

The Isotropic Temperature Factors of $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0, 0.1, 0.5, 0.8, \text{ and } 1.0$)

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The cubic perovskite $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ has a maximum value of a -axis at $x = 0.3$ and a change of spin state of Co^{4+} ion from low to high. To elucidate these properties, the isotropic temperature factor (B) of strontium, cobalt, manganese, and oxygen atoms for $x = 0, 0.1, 0.5, 0.8, \text{ and } 1.0$ have been derived from powder X-ray diffraction measurements. The isotropic temperature factor of oxygen for $x = 0, 0.1, \text{ and } 1.0$ is small and that for $x = 0.5 \text{ and } 0.8$ is large. This fact suggests that the oxygen ion deviates from the center of the Co-O-Mn bond in the solid solutions with $x \geq 0.3$. Larger CoO_6 octahedra and smaller MnO_6 octahedra, which are connected by corner sharing of oxygens of the octahedron, are distributed statistically.

Introduction

The perovskite structure oxides $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ ($0 \leq x \leq 1.0$) were prepared under high oxygen pressures of 140 MPa and their magnetic properties investigated (1). X-Ray powder diffraction patterns of these oxides were indexed as the cubic perovskite structure. The relation of the lattice parameter vs composition (X) in the whole range is shown in Fig. 1. The lattice parameter increased linearly with increasing x in the range $0 \leq x \leq 0.3$ and then it decreased linearly in the range $0.3 \leq x \leq 1.0$.

SrCoO_3 is ferromagnetic with a Curie temperature of 222 K (2) and SrMnO_3 is antiferromagnetic with a Néel temperature of 260 K (3). In the system $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$, the change from ferromagnet to antiferromagnet occurred at about $x = 0.3$. The Curie temperature decreased linearly with increasing x in the ferromagnetic region. The Néel temperature increased monotonically with increasing x in the antiferromagnetic region. From the results of the magnetic susceptibility measurements, Co^{4+} ion changed its spin state from low $(d\epsilon)^5(d\gamma)^0$ to high $(d\epsilon)^3(d\gamma)^2$ at about $x = 0.3$. It is considered that this change of spin state in Co^{4+} ion strongly relates to the lattice parameter.

To examine the stability of Co^{4+} ion with the high spin state, the isotropic tempera-

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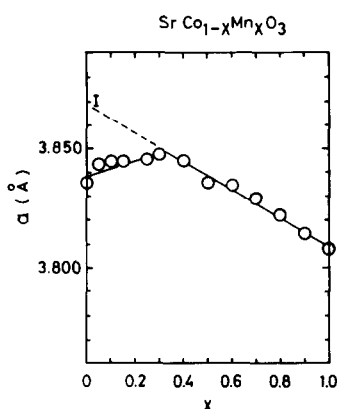


FIG. 1. The relation between a -axis and composition (X) in the system $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$.

ture factor (B) of the atoms (Sr, Co, Mn, and O) were calculated from powder X-ray diffraction measurement.

Experimental

The samples were prepared by standard ceramic technique (1). Powders of SrCO_3 , $\text{CoCO}_3 \cdot 6\text{H}_2\text{O}$, and MnCO_3 were weighed in the desired proportions and milled for 24 hr with acetone. After drying of the mixed powders at 100°C , they were pre-fired in air at 800°C for 24 hr. Then they were reground and fired at 1000 – 1350°C in pure oxygen gas for 24 hr. The firing was repeated three times. The oxygen-deficient oxides obtained in this way were annealed under oxygen pressures of 140 MPa at 300°C for 48 hr.

Phases of the products were identified by X-ray powder diffraction. To calculate the isotropic temperature factor of powder samples, reflections were measured with Ni-filtered $\text{CuK}\alpha$ radiation in the range $20^\circ \leq 2\theta \leq 100^\circ$. After correction for background, absorption and extinction, the observed structure factors $|F_{\text{ob}}|$ were calculated under the assumption that strontium, cobalt, manganese, and oxygen atoms occupied the special positions 1a, 1b, 1b, and

3c, respectively, in the space groups $P\bar{4}3m$, $P432$, and $Pm3m$. A least square refinement was made with UM BADTEA program (4) on the temperature factor. In the refinement program, neutral atomic form factors were taken from the international Table for X-Ray Crystallography (1962). After six cycles of least square refinement using the isotropic temperature factors, the final conventional R values were 5.4, 5.3, 5.8, 9.4, and 5.3% for $x = 0, 0.1, 0.5, 0.8,$ and 1.0 , respectively, in the system $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$.

Results and Discussion

The x-ray powder diffraction patterns of samples with $x = 0, 0.1, 0.5, 0.8,$ and 1.0 were completely indexed as the cubic perovskite structure. SrMnO_3 prepared under high pressures of 5 GPa was hexagonal perovskite structure with $a = 5.431 \text{ \AA}$ and $c = 13.396 \text{ \AA}$ (5), but the present samples prepared under 140 MPa of oxygen pressure had cubic symmetry. The oxygen deficiency of samples annealed under high oxygen pressures was small. The relation between the annealing condition under high oxygen pressures and the physical properties for $\text{SrCoO}_{3-\delta}$ was investigated by the present authors (6).

