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Magnetic Properties in the System $BaCo_{1-x}Mn_xO_3$ and $SrCo_{1-x}Mn_xO_3$ $(0 \leqq x \leqq 1)$

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The compounds in the systems of $BaCo_{1-x}Mn_xO_3$ $(0 \leqq x \leqq 1)$ and $SrCo_{1-x}Mn_xO_3$ $(0 \leqq x \leqq 1)$ were prepared at an oxygen pressure of 1400 bars. The former had a two-layer hexagonal structure and that of the latter was cubic perovskite type. From the variation of the unit-cell parameters and of the magnetic properties, it is found that the Co^{4+} ions change from the low-spin to the high-spin state. In the system of $SrCo_{1-x}Mn_xO_3$, the change of magnetic property from ferromagnet to antiferromagnet is related to the spin state of Co^{4+} ions located at the octahedral sites.

Introduction

Since Yakel (*1*) synthesized $SrFe^{4+}O_3$, interest in the perovskite oxides with the chemical formula $A^{2+}B^{4+}O_3$ (A, alkaline earth ions; B, first-row transition metal ions) has been great. Their crystal structure stabilizes the tetravalent state of the first-row transition metal ions such as Fe^{4+}, Co^{4+}, and Ni^{4+} more easily than any other oxides.

The ideal perovskite structure has the cubic unit cell, in which octahedra share corners and the B^{4+}–O–B^{4+} angle is 180°. In the case where the A cation is large, the stacking sequence of the closed-packed AO_3 layers is changed from cubic to hexagonal. In the two-layer hexagonal structure 2*H* (*2*), octahedra share faces with each other to form linear chains parallel to the hexagonal *c*-axis.

Both $BaMnO_3$ and $BaCoO_3$ have the 2*H* hexagonal structure and their magnetic properties were investigated by Christensen *et al.* (*2*) and Krischer *et al.* (*3*). Both oxides are antiferromagnetic. The Co^{4+} ion was in the low-spin state with $(d\varepsilon)^5(d\gamma)^0$ electron configuration.

The compounds, $SrMnO_3$ and $SrCoO_3$, have a cubic perovskite structure. The magnetic properties of these oxides, reported by Takeda *et al.* (*4*) and Watanabe *et al.* (*5*), indicated that $SrMnO_3$ was an antiferromagnet with a Néel temperature of 260°K, $SrCoO_3$ was a ferromagnet with a Curie temperature of 200°K, and the Co^{4+} ion was in the low-spin state. In both structures, the Co^{4+} ion was in the low-spin state, and J^s_{90} for Co^{4+} $(d\varepsilon)^5(d\gamma)^0$ was antiferromagnetic, but J^s_{180} was ferromagnetic.

In the present study, an attempt was made to synthesize compounds with the chemical compositions of $BaCo_{1-x}Mn_xO_3$ and $SrCo_{1-x}Mn_xO_3$ to study the effect of replacement of Co^{4+} ions with Mn^{4+} ions on the magnetic property and the spin state of the Co^{4+} ion in both of 2*H* and cubic perovskite structures.

These results will also provide some information on the Co^{4+}–O–Mn^{4+} interaction in both the 90° and 180° cases.

Experimental

For the preparation of the compounds, mixtures of raw materials, $BaCO_3$, $SrCO_3$, $CoCO_36H_2O$, and $MnCO_3$, in the desired ratios were fired at 1050°C for 24 hr in air for the $BaCo_{1-x}Mn_xO_3$ ($0 \leqq x \leqq 1$) system, and at 1000–1350°C in pure oxygen gas for 24 hr for the $SrCo_{1-x}Mn_xO_3$ ($0 \leqq x \leqq 1$) system. The firing was repeated three times. The oxygen-deficient materials obtained in this way were annealed under oxygen pressures of 1400 bars at 650°C for the former and at 400°C for the latter for 48 hr (*6*).

Phases of the powder samples in the products were identified by X-ray diffraction with filtered Cu$K\alpha$ radiation. Lattice constants of the compounds were determined using α-SiO_2 as a standard material.

Magnetic properties were measured by an automatic recording magnetic balance in the temperature range from 77 to 300°K.

Results and Discussion

X-ray powder diffraction patterns of all samples of $BaCo_{1-x}Mn_xO_3$ ($0 \leqq x \leqq 1$) were completely indexed as the $2H$ structure. The relation between composition and lattice constants is shown in Fig. 1. In this system, a single crystal of $BaCoO_3$ ($x = 0$) was prepared under high oxygen pressures, and the results of X-ray analysis showed that the space group was $P6_3/mmc$ with the cell dimensions $a = 5.649$ and $c = 4.760$ Å (*7*). As seen in Fig. 1, the a-axis increased linearly with increasing x. The c-axis expanded linearly with increasing x from $x = 0$ to 0.5 and from $x = 0.5$ to 1.0. The atomic distance between transition metals along the c-axis was elongated from 2.380 Å for $BaCoO_3$ to 2.405 Å for $BaMnO_3$. From these results, it appears that the distance of Mn^{4+}–O is longer than that of Co^{4+}–O.

