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Journal of Crystal Growth 237–239 (2002) 787–791

JOURNAL OF CRYSTAL GROWTH

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

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Abstract

We report a single-crystal growth technique for strontium ruthenates. Strontium ruthenates exhibit intriguing magnetic properties such as spin-triplet superconductivity in Sr_2RuO_4. To obtain pure single crystals of strontium ruthenates (Sr_2RuO_4, $Sr_3Ru_2O_7$ and $SrRuO_3$), we employed a conventional floating-zone method. For the crystal growth of Sr_2RuO_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_2RuO_4. However, for $Sr_3Ru_2O_7$ and $SrRuO_3$, 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_2RuO_4 shows superconductivity below 1.5 K [2] and the superconductivity was concluded to be spin-triplet type by ^{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_2RuO_4.

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PII: S0022-0248(01)02033-4

Concerning the crystal growth of Sr_2RuO_4, Mao et al. reported that the highest $T_c \sim 1.5\,K$ 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 $Sr_2RuO_4 + 0.15RuO_2$, 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($\sim 15\%$) 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_2RuO_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 ($Sr_3Ru_2O_7$ and $SrRuO_3$) led to the single crystals of Sr_2RuO_4 with Ru metal islands ($\sim \mu m$) due to the eutectic solidification [8,9]. This embedded metallic micro-domains of Ru metal enhance T_c of Sr_2RuO_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 $Sr_3Ru_2O_7$ and $SrRuO_3$ in the same condition.

The crystal structures of the three strontium ruthenates (Sr_2RuO_4, $Sr_3Ru_2O_7$, and $SrRuO_3$) are shown in Fig. 1. The single crystals by the FZ method have been known only for Sr_2RuO_4, not for either $Sr_3Ru_2O_7$ or $SrRuO_3$. On the other hand, single-crystal growth of $Sr_3Ru_2O_7$ and $SrRuO_3$ was reported by using a $SrCl_2$ flux method [10,11].

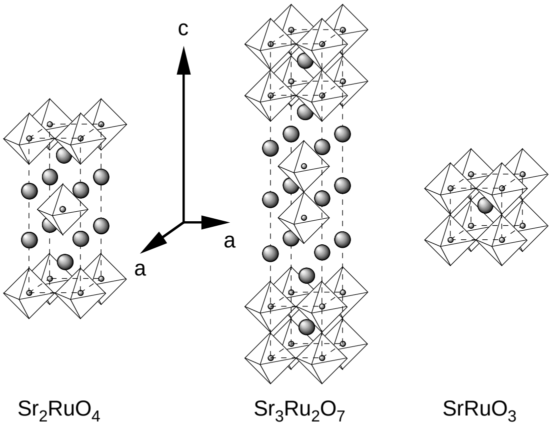

Fig. 1. The crystal structures of strontium–ruthenium oxides; (a) Sr_2RuO_4 (b) $Sr_3Ru_2O_7$ and (c) $SrRuO_3$. The large circles represent Sr and the small circles Ru. The cubes indicate RuO_6 octahedra.

In this paper, we show that the role of oxygen partial pressure is quite essential to growth of single crystalline $Sr_3Ru_2O_7$ and $SrRuO_3$ by a FZ method. We have succeeded in growing single crystalline $Sr_3Ru_2O_7$. 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_α radiation for the powder X-ray diffraction.

For single crystals growth of $Sr_3Ru_2O_7$, 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_2RuO_4–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 $Sr_3Ru_2O_7$ and $SrRuO_3$ do not exist in 0.1 MPa air at higher temperatures than

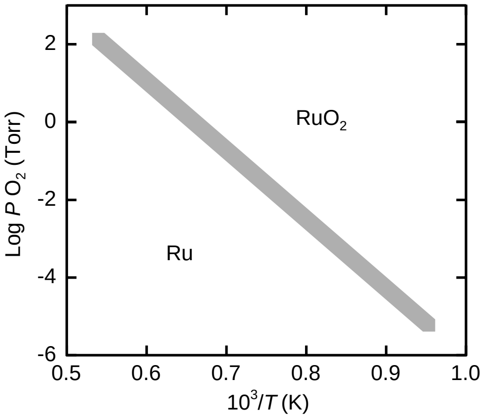

Fig. 2. Schematic phase diagram of equilibrium O_2 pressure for the reaction $RuO_2 \rightarrow Ru + O_2$ investigated by several groups [12–15].

