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Growth and properties of strontium cobaltate single crystals

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Single crystals of strontium cobaltate with oxygen-deficient composition have been prepared by the floating-zone method using a lamp image furnace. Chemical and X-ray analyses showed that the composition was $SrCoO_{2.70}$ with a doubled perovskite structure of cubic cells, $a_0 = 7.710 \pm 0.001$ Å. The crystal was ferromagnetic and its Curie temperature was 150 K. The effective Bohr magneton per ion of Co^{4+} was 1.21, suggesting that Co^{4+} is almost in the low spin state.

1. Introduction

Strontium cobaltate is very interesting material because of its ferromagnetism, which is largely dependent on oxygen stoichiometry. The previous studies by Takeda *et al.* revealed that the composition of this compound varied from $SrCoO_{2.5}$ to $SrCoO_{2.95}$ according to oxygen pressure and temperature of preparation, and that there appeared to be a strong relationship between the composition and magnetic properties [1, 2]. These studies, however, were performed on powder samples and some ambiguities arising from the nature of the polycrystals remained. To obtain further information on this material, single crystals suitable for experiments on X-ray, magnetic and electrical properties were needed.

In the present study, oxygen-deficient crystals of strontium cobaltate, $SrCoO_{3-x}$ where x is about 0.3, were grown by the floating-zone method. X-ray and magnetic properties were investigated.

2. Experimental procedure

2.1. Preparation of raw materials

Powders of $SrCO_3$ and CoO of reagent grade (99.9% purity) supplied from Wakō Pure Chemicals Co, were weighed in stoichiometric proportions and mixed in a polyethylene blender. The mixture was heated in a platinum crucible for 10 h at 1050° C under an oxygen gas flow and was quenched to room temperature. The powders thus prepared were pressed hydrostatically into a rod 10 mm in diameter and 100 mm long under a pressure of 1 torr cm^{-2}. The rod was sintered at 1250° C for 1 h in an oxygen atmosphere.

2.2. Crystal growth

The crystal growth was carried out using a lamp image-type floating-zone furnace which was developed by Akashi *et al.* for the preparation of ferrite single crystals [3]. The radiation source was a halogen enclosed *W*-lamp whose maximum power was 1.5 kW. The sintered rod was used as a nutrient and was fed on to a seed through the molten zone. A single-crystal seed was prepared from a polycrystalline rod by spontaneous nucleation. The optimum growth conditions were as follows; the growth rate was 2 mm h^{-1}, the rotation rates of the crystal and the nutrient were both 30 rpm in opposite directions, the oxygen gas flow rate was about 1 litre min^{-1}, the length of the molten zone was about 10 mm and the cooling rate of the boule was 500° C h^{-1}. The melting point was estimated by means of a DTA apparatus to be 1335 ± 5° C.

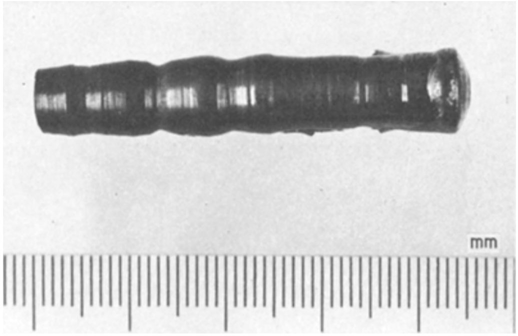

Figure 1 As-grown boule of $SrCoO_{2.70}$.

2.3. Analysis of the crystal

The composition of the crystals was determined by wet chemistry and neutron activation analyses. Sr was analysed by atomic absorption spectrometry and Co was determined by EDTA titration at pH3. The amount of Co^{4+} ions was analysed by the iodometric oxidation–reduction titration. To confirm these results, gravimetric data were obtained from calcination of specimens of several hundred mg at about 1200° C in air. Neutron activation analysis was carried out in order to examine the uniformity of the crystal composition. X-ray powder patterns were obtained with Ni-filtered Cu radiation using internal standards of MgO and Si powder, and the degree of crystallinity of the as-grown boule was determined by the X-ray back reflection Laue method. Single crystal analyses were also made by the Buerger precession method using Zr-filtered Mo radiation.

Magnetic measurements were made with applied field up to 10 kOe between 4.2 K and room temperature using a pendulum-type magnetometer.

3. Results and discussion

A typical as-grown boule is shown in Fig. 1. The boules were black and opaque and possessed no crystal habit on their surfaces. X-ray Laue analyses showed that a major part of the boule was single crystal even when the polycrystalline seed was used. Fig. 2a shows a cross-section view of the boule, where the sudden change from poly- to single-crystalline part is observed. Fig. 2b is a Laue photograph of the single-crystal part. The imperfections commonly observed were cracks, as shown in Fig. 2a. These were probably introduced by thermal strain during cooling.

