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Magnetic Property in the System $BaCo_{1-x}Ni_xO_3$ ($x = 0 \sim 1$)

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The system of $BaCo_{1-x}Ni_xO_3$ ($x = 0 \sim 1$) with a two-layer hexagonal perovskite-type structure are prepared at an oxygen pressure of 2000 bars. The change in unit cell parameters is not linear. Magnetic measurements indicate that $BaCoO_3$, $BaCo_{0.9}Ni_{0.1}O_3$ and $BaCo_{0.8}Ni_{0.2}O_3$ are antiferromagnetic with $T_N = 8$, 10, and 10°K, respectively.

Introduction

Both $BaNiO_3$ and $BaCoO_3$ have a two-layer hexagonal perovskite-type structure (*1*, *2*). These compounds are composed of the hexagonal close packing of BaO_3 layers with Ni^{4+} or Co^{4+} ions occupying the O_6 octahedra. Every octahedron share an opposite face to form linear chains of octahedra parallel to the hexagonal *c*-axis.

The magnetic properties of these compounds have been studied by several investigators. $BaNiO_3$ shows a diamagnetic behavior (*3*, *4*) which indicates that the Ni^{4+} ion has no magnetic moment and is therefore in a low-spin state. On the other hand, $BaCoO_3$ annealed at 350°C in an oxygen atmosphere is antiferromagnetic with $T_N = 4$°K (*5*). From the magnetic measurement, Co^{4+} was determined to be in a low-spin state.

It is well known that a magnetic moment or a magnetic transition temperature decreases linearly by increasing the contents of nonmagnetic ions. This occurs when magnetic ions in the crystal sublattice are partly replaced by nonmagnetic ions. In this case, all kinds of nonmagnetic ions with $3d^0$ or $3d^{10}$ electron configuration such as Zn^{2+}, Al^{3+}, Ca^{3+}, etc., can be substituted. Although many papers have been published on derivatives containing such typical nonmagnetic ions, there has been little investigation into the effect of replacement of nonmagnetic ions with electrons in $d\gamma$ or $d\varepsilon$ orbitals. The Ni^{4+} ion in $BaNiO_3$ is in a ($3d^6$) configuration, but it is nonmagnetic since it is in a low-spin state. In the present study, an attempt was made to synthesize a series of compounds with the chemical compositions $BaCo_{1-x}Ni_xO_3$ to see the effect of replacement of Co^{4+} ion by Ni^{4+} ion on its magnetic properties. These results could also yield some information concerning the properties of Co^{4+}–Co^{4+} interaction within the linear chains in $BaCoO_3$.

Experimental

Starting materials with the chemical composition of $BaCo_{1-x}Ni_xO_3$ ($0 \leqslant x \leqslant 1$) were prepared by weighing oxides of Co_3O_4 and NiO or the carbonates $BaCO_3$, $CoCO_3$, and $NiCO_3$ of high purity and by mixing them with acetone in a ball mill. After drying, the mixtures were heated at 1000°C for 48 hr in a stream of O_2 gas, and then ground and reheated. These products were charged in gold tube capsules with an open end and placed in a test-tube type reactor. Finally, the specimens were oxidized at 600°C and 2000 bars (Po_2) for 48 hr.

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The samples synthesized by the above treatments were identified by X ray powder diffraction with $CoK\alpha$ radiation using Si metal as a standard. The chemical compositions of these products were determined by means of gravimetric and thermogravimetric analysis. Magnetic properties from 4.2°K to room temperature were measured by an automatic recording magnetic balance.

Results and Discussions

The X ray powder diffraction patterns of all the products in this system were completely indexed on the basis of a two-layer hexagonal structure. Single crystals of $BaNiO_3$ and $BaCoO_3$ corresponding to the samples of end member were easily prepared under a high oxygen pressure of 2000 bars, as was previously reported (*3*, *6*). The X ray data of powdered specimens prepared by grinding these single crystals were in good agreement with those of the present samples where $x = 0.0$ and $x = 1.0$. From their crystal structure, the cation–cation distance was determined from the value of $c/2$, where c is a cell dimension in the hexagonal symmetry. The oxygen content of each phase was calculated by using the phase transformation from $BaCo_{1-x}Ni_xO_3$ to $BaCo_{1-x}Ni_xO_{2.5}$.

The details of relationship between the value of x and crystal parameter are shown in Fig. 1. As seen in this figure, the cell dimension along the a-axis was slightly decreased with increasing x. On the other hand, the cell dimension c expanded with increasing x, but did not change linearly. Little change was observed in the Co-rich region, but in the Ni-rich region the change was large. The atomic distance between transition metals along the c-axis was increased from 2.380 Å for $BaCoO_3$ to 2.405 Å for $BaNiO_3$.

