

Growth of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ Single Crystals from KOH Melt and Their Magnetocrystalline Anisotropy

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Single crystals of a metallic ferromagnet $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ ($x = \sim 0.44$) were grown from KOH melt at 773 K under $\text{H}_2\text{O}/\text{O}_2$ mixed gas flow. The grown crystals had a parallelepiped form, and their surfaces were (100) planes of the pseudocubic unit cell. The edges of the largest crystal were about 0.1 mm. The XRD and magnetic susceptibility measurements indicated that the grown crystals are highly homogeneous with respect to La/Sr contents. The magnetization versus magnetic field curve was dependent on the applied field direction to the crystallographic axis, evidencing the presence of magnetocrystalline anisotropy in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$.

Introduction

Perovskite-type cobalt oxides have attracted many researchers because of their unique electronic and spin states.^{1–9} $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ is a typical perovskite-type cobalt oxide. LaCoO_3 is an insulator (or semiconductor) below about 500 K and a metal above about 500 K.⁵ $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ is an insulator at low temperatures below about $x = 0.2$ and a metal even at 0 K above about $x = 0.2$.⁶ The electronic and spin states have been clarified only for Co^{3+} ions in LaCoO_3 at 0 K. The electronic configuration is $t_{2g}^6e_g^0$, and the spin quantum number is 0. The electronic and spin states have not been clarified yet for the metallic phases; however, it has been considered that finite population of e_g orbitals (or band) is essential for the metallic nature.⁶

High-quality $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ single crystals are desirable to investigate the physical properties of the metallic phases, such as magnetization, electric conductivity, Hall effect, and so on, and then to clarify their electronic and spin states. However, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ single crystals have been grown only in a limited x region as described below. Matsuura et al. have reported that $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ single crystals with $x = 0$, 0.02, and 0.1 were grown by a floating-zone method, but the crystals with $x = 0.2$ and 0.3 decomposed into CoO

and K_2NiF_4 -type $(\text{La},\text{Sr})_2\text{CoO}_4$ phases.¹⁰ Single crystals of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ with $x = \sim 0.3$ have been grown also by a floating-zone method,^{11–13} however, there is inconsistency on their preparation conditions. Prabhakaran et al. have reported that $\text{La}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$ single crystal was successfully grown under high oxygen pressure (7–9 atm).¹¹ However, Onose et al. have reported that $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ crystals grown under oxygen pressure of 10 atm included a trace of impurity of an $(\text{La},\text{Sr})_2\text{CoO}_4$ phase.¹² On the other hand, Fita et al. have reported that $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ were grown under oxygen pressure of 1 bar.¹³ Judging from these reports, it is supposed that the single crystal growth of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ with large x is difficult by a floating-zone method possibly because the crystals are unstable at high temperatures due to the high oxidation state of Co. Shivakumara et al. have reported that KOH melt stabilizes high oxidation states of many kinds of metals, and, in fact, they synthesized $(\text{La},\text{K})\text{NiO}_3$ crystals from KOH melt at 673 K.¹⁴ This method would be applicable to the single crystal growth of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ with large x .

In the present study, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ ($x = \sim 0.44$) single crystals were successfully grown from KOH melt. It is the first time in which $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ single crystals were grown with x larger than 0.33. Although the size of the present crystals (~ 0.1 mm) was 1-order smaller than the crystals grown by a floating-zone method,^{11–13} the present crystals have clear crystallographic planes, which made it easy to investigate magnetic anisotropy. The present results suggested uniaxial magnetocrystalline anisotropy with an easy plane of magnetization perpendicular to c axis of the

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Table 1. Starting Quantities for Crystal Growth

no.	KOH (g)	La _{0.5} Sr _{0.5} Co carbonates (g)	SrCO ₃ (g)	La (mmol)	Sr (mmol)	Co (mmol)
1	12	1.5	0.0	4.65	4.65	9.30
2	12	0.5	0.5	1.55	4.94	3.10
3	12	0.5	1.0	1.55	8.32	3.10
4	12	0.5	2.5	1.55	18.49	3.10

hexagonal unit cell, although earlier studies have not clarified the details of magnetic anisotropy.^{11,13}

