Bulk single-crystal growth of strontium ruthenates by a floating-zone method

Shin Ichi Ikeda\textsuperscript{a,*}, Uichiro Azuma\textsuperscript{a,b}, Naoki Shirakawa\textsuperscript{a}, Yoshikazu Nishihara\textsuperscript{b}, Yoshiteru Maeno\textsuperscript{c,d,e}

\textsuperscript{a} Condensed Matter Physics Group, Nanoelectronics Research Institute (NeRI), National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba, Ibaraki, 305-8568, Japan
\textsuperscript{b} Faculty of Science, Ibaraki University, Mito 310-8512, Japan
\textsuperscript{c} Department of Physics, Kyoto University, Kyoto 606-8502, Japan
\textsuperscript{d} Kyoto University International Innovation Center, Kyoto 606-8501, Japan
\textsuperscript{e} CREST-JST, Kawaguchi, Saitama 332-0012, Japan

Abstract

We report a single-crystal growth technique for strontium ruthenates. Strontium ruthenates exhibit intriguing magnetic properties such as spin-triplet superconductivity in Sr\textsubscript{2}RuO\textsubscript{4}. To obtain pure single crystals of strontium ruthenates (Sr\textsubscript{2}RuO\textsubscript{4}, Sr\textsubscript{3}Ru\textsubscript{2}O\textsubscript{7} and SrRuO\textsubscript{3}), we employed a conventional floating-zone method. For the crystal growth of Sr\textsubscript{2}RuO\textsubscript{4}, no severe difficulties are known. Even in air, it is possible to grow that single crystal from the molten zone of polycrystalline bar of Sr\textsubscript{2}RuO\textsubscript{4}. However, for Sr\textsubscript{3}Ru\textsubscript{2}O\textsubscript{7} and SrRuO\textsubscript{3}, it is impossible to obtain single crystals by the same procedure. We herein show the importance of oxygen-partial pressure in the atmosphere for the crystal growth of strontium ruthenates based on our successful results.

PACS: 71.27.+a; 81.10.Fq; 64.75.+g; 61.10.−i

Keywords: A2. Floating zone technique; A2. Growth from melt; B1. Oxides; B1. Perovskites; B2. Magnetic materials

1. Introduction

Single-crystal growth of perovskite oxides has been important for understanding the intrinsic electronic and magnetic properties. Especially, for high-temperature superconductors in layered perovskite cuprates, excellent single crystals obtained by a floating-zone (FZ) method provided the decisive results of physical properties [1]. Thus, the FZ method has been known as a typical single-crystal growth method for transition metal oxides.

Recently, it was discovered that a perovskite ruthenate Sr\textsubscript{2}RuO\textsubscript{4} shows superconductivity below 1.5 K [2] and the superconductivity was concluded to be spin-triplet type by \textsuperscript{17}O NMR measurements [3]. At the first stage of this study on the ruthenates, single crystals grown in air by the FZ method played an vital role in finding the superconductivity [1,4]. Both superconducting signals and zero-resistivity below \( T_c \) was observed only for the single crystals of Sr\textsubscript{2}RuO\textsubscript{4}.

\*Corresponding author. Tel.: +81-298-61-5389; fax: +81-298-61-5387.
\textit{E-mail address:} ikeda-shin@aist.go.jp (S.I. Ikeda).

0022-0248/02/$-see front matter \copyright 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-0248(01)02033-4
Concerning the crystal growth of Sr$_2$RuO$_4$, Mao et al. reported that the highest $T_c$ ~1.5 K was obtained by adjusting the crystal growth conditions using a Ru self-flux FZ technique [5]. For the best condition, the starting composition of the feed rod is Sr$_2$RuO$_4$ + 0.15RuO$_2$, the growth atmosphere is 0.25 MPa Ar mixed with O$_2$ (Ar:O$_2$ = 9:1), and the crystal growth speed is about 40 mm/h which is much faster than that (~0.05 mm/h) for the case of Bi-2223 HTSC cuprates [6]. It is necessary to add excess RuO$_2$ (~15%) as a self-flux because of the high vapor pressure of Ru oxides at high temperature during the crystal growth.

