sodium cobaltates and iron pnictides. It gives a major review of preparation, synthesis and growth of high-quality single crystals, as well as their characterization to achieve the new perspective of high- T_c superconductors and deeper theoretical understanding of superconducting mechanisms. There is an increasing number of fundamental properties of these compounds which are relevant to future applications, opening new possibilities. The layout of this book consists of five chapters. Chapter 1 is devoted to the description of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{Ba}, \text{Sr}, \text{Ca}$) cuprate superconductors. In this chapter, the growth technique including its up-to-date improvements with respect to the detailed growth method is discussed. Large and high-quality $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ single crystals were produced by traveling solvent floating zone (TSFZ) technique. The compounds show a simple layered structure of CuO_2 planes featured with hole-doping dependent anomalies. The doping effects of $\text{M} = \text{Ba}$ and Sr on the superconductivity in the compounds, especially at certain specific *magic* hole concentrations, are given.

Chapter 2 gives a generalization of the growth of high-quality and centimeter-sized YBCO and REBCO ($\text{RE} = \text{rare earth}$) single crystals using either flux or top seeded solution growth (TSSG) method. The superconducting behavior of YBCO shows a “dome” shape when under-, optimal-, and over-doped respectively to deficient, optimum, and over-doped oxygen contents in the compound. The oxygen content of the crystal can be tuned by post-growth treatment of oxygenation/deoxygenation. The as-grown single crystals exhibit twin domains and can be detwinned by ferroelastic polling and enabled to probe the charge reservoir in the CuO_2 planes. $\text{YBa}_2\text{Cu}_4\text{O}_8$ is another important single crystal for the study of its chemical and physical properties, since it is twin-free and shows higher thermal stability with oxygen stoichiometry. The KOH flux growth of $\text{YBa}_2\text{Cu}_4\text{O}_8$ single crystal provided a simple way to access the reasonable size of samples. In this chapter, we present detailed procedures for the best quality crystal growth. Various attempts to improve the crystal quality are described. Large single crystal growth of some other rare earth cuprates is also presented in this chapter.

In Chap. 3, we have summarized the growth of $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ (denoted as 2201 for $n = 1$, 2212 for $n = 2$ and 2223 for $n = 3$) single crystals, which has been hampered by the complexities of the materials and the lack of their phase diagrams. The most common crystal growth technique adopted for these oxides is the “flux” method, where the starting materials are dissolved in a melt, which is usually formed by excess of CuO , Bi_2O_3 , or KCl/NaCl mixture. The crystals are produced by slow cooling of the melt. This method, however, suffers from several drawbacks: (1) crystals are contaminated with a crucible material, (2) crystals are difficult to detach from a crucible, (3) crystals contain flux inclusions. In most cases these drawbacks can be overcome by the traveling solvent floating zone method. Moreover, this method is suitable for growing crystals of incongruently melting compounds and has been thus successfully used to grow large crystals of the high- T_c $\text{La}_2\text{Sr}_x\text{CuO}_4$ and $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ ($n = 1, 2$, and 3) superconductors. In this chapter, we describe the growth of large, undoped and doped, high-quality Bi-2201, Bi-2212, and Bi-2223 crystals as well as their characterization.

Chapter 4 presents a systematic study on growing single crystals of Na_xCoO_2 ($x = 0.32\text{--}1.00$) and hydrated $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ ($x = 0.22\text{--}0.47$, $y = 1.3$). The experiments demonstrate that nearly pure α - ($x = 0.90\text{--}1.00$) and α' - ($x = 0.75$) phases of Na_xCoO_2 large crystals could be obtained using the optical floating zone method. The detailed processes of Na-extraction and hydration in the crystals to expand the c -lattice parameters are presented. A review on the single crystal growth of Na_xCoO_2 family and the hydrated cobaltates becoming superconductors is described in this chapter. The property of the parent crystal and the superconductor derived from them is also reported.

The last chapter of the book, Chap. 5, is devoted to the “iron age”, i.e., superconducting pnictides and chalcogenides. This chapter focuses on the various single crystal growth techniques applied to the new class of high-temperature superconductors, iron-based layered pnictides, such as the parent compounds AFe_2As_2 ($A = \text{Ba, Sr, Ca}$) (122), hole-doped $\text{A}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, electron/hole-doped $\text{AFe}_{2-x}\text{M}_x\text{As}_2$ ($M = \text{Co, Ni, Mn, Cr}$), isovalently doped $\text{AFe}_2\text{As}_{2-x}\text{P}_x$, $\text{A}_x\text{Fe}_{2-y}\text{Se}_2$ ($A = \text{K, Rb, Cs}$) (122), the chalcogenides $\text{Fe}_{1-\delta}\text{Te}_{1-x}\text{Se}_x$ (11), AFePn ($A = \text{Li and Na; Pn = P and As}$) (111), Ln(O/F)FePn (1111) and type $(\text{Li}_{1-x}\text{Fe}_x)\text{OHFe}_{1-y}\text{Se}$ (FeSe1111). Detailed single crystal growth methods (fluxes, Bridgman, floating zone), the associated procedures, and their impact on crystal size, quality, and physical properties are demonstrated. A number of detailed growth parameters on FeSe1111 layered superconductors using hydrothermal growth for ion-exchange method are also included.

This book has been written aiming to provide materials scientists with an in-depth overview of the past, present, and future of high-temperature superconductors. Specialist readers will be given updated information on the research forefront of the study of various high- T_c families and some hints on the possibility of enhancing T_c and on finding new high- T_c compounds. The high- T_c superconductivity is real and there is no reason that T_c does not increase beyond 135 K. So, it is a realistic challenge in materials sciences to search for new superconducting

materials with higher T_c and/or to enhance T_c of the known superconducting materials. A message that the author would like to pass to researchers, especially young researchers and graduate students, is not to give up the challenges to the problems of high-temperature superconductivity.

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