The isotropic temperature factor calculated using the space group $Pm3m$ is as follows: Sr:2.38, Co:4.25, and O:7.94 for $x = 0$ ($R = 5.7\%$) and Sr:1.97, Mn:4.47, and O:7.60 for $X = 1.0$ ($R = 5.8\%$). From these results, the isotropic temperature factor of strontium is ca. 2.00 and that of cobalt and manganese is ca. 4.00. To compare the isotropic temperature factors of oxygen for all samples, the isotropic temperature factors of oxygen for all samples, the isotropic temperature factors of strontium, cobalt, and manganese were fixed as 2.00, 4.00, and 4.00, respectively. Least-square refinement on oxygen was performed for $X = 0, 0.1, 0.5, 0.8,$ and 1.0 . The isotropic

temperature factor, final conventional R factor, and the list of the observed and calculated structure factors (F) are listed in Table I. Conventional R factors of samples being 5–6%, $Pm3m$ was considered to be correct.

The isotropic temperature factor of oxygen for $x = 0.1$ was nearly equal to those for $X = 0$ and 1.0, but those for $X = 0.5$ and 0.8 were larger than those for $X = 0$ and 1.0. Cobalt and manganese ions in the system $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ were determined to be tetravalent from the results of magnetic measurement. The relation of the effective magnetic moment (μ_{eff}) and the composition (X) is shown in Fig. 2. Circles indicate the observed values, and a dotted line is drawn for the theoretical values calculated in case of high and low spin states of Co^{4+} ion located at the octahedral site, respectively. One is the high spin state with $(d\epsilon)^3(d\gamma)^2$ and the other is the low spin state with $(d\epsilon)^5(d\gamma)^0$. Mn^{4+} ion ($3d^3$) was $(d\epsilon)^3(d\gamma)^0$. The observed and calculated μ_{eff} were nearly equal to each other under the assumption of $S = \frac{1}{2}$ for Co^{4+} ion and $S = \frac{3}{2}$ for Mn^{4+} ion in the range $0 \leq X < 0.3$ and $S = \frac{5}{2}$ for Co^{4+} ion and $S = \frac{3}{2}$ for Mn^{4+} ion in the range $0.3 \leq X \leq 1.0$. From Fig. 2, it was considered that the spin state of Co^{4+} ion changed from low to high at $X = 0.3$. The large isotropic temperature factors for $X =$

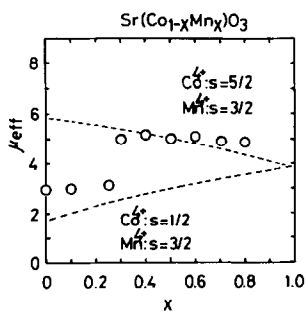


FIG. 2. The relation between the effective magnetic moment and composition (X) in the system $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$.

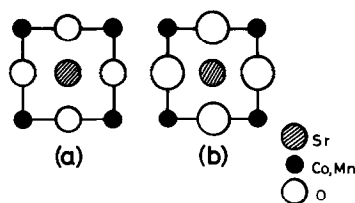


FIG. 3. The schematic model of (110) plane: (a) for $X = 0, 0.1,$ and $1.0+$ (b) for $X = 0.5$ and 0.8 .

0.5 and 0.8 would correspond to the change of spin state in Co^{4+} ion.

MnFe_2O_4 was cubic and normal spinel structure. Cervinka *et al.* (6) investigated using X-ray measurement whether the octahedra containing Mn^{2+} ion ($3d^5$) were tetragonally distorted or were cubic symmetry. From the large isotropic temperature factor of oxygen in MnFe_2O_4 , they concluded the existence of tetragonally deformed octahedra caused by Jahn–Teller distortion of Mn^{2+} ion. In the system $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$, $0.3 \leq x \leq 0.8$, it was considered that the large isotropic temperature factor of oxygen was caused by fluctuation in the Me^{4+} –O distance. The electron clouds of oxygen for $X = 0.5$ and 0.8 spread more widely than those for $X = 0, 0.1,$ and 1.0. This is schematically shown in Fig. 3. This assumption corresponded to the large isotropic temperature factor for $X = 0.5$ and 0.8.

In the range $0 \leq X \leq 0.3$, the increase of a -axis was assumed to be based on the Vegard rule; the distance of Co^{4+} (low spin state)–O is 1.918 Å (6) and that of Mn^{4+} –O is 1.940 Å, assuming that Mn^{4+} ion in $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ ($0 \leq X \leq 0.3$) normally behaved as a tetravalent ion as in the case of Mn^{4+} ion in Mg_6MnO_8 , ZnMn_3O_7 , $3\text{H}_2\text{O}$, and DyMn_2O_5 (7). The variation of a -axis with increase of Mn^{4+} ion content was represented as follows by assuming an Mn^{4+} –O bond with ionic character.

$$\begin{aligned} a &= 2(r_{\text{Mn-O}}X + r_{\text{Co-O}}(1 - X)) \\ &= 2(1.940X + 1.918(1 - X)). \end{aligned}$$

The *a*-axis expanded with increasing *X*. Consequently, the electron state of Co⁴⁺ ion in the high spin state becomes more stable than that in the low spin state, because the ionic radius of Co⁴⁺ ion in a high spin state is larger than that in a low spin state as is true for other transition metal ions.

