Rare Metal Materials and Engineering
Volume 50, Issue 2, February 2021
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2021, 50(2): 0425-0429.

ARTICLE

Large FeSe Single Crystal Growth and Its Superconducting Property

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Abstract: Large crystals with a typical size of 7 mm×2 mm×2 mm were obtained simply by KCl flux with a controlled temperature gradient inside the flux. Superconducting tetragonal β-FeSe phase with the basal plane of (101) is identified by X-ray diffraction analysis. The super large crystals show outstanding superconducting performance with transition happened at 9.05 K according to the DC magnetization measurements and broad resistive transition to zero resistance at 9.91 K with an onset temperature of 15.26 K. The research provides a convenient method to synthesize large FeSe single crystals which is promising in investigations of FeSe-based superconductors.

Key words: FeSe; single crystal; KCl flux

Superconductors have attracted tremendous interest due to their special characteristics like zero resistance effect and Meissner effect, showing huge potential in fields of power generation and transmission, energy storage and microwave devices[1]. As one of the iron-based superconductor family, compared with the first discovered La[$O_{1-x}F_x$]FeAs with superconductivity at 26 K[2], FeSe has a simple structure with rich sources, non-toxicity and easy preparation with lower superconducting transition temperature T_c of 8 K[3]. Therefore, many studies focus on how to improve T_c. Even though several attempts have been made on interface effect of single-layer FeSe films[4] and intercalation of alkali, alkali earth and rare earth elements[5-12], enhancement of T_c is restricted because the underlying superconducting mechanism of FeSe is not explicit, and the mechanism studies are mainly obstructed by the restriction of crystal growth. How to prepare large FeSe single crystals of high quality becomes a critical issue.

To solve this problem, various techniques are adopted for the FeSe crystal growth. Vapor self-transport method is often used to attain crystals of high purity and large size, but it is quite time-consuming (over a month) and sophisticated equipment like the three-zone furnace is necessary, leading to expensive cost and poor efficiency. For example, Patel et al[13] spent more than 35 d to obtain crystals with lateral dimension of 1~2 mm and thickness of tens of micrometers by vapor self-transport method. The optical zone-melting technique is another traditional and useful method to synthesize large crystals (~1 mm×3 mm) of good quality in a shorter time. However, the components of an optical floating-zone furnace including halogen lamps and rotary sample holder are more complicated[14], resulting in difficulties in the selection of experimental parameters and operations. Besides, FeSe crystals can grow in a solvent such as KCl and NaCl[15-17] solution heated in a normal furnace by flux method. Though lack of temperature gradient and fast cooling rate result in smaller crystal size, this simple, fast and convenient technique is still popular in the fields of synthesis of FeSe superconductors.

It is known that the growth of single crystals includes the process of nucleation and growth, in which undercooling plays

Received date: February 23, 2020
Foundation item: National Natural Science Foundation of China (51590893, 51788104); National Key R & D Program of China (2017YFA0700705); 1000 Plan Program for Young Talents of China
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an essential role in affecting nucleation rate and growth rate. Based on this concept, large single crystal was successfully obtained by a modified flux method using KCl as solvent in this research. With a controlled temperature gradient and a slow cooling rate, under the specific undercooling condition, FeSe crystals with dimensions of 7 mm×2 mm×2 mm were successfully grown. The crystal structure was analyzed by X-ray diffraction and superconducting properties were verified by both magnetization and resistivity measurements.

1 Experiment

Powders of Fe (Sinopharm Chemical, spectroscopically pure), Se (Aladdin, 99.99%) and KCl (Beijing Chemical, analytically pure) were ground and mixed with the molar ratio of Fe:Se:KCl=1.01:1:10. The KCl powders were heated to 450 °C before mixing to remove traces of moisture. After the mixture of Fe, Se and KCl (about 9.5 g) was pressed into pellets, it was easily sealed in an evacuated round-bottom quartz tube with an internal diameter of 17 mm. Then the quartz tube was placed in an alumina crucible filled with alumina powder to provide temperature stability. The temperature of the furnace was increased to 840 °C at a heat speed of 100 °C/h and held for 30 h to homogenize the solution. It was cooled to 820 °C in 1 h to provide supersaturated nucleation. Then the solution was slowly cooled down to 770 °C in 125 h then rapidly cooled down to 400 °C in 1.5 h. After being held at 400 °C for 24 h to stabilize the tetragonal phase, the sample was quenched in water. By breaking cooled quartz tube and dissolving mixtures in deionized water, FeSe crystals were obtained. The crystals were then rinsed in alcohol and dried in an oven. Washing crystals may be harmful to the crystals but no visible damage was found in this research.