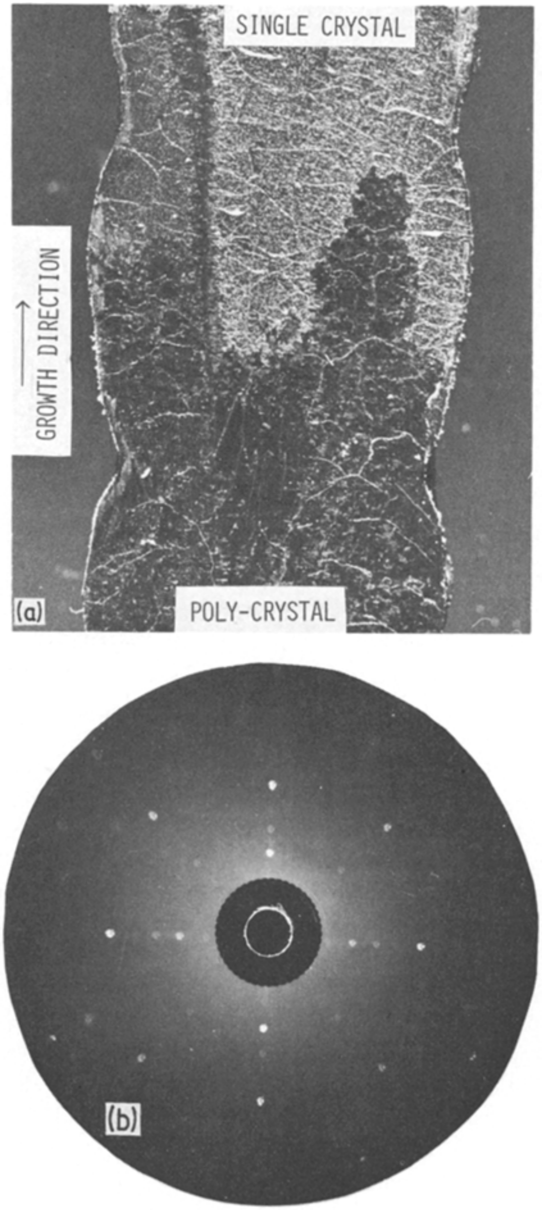

Figure 2 (a) Cross-sectional view of the $SrCoO_{2.70}$ boule. (b) Back reflection Laue photograph of the single crystal part of the boule; Mo radiation was used.

Table I gives chemical analysis compositions of the boules. The results indicate that the mean chemical formula is very close to $SrCoO_{2.70}$, or $SrCo^{4+}_{0.40}Co^{3+}_{0.60}O_{2.70}$. The thermogravimetric analyses support these results within the experimental error. It should be noted that the oxygen content in $SrCoO_{3-x}$ increased with crystallization (see Table I): the value x of the crystal was considerably smaller than that of the nutrient rod. This fact is a contrast to the case of $SrFeO_{3-x}$, where

TABLE I Analytical data of $SrCoO_{3-x}$ crystals

Specimen	Composition (wt%) Sr^{2+}	Co^{4+}	Co^{3+}	x	$3-x$	Atomic ratio Sr/Co	Crystal structure
1	46.30	11.64	19.48	0.311	2.689	1.008	Perovskite†
2	46.37	12.36	18.46	0.299	2.701	1.016	Perovskite†
3	45.97	12.42	18.28	0.298	2.702	1.007	Perovskite†
S. M.*	46.42	2.95	28.38	0.453	2.547	0.997	Brown-millerite
Theoretical value							
$SrCoO_{3.0}$	45.04	30.29	–	0.000	3.000	1.000	Perovskite
$SrCoO_{2.5}$	46.97	–	31.59	0.500	2.500	1.000	Brown-millerite

*Starting material (sintered rod)
†Doubled cubic perovskite cell

this compound decomposed under 1 atm oxygen pressure into a form of $SrFeO_{2.5}$ by melting [4]. The neutron activation analysis, performed on 1 to 2 mg samples, showed that the difference in the atomic ratio (Sr/Co) between the boule and the coexisted melt was below 1%.

The X-ray precession (Fig. 3) and the powder diffraction analyses revealed that the crystal structure was cubic with unit cell dimension $a_0 = 7.710 \pm 0.001$ Å. This value is twice as large as the lattice parameter of the primitive perovskite structure. Such doubling of the cell dimension has been observed in many cubic perovskites such as $CaMnO_3$ [5, 6], $SrSnO_3$ [7, 8], $SrZrO_3$ [8] and $BaThO_3$ [8]. Katz *et al.* have found the doubled cubic cell in defect structures containing an alkaline earth cation with niobium or tantalum [9]. Yakel suggested from the X-ray powder diffraction studies that $SrCoO_3$ containing only 1.4 at.% of Co^{4+} crystallized in cubic structure with the doubled perovskite cell edge of 7.725 (= 3.8625 x 2) Å [10]. This doubling was presumably explained by "puckering"; antiparallel displacements of ions, as found by Vousden in $NaNbO_3$ [11].