Experimental Section

(La,Sr,K)CoO_{3+δ} single crystals were grown as follows. At first, mixed carbonates of La, Sr, and Co with their molar ratio of 1:1:2 were prepared by adding K₂CO₃ aqueous solution to La, Sr, and Co nitrates solution prepared by dissolving La₂O₃, SrCO₃, and Co in nitric acid. The obtained mixed carbonates were filtered and dried at 393 K. The contents of La, Sr, and Co of the mixed carbonates were determined by thermogravimetry. The mixed carbonates, KOH, and excess SrCO₃ were placed in a zirconium–metal crucible with a lid. (Alumina and nickel–metal crucibles were also used, but appreciable contamination was observed from the crucibles.) Their starting quantities are tabulated in Table 1 with sample numbers 1–4. The mixture was held at 773 K for 6 h in an electrical furnace with flowing O₂/H₂O mixed gas and then furnace-cooled to room temperature. By addition of H₂O gas to the flowing O₂ gas, the yield of the impurity phase (KCo₂O₄) was decreased, although the role of H₂O is unclear at present. KOH flux was removed by dissolving it in ion-exchange water. The obtained crystals were then cleaned with ion-exchange water several times and at last by soaking in dilute nitric acid for about 1 min to remove water-insoluble compounds such as SrCO₃.

The crystal structures of samples were investigated by powder X-ray diffraction (XRD) with Cu K α radiation (Rigaku, RINT2200). The lattice constants were calculated by least-squares method using angles of diffraction peaks of Cu K α_1 radiation observed in 2 θ region of 126–143°. The peak angles were corrected using Si crystalline powder as an internal standard. The form and size of grown crystals were observed using an optical microscope and a scanning electronic microscope (SEM) (JEOL, JSM-6330F). La, Sr, Co, and Zr contents of samples were determined by an inductively coupled plasma atomic emission spectrometry (Shimadzu, ICPS-1000III), K contents were determined by a flame spectrochemical analysis (Hitachi, Z-5310), and O contents were determined by an iodometric titration using an autotitrator (Hiranuma COM-450). Magnetization was measured using a superconducting quantum interference device (Quantum Design, MPMS-5SW) for a set of many crystals (1–11 mg) and for one crystal ($\sim 6 \mu\text{g}$).

Results

Figure 1a shows a powder XRD pattern of as-prepared sample (No. 2 sample). Figure 1b and c shows SEM photographs of the sample. The as-prepared sample was composed of two kinds of crystals. One is a (La,Sr,K)CoO_{3+δ} crystal with a parallelepiped form, and the other is a KCo₂O₄ crystal with a hexagon plate form. These crystal forms are consistent with their crystal structures, because the crystal system of La_{1-x}Sr_xCoO_{3+δ} is pseudocubic (rhombohedral distorted slightly from cubic) and KCo₂O₄ hexagonal. The edges of the largest (La,Sr,K)CoO_{3+δ} crystal were about 0.1

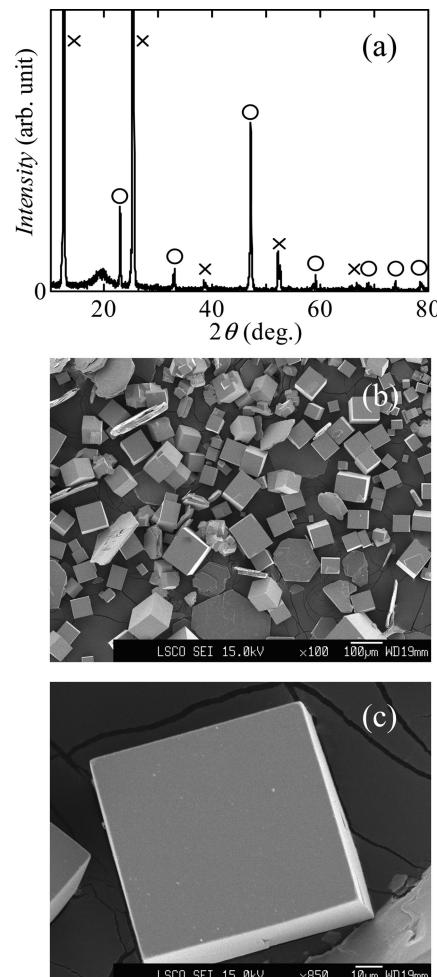


Figure 1. (a) Powder X-ray diffraction pattern of as-prepared No. 2 sample. Circles and crosses indicate peaks of (La,Sr,K)CoO_{3+δ} and KCo₂O₄, respectively. (b,c) SEM photographs of the sample.

mm. The surfaces of (La,Sr,K)CoO_{3+δ} crystals were flat. Almost similar results were obtained for the other as-prepared samples.

