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Structure and magnetic properties of $Sr_{2-x}A_xIrO_4$ (A =Ca and Ba)

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The effects of Ca and Ba substitutions for Sr on the structure and properties of Sr_2IrO_4 were studied. Increase in the Ir-O(2)-Ir bond angle in the IrO_2 plane was found after the substitutions of Ca and Ba for Sr. However, the Ir-O(2) distance is found to be unchanged by the Ba substitution, while it decreases by the Ca substitution. Regardless of these structural changes, the magnetic transition temperature at 240 K was found to be unchanged. Semiconductive behavior of the resistivity was found for all compounds with the increase in activation energy above 200 K. Both the electrical resistivity and the Seebeck coefficient showed no remarkable anomaly around the magnetic transition temperature.

Sr_2IrO_4 is the only K_2NiF_4-type structure oxide containing 5d transition-metal ions. Up to now, five iridium oxides with layered perovskite-type structure have been known, $Sr_{n+1}Ir_nO_{3n+1}$ (n =1, 2, 3, and ∞) and $CaIrO_3$. $SrIrO_3$ and $Sr_4Ir_3O_{10}$ can be obtained by a high-pressure treatment.[1,2] Sr_2IrO_4, $Sr_3Ir_2O_7$, and $CaIrO_3$ have been synthesized without a high-pressure treatment.[3-5] Both $SrIrO_3$ and $CaIrO_3$ have $GdFeO_3$-type distorted perovskite structure. They are metallic conductors and exhibit a Pauli paramagnetism,[1,3] but their magnetic and electrical properties have not been reported yet. It is known that Sr_2IrO_4 shows a magnetic transition around 240 K and below this temperature it exhibits spontaneous magnetization.[3,6] A rapid decrease of the transition temperature with Ru substitution for Ir was reported.[7] Recently, it was shown that Sr_2IrO_4 has an alternative rotation of IrO_6 octahedra in the IrO_2 plane from a structural analysis with the powder-neutron-diffraction technique, and so the proper space group for Sr_2IrO_4 should be tetragonal $I4_1/acd$ rather than $I4/mmm$.[8,9] Crawford *et al.*[8] concluded that the magnetic transition in Sr_2IrO_4 is a weak-ferromagnetic transition due to the Dzialoshinsky-Moriya interaction from the structural aspect and from the value of the saturated magnetic moment at 5 K.

In this paper, substitutions of Ca and Ba for Sr were attempted. With these substitutions structural change is expected without a change in the valence of Ir. In this situation the structural change should be reflected in the structural dependence of the magnetic interaction. It is well known that Ca substitution for Sr decreases T_c and it vanishes when the amount of substitution exceeds 60% (Refs. 10 and 11) in the ferromagnet $SrRuO_3$ with perovskite-type structure. In the case of perovskite-type structure, the octahedra make a three-dimensional linkage by sharing apical oxygens. $Sr_{1-x}Ca_xRuO_3$ has an orthorhombic distorted perovskite-type structure ($GdFeO_3$ type) having a distortion of the Ru-O-Ru bonding angle smaller than 180°. The change in T_c indicates that the magnetic interaction depends both on the Ru-O length and Ru-O-Ru bonding angle. In Sr_2IrO_4, because of the rotation of IrO_6 around the tetragonal c axis, the Ir-O-Ir bonding angle is smaller than 180° and the Ir-O bonding length is larger than one-half of tetragonal a axis. In this case the change in the lattice constant with the substitution may change both the Ir-O length and Ir-O-Ir angle similar to $Sr_{1-x}Ca_xRuO_3$. The structural and magnetic investigation for $Sr_{2-x}A_xIrO_4$ (A =Ca and Ba) should offer valuable information about the structure dependence of the magnetic interaction in the K_2NiF_4-type oxide.

$Sr_{2-x}A_xIrO_4$ (A =Ca and Ba) samples were prepared with the conventional solid-state reaction method. The starting materials were IrO_2, $SrCO_3$, $CaCO_3$, and $Ba(NO_3)_2$. Sr_2IrO_4 was sintered at 1423 K. Single-phased samples were obtainable for the composition up to x =0.10 for A =Ca by sintering at 1353 and 1423 K for x =0.05 and 0.10, respectively. Single-phased samples were obtainable for the composition up to x =0.20 for A =Ba by sintering at 1523 K.