Crystals were grown in a small box furnace (KSL-1100 from Hefei Kejing Material Technology Co., Ltd). Morphology of the crystals was observed by scanning electron microscopy (SEM, Merlin Compact, Zeiss) and element distribution was characterized by energy dispersive spectroscopy (EDS, Oxford Instrument). X-ray diffraction (XRD) measurements of powder (crushing crystals into fine powder) and single crystals were conducted at room temperature on X-ray diffractometers (V2500 and Spider). Magnetic and resistivity measurements were carried out using a magnetic property measurement system (MPMS) and a physical property measurement system (PPMS) of Quantum Design.

2 Results and Discussion

The large crystals of FeSe were fabricated by temperature-gradient flux method where the temperature program is carefully designed to create the undercooling condition. The furnace was first heated to high temperature (840 °C) to dissolve Fe/Se mixtures as much as possible and rapidly cooled to 820 °C to form the undercooling condition. Then the slow crystallization process continues until temperature reaches the melting point of KCl, 770 °C. Because the superconducting tetragonal phase maintains stable between 300 and 455 °C[17], crystals are held at 400 °C for 24 h followed by quenching. To maintain temperature stability, alumina powder around the bottom of the quartz tube was used. Furthermore, it is worth emphasizing again that the temperature gradient plays an important role in crystal growth. To investigate this effect, two thermocouples were applied to measure the temperature difference (ΔT) between the surface temperature (T_s) and bottom temperature (T_b) of the mixture. The definition of ΔT is shown in Fig.1. During the crystallization process, the measured value of ΔT is 14±1 K. T_s is higher because the surface of the mixture is closer to the heating element of the furnace. Crystals grow from the hot side to the cold side and larger ΔT leads to faster nucleation rate and growth rate of the crystals. This relatively large temperature gradient significantly affects the crystal growing process, contributing to the final large size of the crystals.

Fig.2 shows the appearance of the FeSe crystals broken from a large crystal. The crystals of 2~7 mm in length and 2~3 mm in thickness have irregular shapes and all FeSe crystals exhibit a smooth and shiny surface. One side of the crystals is the cleavage plane and the other side is the arc surface which is grown by the bottom of the quartz tube. SEM and EDS analyses of the FeSe crystals are shown in Fig.3, which indicate the layered structure of the crystals and uniform distribution of almost equivalent amount of Fe and Se elements.

As shown in Fig.4, the XRD pattern of FeSe crystal powder is fitted to the tetragonal space group P4/nmm of the β-FeSe. Fig.5 illustrates the XRD pattern obtained from a cleavage plane of FeSe crystals. A sharp and intense peak (101) at 2θ=28.50° and a weak reflection of (202) at 2θ=59.16° belong to the tetragonal phase. It is easy for FeSe crystals to cleave along the (101) orientation[18]. The main diffraction peaks in both crystals are found to shift slightly to a lower 2θ compared to the standard values, indicating an increase in the lattice parameters

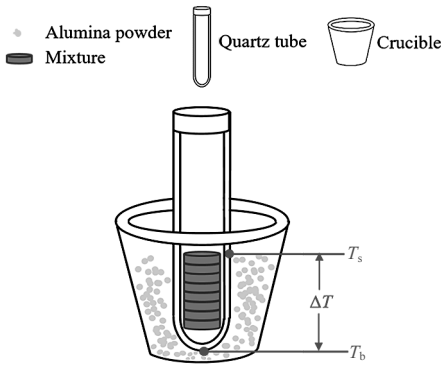

Fig.1 Schematic diagram of the temperature difference (ΔT) between surface temperature (T_s) and bottom temperature (T_b) of the mixture