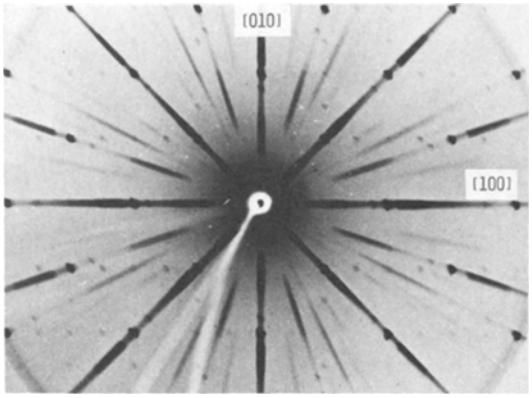

Figure 3 Precession photograph of the $SrCoO_{2.70}$ crystal; (0 0 1) plane, zero-level. The same superstructure pattern was observed on (0 1 0) and (1 0 0) planes.

Another possible explanation of the doubling in cell edge can be made by considering superstructure due to an ordered arrangement of anion defects. Recently, Tofield *et al.* have reported that superstructure reflections of perovskite lattice were observed in electron diffraction study of $SrFeO_{3-x}$, which is possibly considered as isostructure with $SrCoO_{3-x}$ [4]. They suggested that the superstructure reflections were attributable to a new phase, $Sr_4Fe_4O_{11}$, whose cell was constructed by tetragonal lattice with dimensions related to the cubic parameter, a_c, by $a \sim 2\sqrt{2}\ a_c$, $b \sim 2a_c$, and $c \sim 2\sqrt{2}\ a_c$. Though the results obtained in the present study seem to be different from those of Tofield, more detailed analyses are needed to clarify the crystal structure of $SrCoO_{2.70}$.

Fig. 4 is the temperature dependence of magnetization σ in a field of 5.79 kOe after the specimen was cooled to 4.2 K in a field of 10 kOe. It is obvious from the figure that the $SrCoO_{2.70}$ crystal was ferromagnetic at low temperatures. The Curie temperature T_c, which was determined by the plot of σ^2 as a function of $T - T_c$ near T_c, was estimated to be 159 K. By extrapolation of the $\sigma^2 - T$ curve to $H = 0$, T_c of 150 K was obtained. These values are quite different from that of a powder sample, where T_c was supposed to be $-$ 50 K by extrapolation [2]. The disagreement in T_c is attributable to the difference in the shape of $\sigma - T$ curves; the magnetic field dependent anomaly which was observed between 150 K and T_c in powder samples would cause T_c to be lower. Such an anomaly was not observed in the curves of the single crystal specimen, so that the anomaly is apparently characteristic of powder samples.

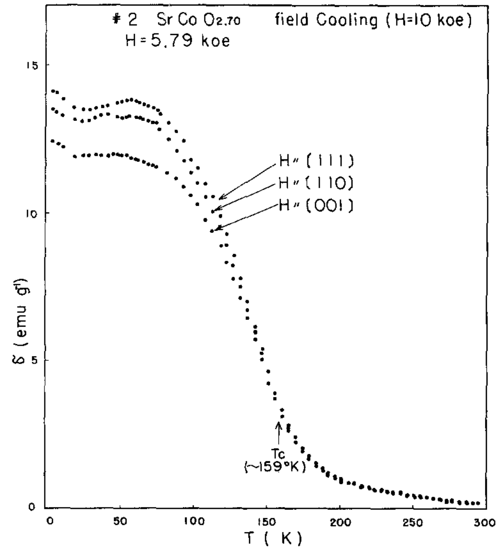

Figure 4 Temperature dependence of magnetization σ of the $SrCoO_{2.70}$ crystal. Specimen 2 crystal was used.

The effective Bohr magneton number μ_B per molecule of $SrCO_{2.70}$ was 0.486 at 77 K from the data of $\sigma = 14.3\,emu\,g^{-1}$ along $\langle 1\,1\,1 \rangle$ direction in the external field of 8 kOe. Thus, the effective Bohr magneton per ion of Co^{4+} was 1.21, where we assumed that Co^{3+} ions in the crystal lie in the low spin state (t_{2g}^6) and possess no magnetic moment [12]. This value is understandable if the major part of Co^{4+} ions are in the low spin state; that is $\mu_B = 1$. Details of these magnetic properties are being investigated by neutron diffraction.

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