Prior to Mao’s study, attempts to grow good single crystals of Sr$_2$RuO$_4$ was performed by changing the composition of the feed rod [7]. The FZ crystal growth in air from the molten zone of the feed rod of two compositions (Sr$_3$Ru$_2$O$_7$ and SrRuO$_3$) led to the single crystals of Sr$_2$RuO$_4$ with Ru metal islands (~μm) due to the eutectic solidification [8,9]. This embedded metallic micro-domains of Ru metal enhance $T_c$ of Sr$_2$RuO$_4$ up to 3 K. This strongly means that the excess RuO$_2$ in the starting materials for the feed rod cannot contribute to the crystal growth of Sr$_3$Ru$_2$O$_7$ and SrRuO$_3$ in the same condition.

The crystal structures of the three strontium ruthenates (Sr$_2$RuO$_4$, Sr$_3$Ru$_2$O$_7$, and SrRuO$_3$) are shown in Fig. 1. The single crystals by the FZ method have been known only for Sr$_2$RuO$_4$, not for either Sr$_3$Ru$_2$O$_7$ or SrRuO$_3$. On the other hand, single-crystal growth of Sr$_3$Ru$_2$O$_7$ and SrRuO$_3$ was reported by using a SrCl$_2$ flux method [10,11].

In this paper, we show that the role of oxygen partial pressure is quite essential to growth of single crystalline Sr$_3$Ru$_2$O$_7$ and SrRuO$_3$ by a FZ method. We have succeeded in growing single crystalline Sr$_3$Ru$_2$O$_7$. However, it was impossible to grow single-phased crystals of SrRuO$_3$.

2. Experimental procedure

For growing single crystals in this study, we employed a self-flux FZ method using two types of image furnace with elliptical mirrors. One has double-elliptical mirrors (NEC Machinery, Model SC-K15HD-HP; at Kyoto University) with two 1.5 kW halogen lamps. The other has four-elliptical mirrors (Crystal System, Model FZ-T-10000-H-II-P-M; at AIST, Tsukuba) with four 1.0 kW halogen lamps. We adopted Cu K$_\alpha$ radiation for the powder X-ray diffraction.

For single crystals growth of Sr$_3$Ru$_2$O$_7$, the starting materials were SrCO$_3$ with purity of 99.99% (Ba < 10 ppm) and RuO$_2$ with 99.9%. The mixture in the molar ratio of Ru/Sr = 0.75 was fired and sintered in air at 1573 K with an intermediate grinding. After being pressed into a rod with a diameter of 6 mm, it was sintered in air at 1623 K for 2 h. The rod was then set in the FZ furnace. The growth of crystals was performed in 1 MPa oxygen atmosphere at the feed speed of 40 mm/h. The rod and seed crystal were rotated oppositely to each other at 30 rpm.

The crystal-growth atmosphere should be kept at high oxygen pressure because of the instability of RuO$_2$ at high temperatures as described below. The Sr$_3$Ru$_2$O$_7$–Ru metal hybrid system has been described by the eutectic solidification at the solidus line in the Sr–Ru–O phase diagram in 0.1 MPa air (~20 kPa oxygen partial pressure). This means that Sr$_3$Ru$_2$O$_7$ and SrRuO$_3$ do not exist in 0.1 MPa air at higher temperatures than...
the melting point (solidus line) in the Sr–Ru–O phase diagram.

As shown in the phase diagram of Ru and oxygen (Fig. 2), RuO$_2$ decomposes into Ru and oxygen at higher temperatures or at lower oxygen partial pressures [12–15]. In other words, high oxygen pressures stabilize RuO$_2$ with tetravalent oxidation state Ru$^{4+}$ at high temperatures. Considering that formal valence number of Ru ion is also four in the three strontium ruthenates as shown in Fig. 1, it is necessary to stabilize Ru$^{4+}$ at higher temperatures ($\sim$2200 K) than melting point during crystal growth by applying high oxygen pressures ($\sim$1.3 MPa) to obtain single crystals of Sr$_3$Ru$_2$O$_7$ or SrRuO$_3$. Therefore, we have tried to grow single crystalline Sr$_3$Ru$_2$O$_7$ and SrRuO$_3$ at 1 MPa oxygen pressure, which is legally attainable maximum pressure for our FZ furnaces.

3. Single-crystal growth of Sr$_3$Ru$_2$O$_7$

For the single-crystal growth of Sr$_3$Ru$_2$O$_7$ at Kyoto, we used the FZ furnace with the double-elliptical mirrors. With increasing the input voltage, the evaporation of RuO$_x$ became obvious. When the input power is about 2 kW, we could have a floating zone (melt). The viscosity of the melt is substantially lower than that in 0.1 MPa air. Thus, it is quite difficult to keep the FZ melt stable during the crystal growth. However, we have succeeded in obtaining the somewhat large ($\sim$mm$^3$) single crystal of Sr$_3$Ru$_2$O$_7$ as shown in Fig. 3.

