Single crystal growth of a layered perovskite V oxide Sr$_4$V$_3$O$_{10}$ with an FZ method under controlled $p$(O$_2$)

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Abstract. We have successfully grown single crystals of a layered compound Sr$_4$V$_3$O$_{10}$ with a floating-zone method under controlled O$_2$ partial pressure ($p$(O$_2$)). We realized that the adjustment of $p$(O$_2$) less than 10$^{-28}$ atm was indispensable for the crystal growth, and achieved that growth condition by an oxygen pump system. Sr$_4$V$_3$O$_{10}$ is a member of the Ruddlesden-Popper type series of Sr$_{n+1}$V$_n$O$_{3n+1}$ with $n = 3$. The crystal structure was indexed in a tetragonal space group $I4/mmm$. The unit cell dimensions of Sr$_4$V$_3$O$_{10}$ were found to be $a = 3.858$ Å and $c = 27.93$ Å. We have measured electrical resistivity from 30mK – 300K and magnetic susceptibility from 1.8K – 300K. The resistivity of Sr$_4$V$_3$O$_{10}$ showed that it is a metallic conductor from 300 K to 30 mK. The magnetic susceptibility of the sample shows the Curie-Weiss type temperature dependence, $\chi = \chi_0 + C/(T-\Theta)$. The values of paramters were obtained as $\chi_0 = 6.93 \times 10^{-5}$ emu/mole, $\Theta = -8.05$ K, and $C = 0.186$ emu·K/mole.

1. Introduction

Sr$_{n+1}$V$_n$O$_{3n+1}$ with the Ruddlesden-Popper(R-P) type structure have been attracting attention for a long time because of having structural and electronic similarities to cuprate superconductors. For example, the single layered perovskite Sr$_2$VO$_4$[1, 2] with $n = 1$ is an antiferromagnetic insulator with $T_N = 47$K, whereas the double layered perovskite Sr$_3$V$_2$O$_7$[3, 4] with $n = 2$, Sr$_4$V$_3$O$_{10}$[5, 6, 7] with $n = 3$, and SrVO$_3$[8] with $n = \infty$ are paramagnetic metals. It seems that these materials exhibit a systematic change of magnetic and transport properties due to the dimensionality effect based on the crystal structure, combined with the band-width effect, where the strong Coulomb interaction between conduction electrons plays an essential role. That is why single crystals of these materials are anticipated. However, these crystals have not been obtained yet, except for SrVO$_3$.

In this study, we have successfully grown single crystals of Sr$_4$V$_3$O$_{10}$ with a floating-zone method under controlled $p$(O$_2$) and have measured electrical resistivity from 30mK – 300K and magnetic susceptibility from 1.8K – 300K. In polycrystalline samples of Sr$_4$V$_3$O$_{9.8}$, Ito et al. have reported that the temperature gradient of the electric resistivity curve changes from slightly negative to positive at 70K and that the magnetic susceptibility shows weak paramagnetism from localized V$^{3+}$ ions[5]. Ohashi et al. have prepared the polycrystalline Sr$_4$V$_3$O$_{10-\delta}$ with controlled oxygen deficiency[7]. They have reported that as its carrier concentration decreases,
the electrical conduction changes from metallic to semiconducting, and the magnetic property changes from the Pauli paramagnetism to the Curie-like paramagnetism with increasing $\delta$-value.

2. Experiments
The single crystals of $\text{Sr}_4\text{V}_3\text{O}_{10}$ were grown in a floating-zone (FZ) furnace equipped with an oxygen pump for $p(\text{O}_2)$ control. High purity $\text{SrCO}_3$ powder (above 99.99%), $\text{VO}_2$ powder (99.9%) and Mo powder (99.9%) were mixed to the off-stoichiometric composition where the molar ratio of $\text{Sr}:\text{V}:\text{Mo}$ was equal to 2 : 9 : 0.1 and ground. The mixed powder was calcinated at 1523K for 24h in flowing Ar 99% + H$_2$ 1% gas. The calcinated powder was packed in rubber tubes and hydrostatically pressed under 2000 atm to be formed into rods. The pressed rods were then sintered at 1323K for 60h in vacuum. The sintered rod was then set quickly in an FZ furnace (Canon Machinery, SC-II-MDH) equipped with an oxygen pump system, which can lower the $p(\text{O}_2)$ of Ar gas down to $10^{-30}$ atm[9]. The value of $p(\text{O}_2)$ is measured by a yttria-stabilized zirconia (YSZ) oxygen sensor. The growth of crystals was performed in Ar gas with $p(\text{O}_2) = 10^{-28}$ atm at the feeding speed of 1.5 mm/h. During the growth, the $p(\text{O}_2)$ in the FZ furnace accrued slightly up to $10^{-25}$ atm. We suppose that the cause of the increase of $p(\text{O}_2)$ was the release of some water absorbed in the sample rod. The crystal growth temperature was made out to be about 1873K with a radiation thermometer.