The distance Mn⁴⁺-O in cubic perovskite SrMnO₃ was 1.905 Å (3). In the perovskite structure oxides, the bonding between manganese and oxygen was stronger than that in manganese oxides with a different crystal structure such as Mg₆MnO₈, ZnMn₃O₇·3H₂O, and DyMn₂O₅. In the range 0.3 ≤ *X* ≤ 1.0, the distance Mn⁴⁺-O decreased from 1.940 to 1.905 Å. It is assumed that the Mn⁴⁺-O bond in the range

0.3 ≤ *X* ≤ 1.0 has a covalent nature. The variation of the *a*-axis with increase of Mn⁴⁺ ion content was represented as follows:

$$\begin{aligned} a &= 1(r_{\text{Mn-O}}X + r_{\text{Co-O}}(1 - X)) \\ &= 2(1.905X + 1.935(1 - X)) \end{aligned}$$

where 1.935 was the distance between Co⁴⁺ (high spin state)-O calculated from the point I in Fig. 1.

It is concluded that the volumes of the CoO₆ and MnO₆ octahedra connected to each other with oxygens at the apex of the octahedron are not so different in the range 0 ≤ *X* ≤ 0.3 resulting in the small isotropic temperature factor of oxygen. In the range 0.3 ≤ *X* < 1.0, there is a large difference

TABLE I
TEMPERATURE FACTOR, *R* FACTOR AND STRUCTURE FACTORS (*F*_{obs} AND *F*_{cal})

	Sr:2.00,	Co:4.00,	O:7.58	<i>R</i> = 5.4%	
<i>X</i> = 0	<i>h k l</i>	<i>F</i> _{obs}	<i>F</i> _{cal}		
	1 0 0	2.28	3.87		
	1 1 0	41.37	42.98		
	1 1 1	20.60	20.23		
	2 0 0	48.68	46.77		
	2 1 1	30.82	30.11		
	2 2 0	29.14	30.46		
	3 1 0	21.49	22.24		
	3 1 1	10.05	10.33		
	2 2 2	19.44	21.61		
	3 2 1	19.39	16.97		
	Sr:2.00,	Co:4.00,	Mn:4.00,	O:6.78	<i>R</i> = 5.3%
<i>X</i> = 0.1	<i>h k l</i>	<i>F</i> _{obs}	<i>F</i> _{cal}		
	1 0 0	5.53	3.99		
	1 1 0	38.77	42.71		
	1 1 1	20.83	20.88		
	2 0 0	47.27	47.20		
	2 1 1	29.56	29.90		
	2 2 0	31.34	30.88		
	3 1 0	22.81	22.12		
	3 1 1	11.01	10.75		
	2 2 2	21.54	21.93		
	3 2 1	22.54	16.90		

TABLE I—Continued

	Sr:2.00,	Co:4.00,	Mn:4.00,	O:8.25	R = 5.8%
$X = 0.5$	$h k l$	F_{obs}	F_{cal}		
	1 0 0	7.60	4.93		
	1 1 0	40.40	42.18		
	1 1 1	20.66	20.70		
	2 0 0	45.87	45.65		
	2 1 1	30.74	29.61		
	2 2 0	30.89	29.65		
	3 1 0	20.38	21.92		
	3 1 1	11.36	10.46		
	2 2 2	18.46	21.06		
	3 2 1	18.81	16.76		
	Sr:2.00,	Co:4.00,	Mn:4.00,	O:13.00	R = 9.4%
$X = 0.8$	$h k l$	F_{obs}	F_{cal}		
	1 0 0	1.76	6.02		
	1 1 0	40.58	42.23		
	1 1 1	19.06	18.93		
	2 0 0	38.85	42.83		
	2 1 1	28.48	29.76		
	2 2 0	29.35	27.66		
	3 1 0	24.62	21.95		
	3 1 1	11.94	9.60		
	2 2 2	19.84	19.82		
	3 2 1	21.53	16.71		
	Sr:2.00,	Mn:4.00,	O:6.99	R = 5.3%	
$X = 1.0$	$h k l$	F_{obs}	F_{cal}		
	1 0 0	5.89	5.83		
	1 1 0	38.54	40.93		
	1 1 1	24.14	22.13		
	2 0 0	46.22	45.32		
	2 1 1	28.93	28.54		
	2 2 0	28.01	29.46		
	3 1 0	21.12	21.11		
	3 1 1	10.41	11.23		
	2 2 2	19.44	20.89		
	3 2 1	19.57	16.15		

between the volumes of CoO_6 and MnO_6 octahedra and each octahedron distributes statistically resulting in the large isotropic temperature factor of oxygen. The stability of Co^{4+} ion with high spin state in $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ would be caused by the large CoO_6 octahedra.

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