In the system, $SrCo_{1-x}Mn_xO_3$, the X-ray patterns of the specimens were indexed as cubic perovskite structure. The relation of cell parameter vs composition in the whole range is shown in Fig. 2. The lattice parameter of the a-axis increased linearly with increasing x from $x = 0$ to $x = 0.3$, and for $x = 0.3$ to $x = 1.0$, it decreased monotonously with increasing of x. The distances between the tetravalent transition-metal and oxygen atoms were calculated using the cell dimension in this solid solution series. The distance of 1.904 Å for Mn^{4+}–O was shorter than that of 1.921 Å for Co^{4+}–O. This result was inverse in comparison with that of the $BaCo_{1-x}Mn_xO_3$ series with the $2H$ structure.

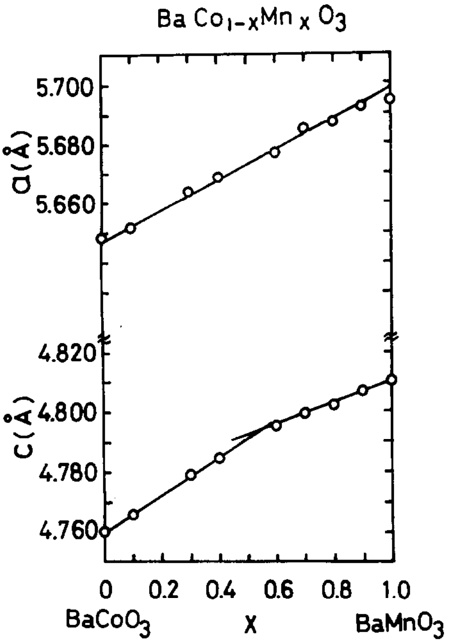

FIG. 1. Cell parameter vs composition in the system $BaCo_{1-x}Mn_xO_3$ ($0 \leqq x \leqq 1$) with a $2H$ structure.

The changes of lattice parameter with a break at $x = 0.5$ for $BaCo_{1-x}Mn_xO_3$ and $x = 0.3$ for $SrCo_{1-x}Mn_xO_3$ indicates that the ionic radius of the tetravalent transition metal ions located at octahedral site changed due to the change of spin state from low to high with increasing x. The results of the structure analysis of the $BaNiO_3$ with the $2H$ structure (*8*) indicated that the c-axis is twice the B^{4+}–B^{4+} distance, but the a-axis corresponds to the length between the chains of octahedron held together by large A^{2+} ions. It is expected, therefore, that the change of

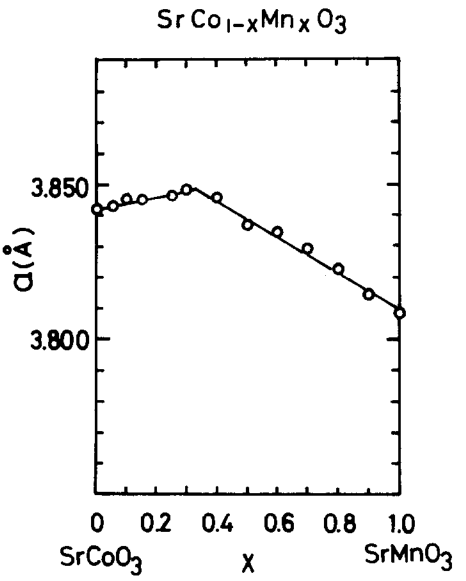

FIG. 2. Cell parameter vs composition in the system $SrCo_{1-x}Mn_xO_3$ ($0 \leq x \leq 1$) with a cubic perovskite structure.

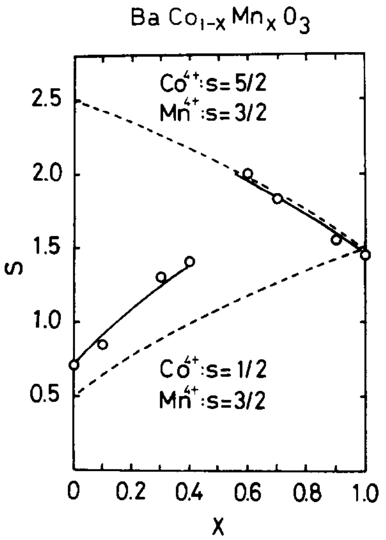

Fig. 3. Total spin angular momenta of S as a function of composition in the system $BaCo_{1-x}Mn_xO_3$.