The obtained sample rod crystallized at the first part of the growing process, while the remaining part was polycrystalline whose main phase was orthorhombic $\text{Sr}_2\text{VO}_4$. The crystallized part was composed of single crystals of $\text{Sr}_4\text{V}_3\text{O}_{10}$, as confirmed by a single crystal X-ray diffractometer. The typical size of the crystals was 0.5 – 1 mm. The composition of the crystal was checked by the energy-dispersive X-ray spectrometer of a scanning electron microscope (SEM-EDX). We applied the AC four-probe technique to measure electrical resistivity from 30 mK to room temperature with a dilution refrigerator. For DC magnetic susceptibility, we employed a commercial SQUID magnetometer (MPMS) from 1.8K to 300K.

3. Results and Discussion
The powder X-ray diffraction pattern for the crystallized part is shown in Fig.1. The sample turned out to be single phase $\text{Sr}_4\text{V}_3\text{O}_{10}$, except for small peaks of $\text{SrO}$. The inset in Fig.1. is the SEM image of the $\text{Sr}_4\text{V}_3\text{O}_{10}$ crystals with the flat surface, but we have not found out the (hkl) index of this surface yet. The crystal structure was successfully indexed in a body-centered tetragonal space group $I4/mmm$. The unit-cell parameters at room temperature were $a = 3.858\text{Å}$ and $c = 27.93\text{Å}$. The composition ratio of $\text{Sr}/\text{V}$ ions was equal to 4.12/3, as determined by SEM-EDX. Mo was not detected by EDX.

The temperature dependence of electrical resistivity from 30mK to 300K is shown in Fig. 2. The direction of applied current is parallel to the flat surface of the crystal as shown in the inset of Fig. 2. The resistivity of $\text{Sr}_4\text{V}_3\text{O}_{10}$ is about $5\times10^{-4}$ ohm cm at room temperature, and decrease almost linearly with decreasing temperature. The obtained $\text{Sr}_4\text{V}_3\text{O}_{10}$ crystal is obviously a metallic conductor. We also detected a small upturn of the resistivity below 7K, which seems to have the logarithmic temperature dependence.

Figure 3 shows the temperature dependence of magnetic susceptibility from 2K to 300K. The direction of applied magnetic field was perpendicular to the flat surface (as shown in the inset of Fig. 3). The $\text{Sr}_4\text{V}_3\text{O}_{10}$ crystal exhibits paramagnetic susceptibility which obeys the Curie-Weiss law, $\chi = \chi_0 + C/(T-\Theta)$, where $\chi_0$ is the temperature-independent paramagnetism, and the second term represents the usual paramagnetic temperature variation with the Curie constant $C$ and the characteristic temperature $\Theta$. The values of the fitted parameters are $\chi_0 = 6.93 \times 10^{-5}$ emu/mole, $\Theta = -8.05$ K, and $C = 0.186$ emu/K/mole. At low temperature below 7K, the hysteresis between the field cooling (FC) and the zero field cooling (ZFC) was observed in the susceptibility.
Figure 1. Powder X-ray diffraction pattern for \( \text{Sr}_4\text{V}_3\text{O}_{10} \). Asterisks indicate a peak of the impurity \( \text{SrO} \).

Figure 2. The resistivity of the obtained crystal \( \text{Sr}_4\text{V}_3\text{O}_{10} \) from 30mK to 300K. The inset is a SEM image of the crystal and shows the direction of electric current.