KCo₂O₄ crystals were removed successfully from as-prepared samples by the following isolation procedures. The isolated (La,Sr,K)CoO_{3+δ} crystals were used for elementary analyses and magnetization measurements. When an as-prepared sample was held in boiling water, KCo₂O₄ crystals were broken into fine powder possibly by intercalation of H₂O molecules into the crystals, but (La,Sr,K)CoO_{3+δ} crystals were not broken. The fine powder of KCo₂O₄ crystals was removed by decantation. This procedure was repeated until KCo₂O₄ was not detected by an optical microscope observation and powder XRD. Figure 2 shows powder XRD patterns of the samples (Nos. 1–4) obtained by the isolation procedure. Only the diffraction peaks of (La,Sr,K)CoO_{3+δ} were observed, and no diffraction peak of KCo₂O₄ was detected in these samples.

Table 2 shows the molar ratio of elements in (La,Sr,K)CoO_{3+δ} crystals for No. 1–4 samples. It is found that the Sr content increases with increasing the starting quantity of excess SrCO₃. On the basis of the standard deviations of calibration curves for the elementary analyses, the experimental errors were estimated to be about 0.01 for each metal

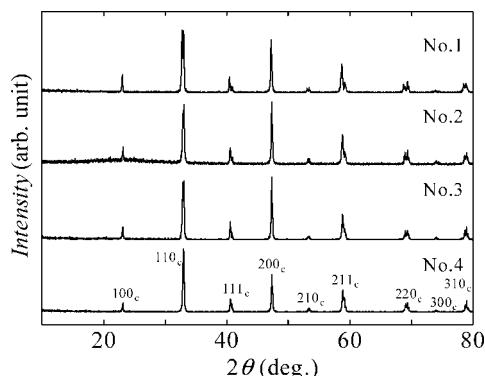


Figure 2. Powder X-ray diffraction patterns of $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ crystals after the isolation procedure with removal of KCo_2O_4 crystals from as-prepared samples. The peaks are indexed by pseudocubic unit cell.

Table 2. Molar Ratio of Elements in $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ Crystals

no.	La	Sr	K	Co	Zr	O
1	0.80	0.12	0.09	1	0.009	
2	0.71	0.25	0.06	1	0.007	
3	0.65	0.34	0.02	1	0.003	
4	0.57	0.44	0.00	1	0.003	3.01

Table 3. Lattice Constants of $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ Crystals

no.	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
1	5.4492(6)	13.201(2)	339.49(8)
2	5.4407(3)	13.216(1)	338.80(5)
3	5.4380(3)	13.218(1)	338.51(5)
4	5.4325(3)	13.2254(3)	338.02(2)

element in Table 2. Taking account of this, K is undoubtedly present in No. 1 and 2 samples. The K content decreased with increasing the starting quantity of excess SrCO_3 . K was not detected in No. 4 sample. The sum of La, Sr, and K contents coincides with the Co content for each sample within the experimental errors. This concludes that K is substituted for La/Sr. This is reasonable because the ion radius of K is close to that of La/Sr rather than Co. In addition, this indicates that KCo_2O_4 was nearly completely removed from as-prepared samples by the isolation procedure. The Zr contents are in the order of the experimental errors for No. 1 and 2 samples, but much less than the experimental errors for No. 3 and 4 samples. The oxygen content was determined only for No. 4 sample by assuming that the chemical formula is $\text{La}_{0.57}\text{Sr}_{0.44}\text{CoO}_{3+\delta}$. No appreciable oxygen nonstoichiometry was observed in the sample within the experimental errors.

It is found from Figure 2 that all $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ crystals have a rhombohedral structure with a space group $\bar{R}\bar{3}c$. The lattice constants for the hexagonal setting are tabulated in Table 3. The lattice constants of No. 4 sample are close to literature values.¹⁵ The XRD peaks of $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ crystals from $(200)_c$ planes observed around 47° are shown in Figure 3 on an enlarged scale in addition to 220 peak of Si crystalline powder, where the subscript c means that these are indexed on the basis of the pseudocubic unit cell. (The 220 peak of Si can be used as an index for crystallinity or homogeneity of $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$, because the diffraction angle is close to the 200_c peaks of $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ by

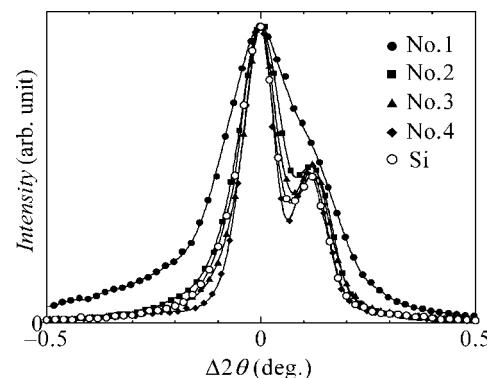


Figure 3. X-ray diffraction peaks from $(200)_c$ plane of the pseudocubic unit cell of $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ crystals and from (220) plane of Si crystals. The peak intensities are normalized. $\Delta 2\theta = 2\theta - 2\theta_{\text{peak}}$, where $2\theta_{\text{peak}}$ is 2θ of the respective peaks.