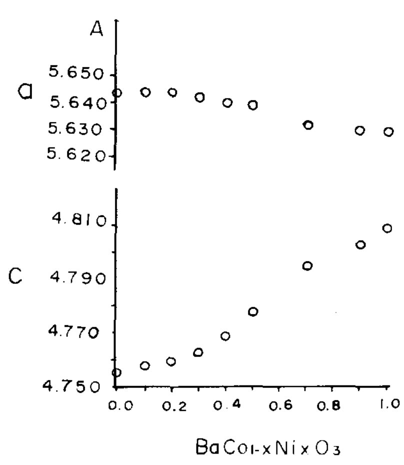

FIG. 1. Cell parameters versus composition in the system $BaCo_{1-x}Ni_xO_3$ ($0.0 \leqslant x \leqslant 1.0$).

Figure 2 shows the magnetic susceptibility and reciprocal magnetic susceptibility per gram versus temperature for $BaCoO_3$, $BaCo_{0.9}Ni_{0.1}O_3$ and $BaCo_{0.8}Ni_{0.2}O_3$.

The Néel temperature was determined from the maximum in the susceptibility curve. The Curie–Weiss θ_p and the molar Curie constant, C_m, were also determined by the use of the Curie–Weiss law for the high-temperature susceptibility data. The results are also listed in Table I.

In the composition range, $0.0 \leqslant x \leqslant 0.2$, the products were antiferromagnetic and their Néel temperature and paramagnetic Curie temperature are given in Table I.

In the composition range $0.3 \leqslant x \leqslant 0.5$, the magnetic ordering was not observed down to 4.2°K, and the magnitude of the susceptibility and the effective magnetic moments per formula unit decreased as x increased. This indicates that Ni^{4+} ions act as nonmagnetic ions, and subsequently, the effect of magnetic dilution of Co^{4+} ions by Ni^{4+} ions was observed.

In the region $0.7 \leqslant x \leqslant 1.0$, the value of the magnetic susceptibility was on the order of 10^{-7} emu/g and the samples showed the temperature-independent paramagnetic susceptibility. In this region, the magnetic properties of specimens were affected by the nonmagnetic Ni^{4+} ions of $(3d)^6$ with low-spin state (*3*).

Assuming that Ni^{4+} ions with low-spin state of $(3d)^6$ electron configuration were nonmagnetic, the total angular momentum of Co^{4+} ions for each specimen in the region $0 \leqslant x \leqslant 0.5$ was determined to be 0.8–0.9 for all specimens. The values scarcely varied despite the change in chemical composition. The value of $s = 0.8$–0.9 is larger than the value of $s = 0.5$ for Co^{4+} ion in a low-spin state. This indicates that the orbital angular

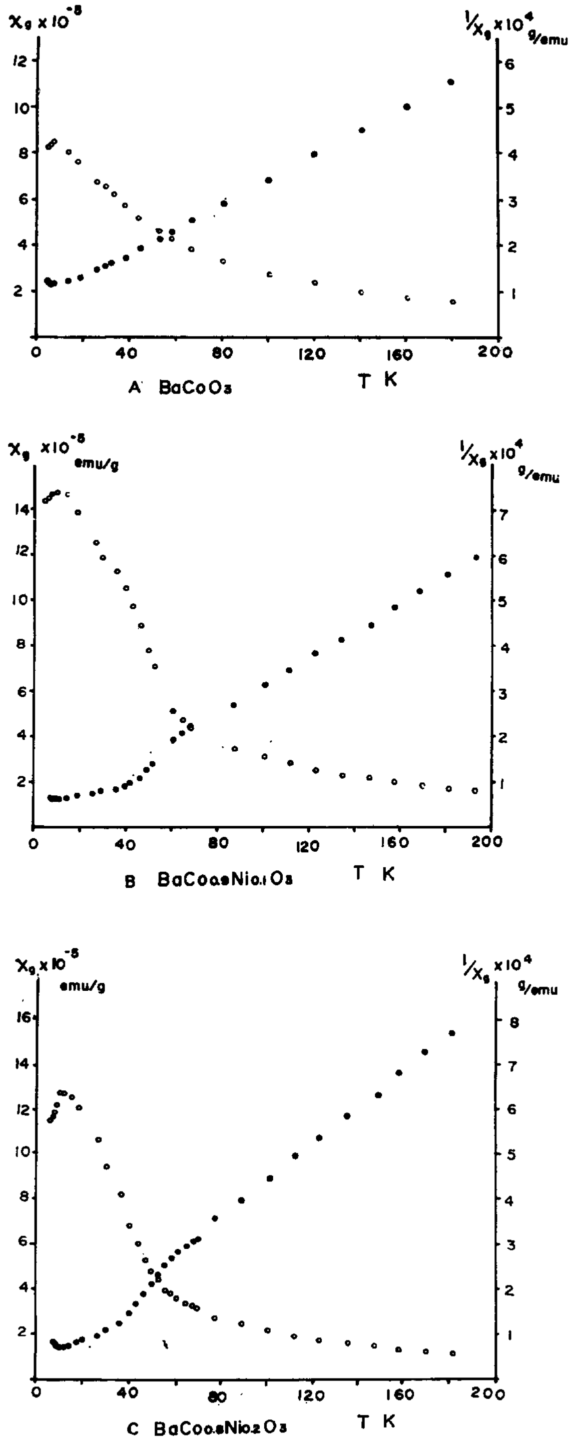

FIG. 2. Magnetic susceptibility versus temperature and reciprocal of susceptibility versus temperature for (A) $BaCoO_3$, (B) $BaCo_{0.9}Ni_{0.1}O_3$, and (C) $BaCo_{0.8}Ni_{0.2}O_3$.