Phase characterization was performed by a powder x-ray-diffraction analysis using a Mac Science MXP[18] x-ray diffractometer. For Sr_2IrO_4, $Sr_{1.95}Ca_{0.05}IrO_4$, and $Sr_{1.90}Ba_{0.10}IrO_4$, a powder neutron-diffraction analysis was performed at room temperature and 10 K. Diffraction data were collected with HRPD angle-dispersive–type diffractometer at the JRR-3 reactor at Japan Atomic Energy Research Institute. A structural analysis was performed for the data using the structural refinement program RIETAN.[12] The magnetic susceptibility was measured by a superconducting quantum interference device (SQUID) magnetometer below 340 K for all compositions and a magnetic balance between 340 and 700 K for Sr_2IrO_4. The electrical resistivities of all of the samples were measured between 50 and 300 K. The Seebeck coefficient for Sr_2IrO_4 was measured between 80 K and room temperature.

Figure 1 shows the lattice parameters and unit-cell volume as a function of x at room temperature for $Sr_{2-x}A_xIrO_4$ (A =Ca and Ba) determined by powder x-ray-diffraction and powder neutron-diffraction analyses. By Ca substitution the lengths of a and c axes and unit-

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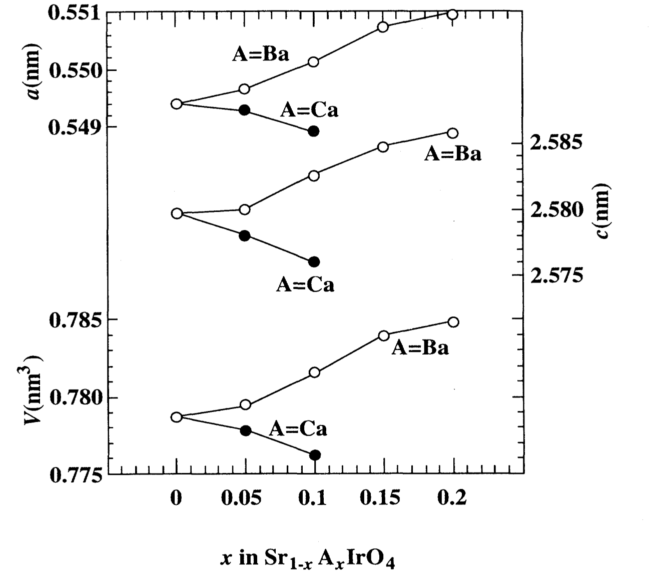

FIG. 1. Lattice parameters and unit-cell volumes of $Sr_2A_xIrO_4$ (A =Ca and Ba) at room temperature.