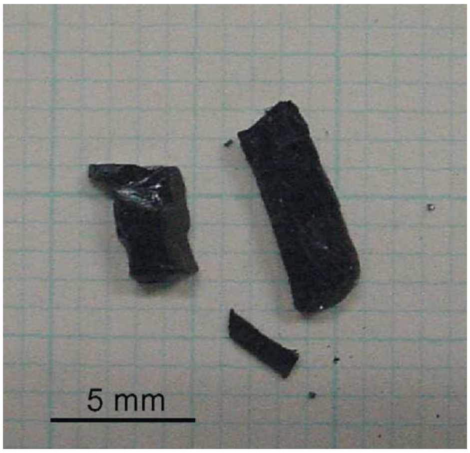

Fig. 3. Single crystals of $Sr_3Ru_2O_7$ with the cleaved surface parallel to the two-dimensional RuO_2 planes.

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 (~ 2200 K) than melting point during crystal growth by applying high oxygen pressures (~ 1.3 MPa) to obtain single crystals of $Sr_3Ru_2O_7$ or $SrRuO_3$. Therefore, we have tried to grow single crystalline $Sr_3Ru_2O_7$ and $SrRuO_3$ at 1 MPa oxygen pressure, which is legally attainable maximum pressure for our FZ furnaces.

3. Single-crystal growth of $Sr_3Ru_2O_7$

For the single-crystal growth of $Sr_3Ru_2O_7$ 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 $Sr_3Ru_2O_7$ 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 $(0\,0\,\ell)$ reflection pattern from several pieces of cleaved plate-like crystals. All $(0\,0\,\ell)$ 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.

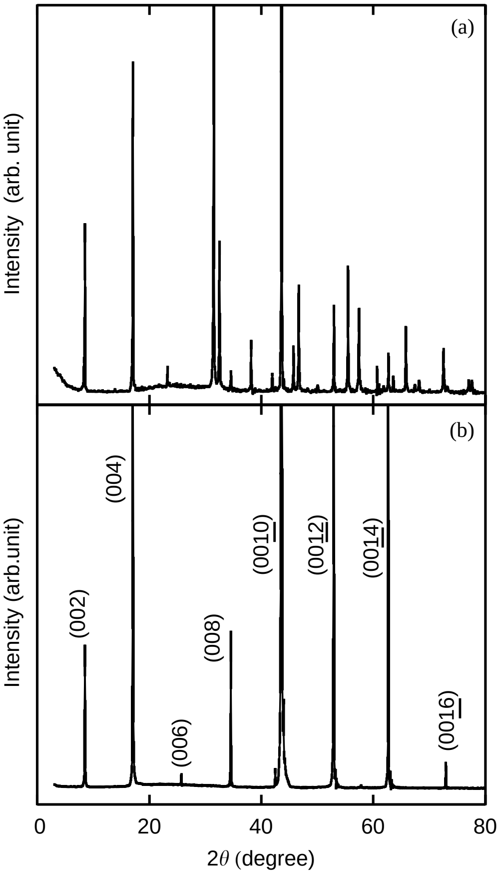

Fig. 4. X-ray diffraction pattern of FZ crystals of $Sr_3Ru_2O_7$. (a) powdered crystals and (b)plate shape crystals for (0 0 ℓ) reflections.

As for the electronic and magnetic properties for FZ crystals of $Sr_3Ru_2O_7$, more detailed results have been reported elsewhere [17,18]. As a brief summary, the ground state of $Sr_3Ru_2O_7$ 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 $Sr_3Ru_2O_7$ 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 $Sr_3Ru_2O_7$ 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 $Sr_3Ru_2O_7$. 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 $Sr_3Ru_2O_7$. 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_2RuO_4, $Sr_3Ru_2O_7$ and $Sr_4Ru_3O_{10}$ 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

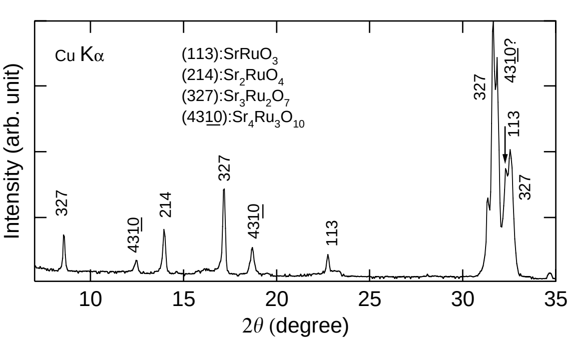

Fig. 5. Powder X-ray diffraction pattern for the crystals with starting composition of (Ru/Sr = 1.3). The peaks corresponding to Sr_2RuO_4, $Sr_3Ru_2O_7$ and $Sr_4Ru_3O_{10}$ as well as $SrRuO_3$ were observed.

crystalline $SrRuO_3$ 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 $Sr_3Ru_2O_7$ and $SrRuO_3$ by the floating-zone method. We have succeeded in growing single crystals of $Sr_3Ru_2O_7$. However, it was impossible to grow single-phased crystals of $SrRuO_3$ 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.

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