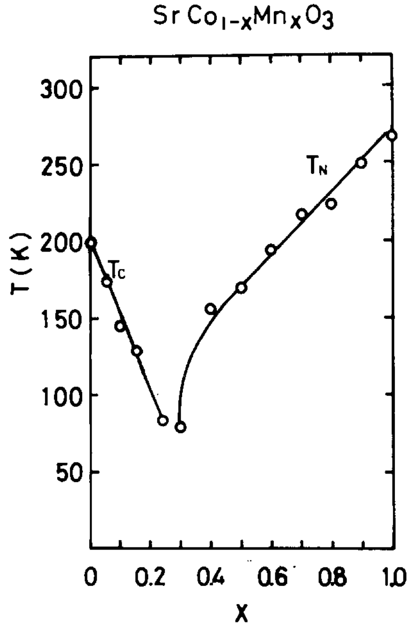

FIG. 4. Curie temperature and Néel temperature as a function of composition in the system $SrCo_{1-x}Mn_xO_3$.

ionic radius of B^{4+} ions strongly influences the variation in the unit cell parameter for c but not for a.

The results of the magnetic susceptibility measurements of the $BaCo_{1-x}Mn_xO_3$ compounds showed that the inverse susceptibility vs temperature curve obeys the Curie–Weiss law above 77°K. The total spin angular momentum of S was calculated and is presented in Fig. 3. A full line indicates the observed values, and a dotted line is drawn for the theoretical values calculated in cases of high- and low-spin states of Co^{4+} ion located at octahedral site respectively; one is the high-spin state with the $(d\varepsilon)^3(d\gamma)^2$ electron configuration and the other is the low-spin state with the $(d\varepsilon)^5(d\gamma)^0$ electron configuration. The Mn^{4+} ion with a $3d^3$ electron configuration has only one spin state with the $(d\varepsilon)^3(d\gamma)^0$ electron configuration. The observed and calculated values of S shown in Fig. 3 were nearly equal to each other under the assumption of $S = \frac{1}{2}$ for Co^{4+} and $S = \frac{3}{2}$ for Mn^{4+} in the compositional range of $0.0 \leq x \leq 0.5$, and in the range $0.6 \leq x \leq 1.0$ the observed values of S lie on the dotted line, calculated assuming that $S = \frac{5}{2}$ for Co^{4+} and $S = \frac{3}{2}$ for Mn^{4+} ion. From these results, it was concluded that the Co^{4+} ion changed its spin state from low to high at $x = 0.5$. This conclusion is supported by the result of the X-ray analysis.

In the system, $SrCo_{1-x}Mn_xO_3$, it is known that $SrCoO_3$ is ferromagnetic and $SrMnO_3$ is antiferromagnetic. In Fig. 4, the Curie temperature (T_C) and the Néel temperature (T_N) are shown as a function of x. $SrCoO_{2.97}$ gave the spontaneous magnetization of 34.0 emu/g at 77°K. From this value, a magnetic moment of 1.18 μ_B/mole at 77°K was obtained, corresponding to the moment caused by one unpaired electron. This fact suggests that cobalt ion is in a low-spin state with the $(d\varepsilon)^5(d\gamma)^0$ electron configuration. As seen in Fig. 4, in the compositional range of $0.0 \leqq x < 0.3$, the products were ferromagnetic and the Curie temperature decreased linearly with increasing x. Around $x = 0.3$ the samples were antiferromagnetic and the Néel temperature increased with increasing x. The Curie temperature and the saturation magnetization at 77°K of $SrCo_{0.9}Mn_{0.1}O_{2.98}$ were determined to be 140°K and 27.1 emu/g, respectively. The decrease of saturation magnetization with an increase of x was explained under the assumption of the antiferromagnetic superexchange coupling between Co^{4+} and Mn^{4+} ion. In the antiferromagnetic region of the solid solution, it is considered that J_{180}^s of the superexchange interactions of Mn^{4+}–O–Mn^{4+} is antiferromagnetic and dominates the magnetic properties of samples. In particular, it is expected that the change of the magnetic properties from ferromagnetic to antiferromagnetic at $x = 0.3$ is strongly influenced by the change of lattice constant, as shown in Fig. 2; that is, the Co^{4+} ion is in the low-spin state at $x < 0.3$ but in the high-spin state at about $x = 0.3$. As for the superexchange interaction, it is expected that in the range $0 \leqq x < 0.3$, J_{180}^s for Co^{4+} $(d\varepsilon)^5(d\gamma)^0$ is strongly ferromagnetic and J_{180}^s for Co^{4+} $(d\varepsilon)^5(d\gamma)^0$–O–$Mn^{4+}$ $(d\varepsilon)^3(d\gamma)^0$ is antiferromagnetic, while, for $0.3 \leqq x \leqq 1.0$, all the J_{180}^s for Mn^{4+} $(d\varepsilon)^3(d\gamma)^0$, Co^{4+} $(d\varepsilon)^3(d\gamma)^2$, and Mn^{4+}–O–Co^{4+} are antiferromagnetic.

It is concluded that tetravalent cobalt ions located at octahedral sites in both solid solution series of $BaCo_{1-x}Mn_xO_3$ with a 2*H* structure and $SrCo_{1-x}Mn_xO_3$ with a cubic perovskite structure change their spin states from low to high at $x = 0.5$ for the former and at $x = 0.3$ for the latter. This change of spin state of the Co^{4+} ion strongly influences the lattice parameters and magnetic properties of the products in both solid solution series.

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