cell volume V decrease. By Ba substitution all these values increase. This tendency reflects simply the order of the ionic radii of Ba^{2+}, Sr^{2+}, and Ca^{2+}.[13] No extra peak other than those originating from the space group $I4_1/acd$ was found to appear in powder x-ray-diffraction patterns and also in powder neutron-diffraction patterns. Tables I and II show the structural parameters for Sr_2IrO_4, $Sr_{1.95}Ca_{0.05}IrO_4$, and $Sr_{1.90}Ba_{0.10}IrO_4$ determined from Rietveld analysis for powder neutron-diffraction data at room temperature and 10 K, respectively. O(1) denotes the apical oxygen of an IrO_6 octahedron. O(2) denotes the oxygen in the IrO_2 plane shared by two IrO_6 octahedra. The bond length of Ir-O(1) is about 4% larger than the Ir-O(2) bond length in $Sr_{2-x}A_xIrO_4$. For the $5d$ transition-metal ion, generally, a low-spin configuration or intermediate-spin configuration is considered to be stabilized in the octahedral coordination site. According to a previous study by Demazeau *et al.*,[14] this small distortion of the octahedron is too small to stabilize the d^5 intermediate-spin state ($d\varepsilon^4 d\gamma^1$). They pointed out that at least 20% of stretch is needed to stabilize the intermediate-spin state for the d^5 ion. Therefore, $5d$ electrons in $Sr_{2-x}A_xIrO_4$ are thought to take the low-spin configuration ($5d\varepsilon^5 5d\gamma^0$). It is clear that Ca substitution decreases the Ir-O(2) length and increases the Ir-O-(2)-Ir angle a little at 10 K and room temperature. On the other hand, Ba substitution does not affect the Ir-O(2) bond length and Ir-O(2) bond angle at both temperatures. The change in the Ir-O(2)-Ir angle with Ba substitution shows a positive dependence, being the same tendency as the changes in Sr_2IrO_4, $Sr_{1.95}Ca_{0.05}IrO_4$, and $Sr_{1.90}Ba_{0.10}IrO_4$ with temperature increase. An increase in the a length with a temperature increase only affects the Ir-O(2)-Ir bond angle. However, this tendency of the structure change with a temperature increase is apparently different from previous reports for Sr_2IrO_4. In previous papers for Sr_2IrO_4, a small increase in the Ir-O(2)-Ir bond angle from 157.0° to 157.9° (Ref. 8) or from 156.6° to 157.3° (Ref. 9) and an increase in the Ir-O(2) bond length from 0.1979 to 0.1981 nm (Ref. 8) or from 0.1980 to 0.1983 nm (Ref. 9) with a temperature increase from 13 to 295 K (Ref. 8) or from 10 K to room temperature (Ref. 9) are reported. In $Sr_{1.95}Ca_{0.05}IrO_4$ a decrease in the Ir-O(2) length of 0.0001 nm with a temperature increase is found. As a result, the effect of Ca substitution appears both in the Ir-O(2) bond length and Ir-O(2)-Ir bond angle, but the effect of Ba substitution clearly appears only in the Ir-O(2)-Ir bond angle. The Ir-O(2) bond length is held constant in spite of the increase in the a axis with Ba substitution. The Ir-O(1) length changes always along with a change of the c length with substitution or a temperature change.

Figure 2 shows the magnetic susceptibilities for $Sr_{2-x}A_xIrO_4$ measured under 0.5 T below 340 K after zero field cooling. The anomaly below 100 K does not appear in the measurement after field cooling. Figure 2

TABLE I. Structural parameters and refinement information for Sr_2IrO_4, $Sr_{1.95}Ca_{0.05}IrO_4$, and $Sr_{1.90}Ba_{0.10}IrO_4$ at room temperature with space group $I4_1/acd$. The four unique positions for (Sr,A), Ir, O(1), and O(2) are $(0,\frac{1}{4},z)$, $(0,\frac{1}{4},\frac{3}{8})$, $(0,\frac{1}{4},z)$, and $(x,x+\frac{1}{4},z)$, respectively.

	Sr_2IrO_4	$Sr_{1.95}Ca_{0.05}IrO_4$	$Sr_{1.90}Ba_{0.10}IrO_4$
a/nm	0.549 56(1)	0.549 33(1)	0.550 10(1)
c/nm	2.579 33(5)	2.577 44(7)	2.582 59(5)
V/nm^3	0.778 99(3)	0.777 78(5)	0.781 53(4)
Atomic positions and thermal parameters			
Sr,A (16d)			
z	0.550 6(3)	0.550 5(4)	0.550 5(3)
B_{eq}/nm^2	0.001[a]	0.002(2)	0.004(1)
Ir (8a)			
B_{eq}/nm^2	0.001[a]	0.002(2)	0.002(2)
O(1) (16d)			
z	0.458 4(4)	0.454 6(5)	0.454 7(4)
B_{eq}/nm^2	0.001[a]	0.002(2)	0.002(2)
O(2) (16f)			
x	0.203 7(6)	0.204 4(22)	0.204 4(15)
B_{eq}/nm^2	0.010(4)	0.013(6)	0.011(4)
Bond length/nm			
Ir-O(1) (×2)	0.205 8(1)	0.205 1(4)	0.205 9(1)
Ir-O(2) (×4)	0.197 7(3)	0.197 4(4)	0.197 7(3)
Sr,A-O(2) (×2)	0.299 6(4)	0.299 4(4)	0.299 9(4)
Sr,A-O(2) (×2)	0.248 7(4)	0.249 3(4)	0.249 6(4)
Sr,A-O(1) (×1)	0.247 1(1)	0.247 2(2)	0.247 3(1)
Sr,A-O(1) (×4)	0.275 1(1)	0.275 0(2)	0.275 1(1)
Bond angle/degree			
Ir-O(2)-Ir	159.1(3)	159.3(3)	159.4(3)
Ir-O(1)-Sr,A	87.4(4)	87.3(4)	87.2(4)
R factors/%			
R_{wp}	12.24	14.60	12.32
R_p	9.46	10.88	9.19
R_e	7.38	7.40	7.93
R_i	6.17	6.64	5.77
R_f	5.01	5.86	5.29