The 327 structure was confirmed using crushed crystals by the powder X-ray diffraction patterns, which indicate no impurity peaks as shown in Fig. 4(a). Details of the crystal structure with atomic coordinates have been determined by neutron scattering measurements for polycrystalline samples [16]. From present results for FZ crystals, lattice parameters at room temperature were deduced as $a = 0.38872(4)$ nm and $c = 2.0732(3)$ nm by assuming tetragonal $I4/mmm$ symmetry, although the symmetry of structure was determined to be quasi-tetragonal Bbcb [16]. These values are in good agreement with those of polycrystals within an experimental error but show significant difference from the reported values for single crystals grown by a flux method [10] as described below. Fig. 4(b) shows the $(00\ell)$ reflection pattern from several pieces of cleaved plate-like crystals. All $(00\ell)$ peaks allowed for the tetragonal symmetry are clearly observed and the corresponding $c$ parameter ($c = 2.0741$ nm) is consistent with that obtained from the powder diffraction measurements. This is a strong evidence that the cleaved surface is a two-dimensional $ab$-plane.
As for the electronic and magnetic properties for FZ crystals of Sr$_3$Ru$_2$O$_7$, more detailed results have been reported elsewhere [17,18]. As a brief summary, the ground state of Sr$_3$Ru$_2$O$_7$ has been concluded to be nearly ferromagnetic metal with Fermi liquid state based upon the investigation for FZ crystals.

We have also tried to grow the crystals of Sr$_3$Ru$_2$O$_7$ using another image furnace with four-elliptical mirrors at Tsukuba. The condition for crystal growth was the same as that at Kyoto. Although we needed to input more power (>3.5 kW) in order to melt the polycrystalline rod, we were also able to obtain a crystal of Sr$_3$Ru$_2$O$_7$ and basically reproduced the former’s results.

4. Single-crystal growth of SrRuO$_3$

In order to find the best composition of starting materials for the crystal growth of SrRuO$_3$, we prepared crystal growth rods with four different compositions of the molar ratio Ru/Sr = 1.3, 1.4, 2.0 and 3.0. The procedure of making polycrystalline rods were the same as that for the case of Sr$_3$Ru$_2$O$_7$. The crystal growth for those four polycrystalline rods was performed at Tsukuba. It was seriously difficult to grow crystals stably due to the same reason described in the part for Sr$_3$Ru$_2$O$_7$. The as-grown samples have single crystal-like shape. The crushed crystals show cleaved surface similar to the appearance shown in Fig. 3.

In Fig. 5, the powder X-ray diffraction pattern is presented for the crystals with starting composition of (Ru/Sr = 1.3). The peaks corresponding to Sr$_2$RuO$_4$, Sr$_3$Ru$_2$O$_7$ and Sr$_4$Ru$_3$O$_{10}$ as well as SrRuO$_3$ were observed. It should be noted that the existence of the phase of SrRuO$_3$ in the molten sample indicates the possibility of crystal growth of SrRuO$_3$. For all compositions (Ru/Sr = 1.3, 1.4, 2.0 and 3.0), results of powder X-ray diffraction are essentially the same. No systematic variation of the results by changing the composition was obtained. This means that it is not easy to have a single crystalline SrRuO$_3$ by adjusting the starting material’s composition. If we can keep the floating zone more stably, we will achieve the single...
crystalline SrRuO₃ without other phases by FZ method with high oxygen pressures.

5. Conclusion

We have clarified that the higher oxygen partial pressure is quite important for growth of single crystalline Sr₃Ru₂O₇ and SrRuO₃ by the floating-zone method. We have succeeded in growing single crystals of Sr₃Ru₂O₇. However, it was impossible to grow single-phased crystals of SrRuO₃ by the same procedure.

Acknowledgements

The authors thank S. Nakatsuji, T. Ishiguro, A.P. Mackenzie, K. Matsushige, H. Bando, H. Kawanaka, and M. Koyanagi for their fruitful advice and kind help. This work was supported in part by a Grant-in-Aid for the Scientific Research on Priority Area “Novel Quantum Phenomena in Transition Metal Oxides” from the Ministry of Education, Culture, Sports, Science and Technology.

References