Figure 3. The temperature dependence of susceptibility from 1.8K to 300K for \( \text{Sr}_4\text{V}_3\text{O}_{10} \). The inset shows the direction of magnetic field with \( H = 1 \text{T} \) for the sample.

The effective moment per one mole of vanadium ions is 0.70 \( \mu_B \), as calculated from the Curie constant. This value is smaller than the free-ion values of 1.73 for V\(^{4+}\) and 2.83 for V\(^{3+}\). According to the previous report by Ohashi et al.\(^7\), polycrystalline \( \text{Sr}_4\text{V}_3\text{O}_{10-0.03} \), which has almost no oxygen deficiency and is occupied by V\(^{4+}\) ions, shows Pauli paramagnetic metal behavior. \( \text{Sr}_4\text{V}_3\text{O}_{10-0.14} \) also shows metallic behavior. On the other hand, \( \text{Sr}_4\text{V}_3\text{O}_{10-0.3} \) exhibits semiconductive and Curie-Weiss like behaviors induced by the oxygen deficiency. Since the ionic composition of \( \text{Sr}_4\text{V}_3\text{O}_{10-\delta} \) is represented by \( \left( \text{Sr}_2^{2+}\text{V}_4^{4+}\right)\left( \text{V}_3^{3+}\right)\left( \text{O}_{2-\delta}\right)_{10-\delta} \), the weak Curie-Weiss behavior would be induced by trivalent V ions involving localized electrons. Using the value of 2.83 \( \mu_B \) for a free-ion V\(^{3+}\), we can estimate the oxygen vacancy \( \delta \) as 0.093 from the obtained
Curie constant. Because this value of oxygen deficiency is within 0.03 to 0.14, it seems that the metallic behavior of our crystalline sample is consistent with Ohashi’s results. However, our residual resistance ratio $\rho_{300K}/\rho_{4.2K}$ is 4.6, which is already greater than that of polycrystalline Sr$_4$V$_3$O$_{10-0.03}$ by Ohashi.

In summary, we have successfully grown single crystals of Sr$_4$V$_3$O$_{10}$ with a floating-zone method under controlled $p$(O$_2$). The $p$(O$_2$) of less than $10^{-28}$ atm was necessary for the crystal growth. The crystal has tetragonal crystal structure with space group of $I4/mmm$, and its lattice constants are $a = 3.858\,\text{Å}$ and $c = 27.93\,\text{Å}$. The magnetic susceptibility shows Curie-Weiss behavior which gives the fitted parameters of $\chi_0 = 6.93 \times 10^{-5} \,\text{emu/mole}$, $\Theta = -8.05$ K, and $C = 0.186\,\text{emu-K/mole}$. The resistivity exhibits metallic conductivity and have a small upturn below 7K.

Acknowledgments

The authors are grateful to S. Hara, S. I. Ikeda, K. Iwata, T. Yanagisawa and S. Koikegami for their support and advice. The research was financially supported by the Sasakawa Scientific Research Grant from The Japan Science Society.

References

[1] Nozaki A, Yoshikawa H, Wada T, Yamauchi H, Tanaka S 1991 Phys. Rev. B 43 181
[2] Imai Y, Imada M 2006 J. Phys. Soc. Jpn. 75 4713
[3] Lee J -G, Ramanujachary K V, Greenblatt M 1995 J. Solid State Chem. 118 292-298
[4] Suzuki N, Noritake T, Yamamoto N, Hioki T 1991 Mat. Res. Bull. 26 1-9
[5] Itoh M, Shikano M, Liang R X, Kawaji H, Nakamura T 1990 J. Solid State Chem. 88 597-600
[6] Suzuki N, Noritake T, Yamamoto N, Hioki T 1991 Mat. Res. Bull. 26 75-83
[7] Ohashi N, Teramoto Y, Ikawa H, Fukunaga O 1992 J. Solid State Chem. 97 434-442
[8] Lan Y C, Chen X L, He M 2003 J. Alloys and Compound 354 95-98.
[9] Nagai I, Shirakawa N, Ikeda S I, Iwasaki R, Nishimura H, Kosaka M 2005 App. Phy. Lett. 87 024105.