[a] B_{eq} was fixed to small positive values when refinements give small negative values.

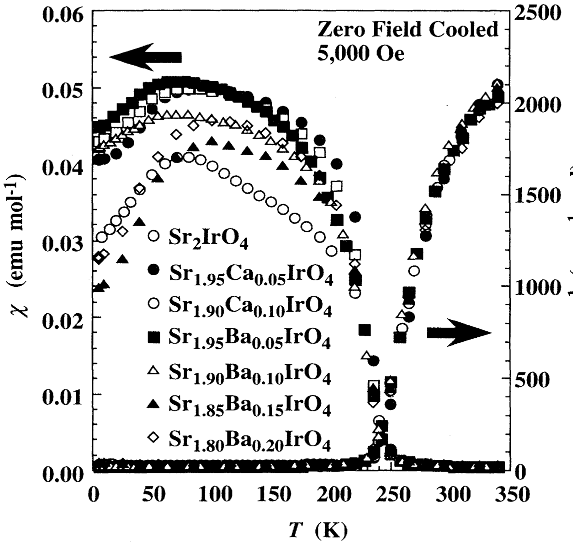

FIG. 2. Temperature dependence of magnetic susceptibilities for $Sr_{2-x}A_xIrO_4$ (A = Ca and Ba) between 5 and 340 K under 5 kOe. A magnetic field was applied after cooling down to 5 K.

TABLE II. Structural parameters and refinement information for Sr_2IrO_4, $Sr_{1.95}Ca_{0.05}IrO_4$, and $Sr_{1.90}Ba_{0.10}IrO_4$ at 10 K with space group $I4_1/acd$.

	Sr_2IrO_4	$Sr_{1.95}Ca_{0.05}IrO_4$	$Sr_{1.90}Ba_{0.10}IrO_4$
a/nm	0.548 164(8)	0.547 94(1)	0.548 718(9)
c/nm	2.580 019(5)	2.578 70(7)	2.583 78(6)
V/nm^3	0.775 30(4)	0.774 22(5)	0.777 95(4)
Atomic positions and thermal parameters			
Sr,A (16d)			
z	0.550 6(3)	0.550 7(4)	0.550 4(4)
B_{eq}/nm^2	0.001[a]	0.001 [a]	0.001[a]
Ir (8a)			
B_{eq}/nm^2	0.001[a]	0.001[a]	0.001[a]
O(1) (16d)			
z	0.454 8(3)	0.454 6(5)	0.454 8(4)
B_{eq}/nm^2	0.001[a]	0.001[a]	0.001(1)
O(2) (16f)			
x	0.199 6(14)	0.200 5(21)	0.201 2(17)
B_{eq}/nm^2	0.006(4)	0.010(6)	0.005(4)
Bond length/nm			
Ir-O(1) (×2)	0.206 0(1)	0.205 3(4)	0.206 3(1)
Ir-O(2) (×4)	0.197 7(3)	0.197 5(4)	0.197 7(3)
Sr,A-O(2) (×2)	0.301 7(4)	0.301 1(4)	0.301 6(4)
Sr,A-O(2) (×2)	0.246 6(4)	0.246 7(4)	0.248 1(4)
Sr,A-O(1) (×1)	0.247 1(1)	0.247 7(2)	0.246 9(1)
Sr,A-O(1) (×1)	0.274 4(1)	0.274 3(2)	0.274 7(1)
Bond angle/degree			
Ir-O(2)-Ir	157.2(3)	157.6(3)	157.9(3)
Ir-O(1)-Sr,A	87.1(4)	87.2(4)	87.2(4)
R factors/%			
R_{wp}	12.47	15.22	14.13
R_p	9.50	11.48	10.78
R_e	7.50	7.45	8.70
R_i	6.35	9.52	9.54
R_f	5.07	7.26	6.95