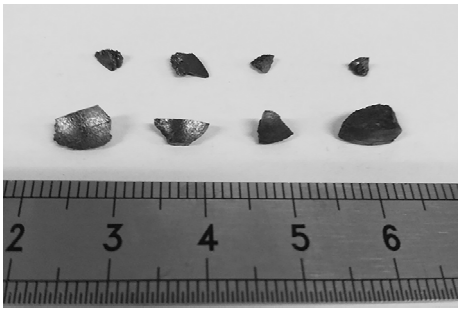

Fig.2 Typical FeSe crystal pieces

(0.313 nm for (101) face). Peaks of the hexagonal phase are also observed in both patterns, showing possible existence of a small amount of the secondary phase. The hexagonal phase may appear during crystal growth at high temperatures and can be reduced by further annealing. Fig.6 shows the well symmetrical X-ray rocking curve of (101) Bragg reflection of the FeSe crystal. The full width at half maximum (FWHM) of 1.2° is smaller than that of other reported FeSe crystals[15,18], proving the good quality of the single crystals. The Laue diffraction pattern of a thin FeSe single crystal is illustrated in Fig.7. The clear spots indicate that the single crystals are of high quality.

As shown in Fig.8, the resistance (R) vs temperature (T) curve

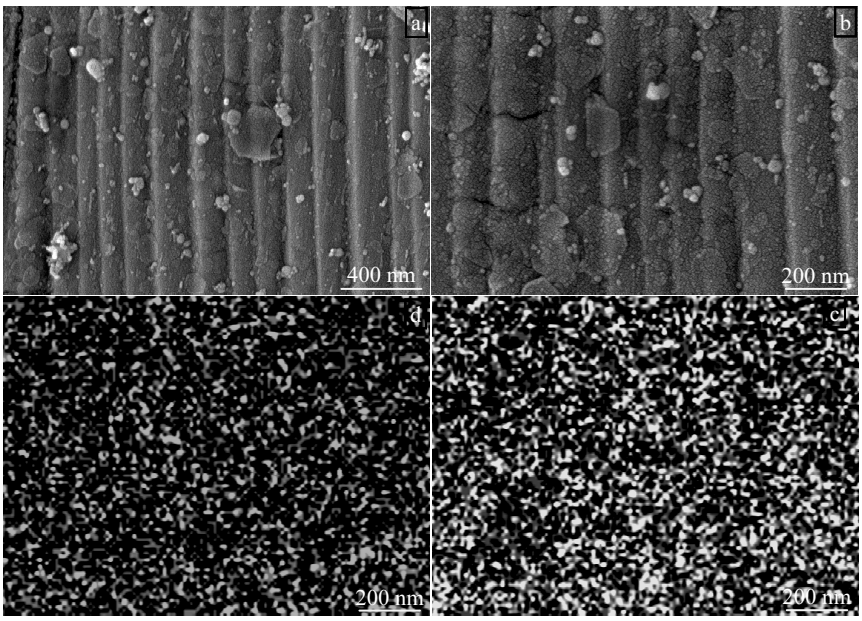

Fig.3 SEM images of FeSe crystals (a, b) and EDS mapping of Fe (c) and Se (d) in Fig.3b

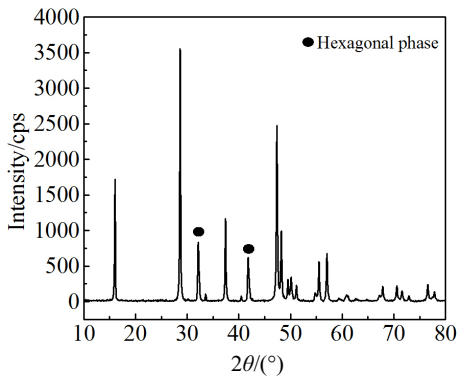

Fig.4 XRD pattern of FeSe crystal powder

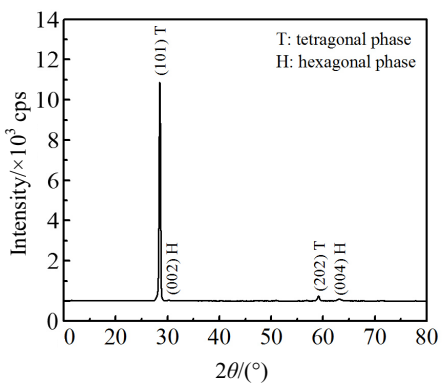

Fig.5 XRD pattern of the cleavage plane of FeSe crystal

shows the metallic behavior of FeSe crystals in the normal state. And the superconducting transition to zero resistance occurs at 9.91 K with a broad transition starting from 15.26 K, which is similar to that of other reported FeSe crystals[15,17]. Fig.9 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility (χ) vs temperature (T) curves for FeSe crystals