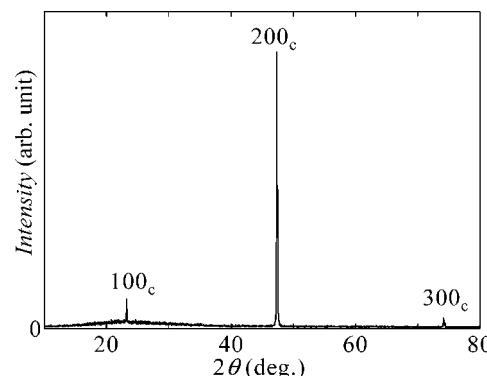


Figure 4. X-ray diffraction pattern of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ single crystals (No. 4 sample), the surfaces of which were carefully arranged parallel to a XRD holder plane.

chance.) In this figure, normalized intensities are plotted against $\Delta 2\theta (=2\theta - 2\theta_{\text{peak}})$, where $2\theta_{\text{peak}}$ is 2θ of the respective diffraction peaks. The diffraction peak is clearly broad for No. 1 sample but clearly sharp for No. 4 sample as compared to Si. The diffraction peak broadens with increasing K content.

The Laue back-reflection method using one $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ crystal showed a few diffraction spots, but it was impossible to determine the mirror index of the surfaces of the parallelepiped crystals because no clear diffraction pattern was observed possibly because the crystal is small. Thus, powder X-ray diffraction was carried out for $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ single crystals, the surfaces of which were carefully arranged parallel to a XRD holder plane. Figure 4 shows the XRD pattern of the arranged crystals of No. 4 sample. Only diffraction peaks from $(100)_c$, $(200)_c$, and $(300)_c$ planes were observed, and thus the mirror index of the surfaces of the grown crystals was concluded to be $(100)_c$.

Figure 5 shows the temperature dependence of inverse magnetic susceptibility of a set of $(\text{La},\text{Sr},\text{K})\text{CoO}_{3+\delta}$ single crystals measured under 100 Oe. The paramagnetic Curie temperature is positive for each sample and increases with decreasing La content. This is reasonable, because the Curie temperature of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ increases with increasing x (or average valence of Co). The inverse magnetic susceptibility versus temperature curve just above the Curie tem-

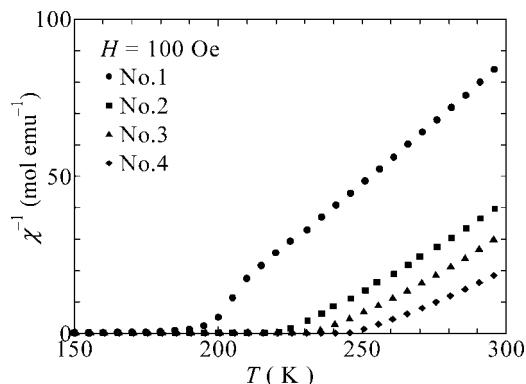


Figure 5. Temperature versus inverse magnetic susceptibility curves of a set of many $(La, Sr, K)CoO_{3+\delta}$ single crystals under a magnetic field of 100 Oe.

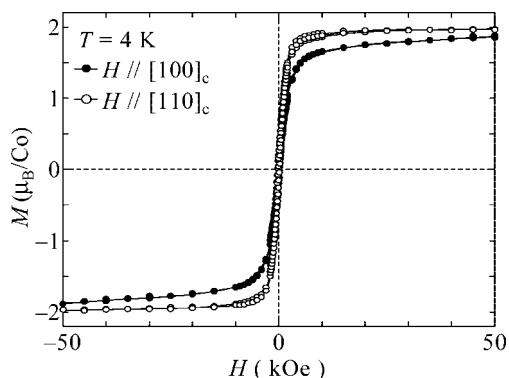


Figure 6. Magnetic field versus magnetization curves of a $La_{1-x}Sr_xCoO_{3+\delta}$ single crystal (No. 4 sample) at 4 K under magnetic fields parallel to $[100]_c$ and $[110]_c$ of the pseudocubic unit cell.