TABLE I

UNIT CELL PARAMETERS AND MAGNETIC CHARACTERISTICS IN THE SYSTEM $BaCo_{1-x}Ni_xO_3$ ($0.0 \leqslant x \leqslant 1.0$)

Sample	θ_p (°K)	T_N (°K)	C_m	Unit cell parameter a (Å)	 c (Å)
$BaCoO_{2.99}$	−27	8	0.89	5.645(4)	4.756(3)
$BaCo_{0.9}Ni_{0.1}O_{3.01}$	− 7	10	0.83	5.646(4)	4.758(3)
$BaCo_{0.8}Ni_{0.2}O_{3.02}$	−10	10	0.61	5.645(4)	4.760(3)
$BaCo_{0.7}Ni_{0.3}O_{3.04}$	−16		0.61	5.642(4)	4.763(3)
$BaCo_{0.6}Ni_{0.4}O_{3.03}$	−19		0.52	5.640(4)	4.770(3)
$BaCo_{0.5}Ni_{0.5}O_{3.04}$	−20		0.43	5.640(4)	4.780(3)
$BaCo_{0.7}Ni_{0.3}O_{3.01}$	—		—	5.633(4)	4.794(3)
$BaCo_{0.9}Ni_{0.1}O_{3.00}$	—		—	5.632(4)	4.800(3)
$BaNiO_{3.00}$	—		—	5.634(4)	4.810(3)

momentum is not fully quenched by the crystal field distortion from cubic to trigonal symmetry.

In the case of $BaCoO_3$ at $x = 0.0$, the Néel temperature, T_N, was near 8°K, and paramagnetic Curie temperature, θ_p, was near −27°K. Candela et al. (*5*) reported the result of magnetic susceptibility measurement for $BaCoO_3$. Although they do not state the Néel temperature and paramagnetic Curie temperature, T_N and θ_p are estimated to be near 10°K and 0°K from a review of their figures. On the other hand, paramagnetic Curie temperature of $BaCoO_3$ prepared by Greaves (*7*) was below 0°K. This discrepancy seems to be due to a difference of oxygen content in this system. In the present study, all specimens were prepared at 2000 bars of oxygen pressure, and from the results of chemical analysis, the chemical formula was determined to be $BaCoO_{3.0}$. On the other hand, Candela et al. prepared the sample in O_2 atmosphere and they indicated the possibility of a slight deviation from $BaCoO_3$ stoichiometry similar to the $BaCoO_{2.95}$ reported by Zanne (*8*).

$BaCo_{0.9}Ni_{0.1}O_3$ and $BaCo_{0.8}Ni_{0.2}O_3$ showed an anomalous susceptibility versus temperature curve, as shown in Fig. 2. A change in Curie constant was observed at about 60°K. It is suggested that the short-range magnetic order, Co^{4+}–Co^{4+} dimer formation, or crystal field distortion could occur below this temperature.

According to the rules for a sign of 90° superexchange magnetic interaction reported by Kanamori (*9*) and Motida et al. (*10*), so-called J^s_{90} is ferromagnetic for Cr^{3+} ($d\varepsilon^3$) and Ni^{2+} ($d\varepsilon^6 d\gamma^2$) but uncertain for Mn^{2+} ($d\varepsilon^3 d\gamma^2$) and Fe^{3+} ($d\varepsilon^3 d\gamma^2$). Especially Motida et al. reported the empirical relations between the bond angle of M–O–M and the paramagnetic Curie temperature or Néel temperature. According to their result, these relations were empirically explained by assuming the presence of two types of exchange interactions: (1) a superexchange interaction, and (2) a direct exchange interaction. In the present results, cobalt ions are in the tetravalent state with $3d^5(d\varepsilon^5 d\gamma^0)$ electron configuration and it would seem that their 90° interaction was negative, if the direct exchange interaction was negligible compared to superexchange interaction.

In the composition range of $0.1 \leqslant x \leqslant 0.2$, the Néel temperature of samples was larger than that of $BaCoO_3$ and θ_p changed drastically despite a mixing of nonmagnetic Ni^{4+} ions. Assuming that the Ni^{4+} ions were in the low-spin state, the direct interactions between Co^{4+} and Ni^{4+} ions were also negligible and the change of Co^{4+}–Co^{4+} and Co^{4+}–O^{2-} distances was quite small in the above range; the above-mentioned facts seem to be attributed to the variation of metal–oxygen–metal angles. In the system $BaCo_{1-x}Ni_xO_3$, the changes of cell dimensions a and c were reciprocal. This indicates that the change of the metal–oxygen–metal angle in the MO_6 octahedron varies with that of x value. The M–O–M angles are not known from the X ray powder diffraction data, but the variation of T_N in the region $0.0 \leqslant x \leqslant 0.2$ could be explained by the change of superexchange interaction related with the angle of metal–oxygen–metal.

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