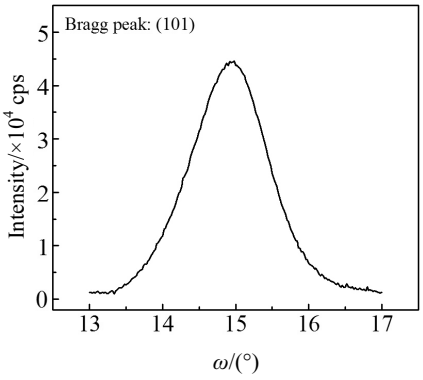

Fig.6 XRD rocking curve of the (101) reflection for the FeSe crystal

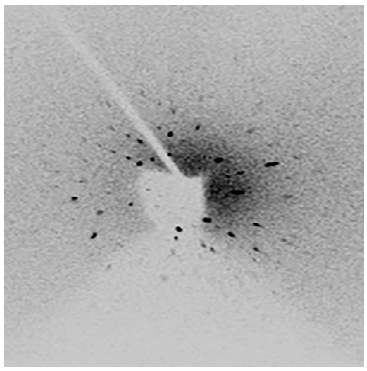

Fig.7 Laue diffraction pattern of a thin FeSe single crystal

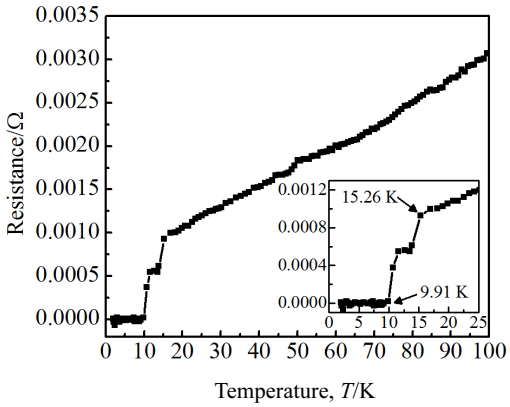

Fig.8 Resistance-temperature curve of FeSe crystals

under a field of H=796 A·m^{-1}. The superconducting transition temperature of 9.05 K is determined from the curve. The broad transition and positive magnetization value may arise from the secondary phase. These values conform to the general values of FeSe crystals[19], demonstrating the superconducting properties of the crystals.

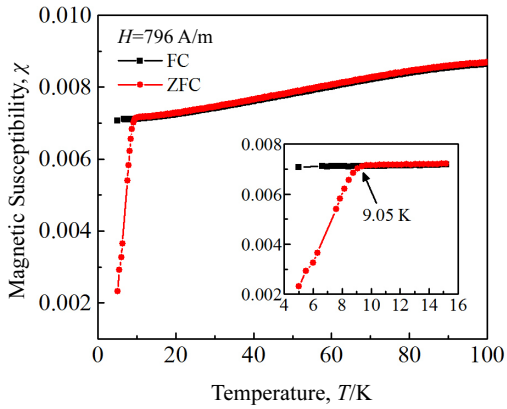

Fig.9 Magnetic susceptibility-temperature curve of FeSe crystals with zero-field-cooling (ZFC) and field-cooling (FC)

3 Conclusions

1) FeSe crystals with a large size of 7 mm×2 mm×2 mm can be successfully fabricated by KCl solution flux method under the temperature gradient. Phase identification indicates that the main phase of the crystals is the superconducting tetragonal β-FeSe. Single crystal X-ray diffraction shows that these single crystals are of good quality. SEM and EDS analysis demonstrate the layered structure and uniform composition of the crystals.

2) The superconducting transition temperatures of the FeSe crystals are 9~10 K by both magnetic and electronic transport measurements. A simple and effective method to synthesize large FeSe single crystals is proposed which is promising in investigations of superconducting mechanism of FeSe superconductors.

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FeSe 晶体生长和超导性能

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摘　要：利用了简单的 KCl 熔盐法生长晶体，通过在熔剂内部控制温度梯度，得到了尺寸为 7 mm×2 mm×2 mm 的大晶体。通过 X 射线衍射分析，确定（101）基面的四方 β-FeSe 为超导相。磁性测量表明晶体在 9.05 K 时发生了超导转变；四探针法测量表明伴随着较宽的转变温度范围，晶体在 9.91 K 时电阻值降为零，起始转变温度为 15.26 K。本研究为制备大尺寸 FeSe 单晶提供了一种简单快捷的方法，对于指导 FeSe 基超导体的研究具有重要意义。

关键词：FeSe；单晶生长；熔盐法

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