perature is S curve for No. 1 sample but downward convex (second derivative of χ^{-1} with respect to T is positive) for the other samples. Figure 6 shows magnetization versus magnetic field curves obtained using one $La_{1-x}Sr_xCoO_{3+\delta}$ single crystal of No. 4 sample under magnetic fields parallel to $[100]_c$ and $[110]_c$ crystalline axes. No demagnetizing-field correction was carried out here. The magnetization easily saturated in the direction of $[110]_c$ but gradually saturated in the direction of $[100]_c$. The coercive forces were about 140 and 220 Oe in the directions of $[110]_c$ and $[100]_c$, respectively.

Discussion

The XRD peaks of $(La, Sr, K)CoO_{3+\delta}$ crystals of No. 1 sample were broad as compared to the other samples (see Figure 3) despite that the crystal sizes are similar for all samples. This implies that La, Sr, and K contents are inhomogeneous in a crystal or between crystals for No. 1 sample. This inhomogeneity is consistent with the results of magnetization measurements. The inverse magnetic susceptibility versus temperature curve of No. 1 sample was S curve above Curie temperature (see Figure 5), which is usually observed in samples with a distribution in Curie temperatures.¹⁶ In addition, a Curie temperature of one crystal of No. 1 sample was different from that of a set of many crystals (not shown). On the basis of these results, No. 1 sample is

concluded inhomogeneous at least between crystals with respect to La/Sr/K contents. On the other hand, there is no evidence indicating inhomogeneity for the other samples, because XRD peaks were sharp and the inverse magnetic susceptibility versus temperature curves were downward convex, which is usually observed in homogeneous ferromagnets due to critical fluctuation.¹⁷ In particular, No. 4 sample is supposed highly homogeneous because the XRD peak is sharper even than Si.

Clear magnetic anisotropy was observed in No. 4 sample. Because the crystal form is pseudocube, the demagnetizing-field effect should be similar in both $[100]_c$ and $[110]_c$ directions. Therefore, the observed magnetic anisotropy originates from magnetocrystalline anisotropy. This is reasonable because some experiments indicate a strong spin-orbit coupling constant in $La_{1-x}Sr_xCoO_{3+\delta}$ crystals.^{12,18,19} Because this crystal is not cubic but rhombohedral actually, uniaxial anisotropy is expected for this crystal. The c axis of the hexagonal unit cell of this crystal is parallel to $[111]_c$ axis of the pseudocubic unit cell. Six equivalent $[110]_c$ axes of the pseudocubic unit cell split into two kinds of axes in the hexagonal unit cell. One is a set of three equivalent axes perpendicular to the hexagonal c axis, and the other is a set of three equivalent axes not perpendicular to the hexagonal c axis. The present results thus suggest that this crystal has an easy plane of magnetization perpendicular to the hexagonal c axis. The magnetocrystalline anisotropy is important to clarify the orbital states of Co ions in $La_{1-x}Sr_xCoO_3$.

Fita et al.¹³ have measured the magnetization of $La_{1-x}Sr_xCoO_3$ single crystals ($x = 0.2$ and 0.3) at 15 kOe and 5 K by changing the angle between applied magnetic field and a crystalline axis, although it was not determined what is the crystalline axis. Two-fold symmetry was observed in the angular dependences of magnetization, suggesting uniaxial magnetic anisotropy. This is consistent with the present results. In the angular dependences, the maximum magnetization was twice larger than the minimum magnetization. This anisotropy is much larger than the present results. The large anisotropy may originate from the rhombohedral distortion larger than the present crystal with $x = \sim 0.44$.

Conclusions

$La_{1-x}Sr_xCoO_{3+\delta}$ ($x = \sim 0.44$) single crystals were grown from KOH melt at 773 K under H_2O/O_2 mixed gas flow. The parallelepiped crystals had the surfaces of $(100)_c$ planes. The edges of the largest crystal were about 0.1 mm. The grown crystals were concluded highly homogeneous with respect to La/Sr contents. The magnetization measurements using one crystal showed clear magnetic anisotropy and suggested uniaxial magnetocrystalline anisotropy with an easy plane of magnetization perpendicular to the c axis of

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the hexagonal unit cell. Further studies are necessary to confirm this anisotropy, because this crystal would have twin structure according to the literature.^{10–13}

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