[a] B_{eq} was fixed to small positive values when refinements give small negative values.

shows that there is no systematic change in the magnetic transition temperature with the substitution. The susceptibilities above 240 K are almost the same for all compositions, and the temperature dependence of the magnetic susceptibility of Sr_2IrO_4 above 240 K does not obey Curie-Weiss-type paramagnetism. This result means that the magnetic transition is neither affected by the change in Ir-O(2)-Ir bond angle nor the change in Ir-O(2) bond length within the measured composition range.

The transition around 240 K is reported to be the breakdown of three-dimensional ferromagnetic ordering between layers.[8] The IrO_2 layer has a small spontaneous magnetic moment due to the ordering of the moment of Ir^{4+} with an angle smaller than 180°. In the case of $Sr_{2-x}A_xIrO_4$, changes in the Ir-O(2) bond length and Ir-O(2)-Ir bond angle do not influence the transition around 240 K. It is considered that they mainly influence the transition temperature at which the two-dimensional ordering vanishes. Curie-Weiss-type paramagnetism may appear above this transition. Any magnetic anomaly in the susceptibility measurement up to 700 K for Sr_2IrO_4 was not found. For $La_2CuO_{4.0}$ quite a high temperature (1500 K) is reported as the two-dimensional magnetic ordering temperature.[8]

The separation between two IrO_2 layers is the same as one-fourth of the c axis, and so it is expected that there is a remarkable change in the c axis with substitution. It means that the strength of the magnetic interaction along the c axis may be affected by the substitution. However, the constant magnetic transition temperature in $Sr_{2-x}A_xIrO_4$ means that the magnetic interaction along the c axis in $Sr_{2-x}A_xIrO_4$ is quite insensible to the change in bond lengths; thereby, this interaction does not work via alkali-earth ions.

Figure 3 shows the temperature dependence of the electrical resistivities (ρ) for $Sr_{2-x}A_xIrO_4$ normalized by the values at 300 K ($\rho_{300\ K}$). All the samples exhibit a semiconductive temperature dependence below 300 K.

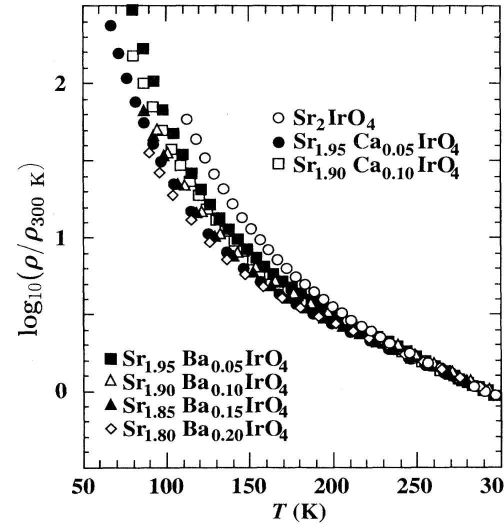

FIG. 3. Normalized resistivities with the values at 300 K for $Sr_{2-x}A_xIrO_4$.

There is no systematic change in the temperature dependence of the resistivity with substitution, although the increase of the resistivity with a temperature decrease is slightly larger in Sr_2IrO_4 than in substituted samples. There is no clear anomaly around 240 K in resistivities, but in the temperature dependence of the activation energy of the conductive carrier (E_a), obvious changes are seen around 240 K. Below 200 K, E_a was almost independent of temperature. It means that in this temperature region the temperature dependence of the resistivity is a gap-type one, generally expressed as $\rho=\rho_0\exp(E_a/k_BT)$. The values of E_a were found to be about 0.06 eV for Sr_2IrO_4 and about 0.03–0.05 eV for substituted samples. Above 200 K, E_a increases with the temperature increase. Because of relatively large scattering of the data, determination of accurate temperature dependences was impossible, but it is certain that the temperature dependence of semiconductive electrical resistivities is a no-gap-type one in the higher-temperature region. The sign of the Seebeck coefficient was positive with 320 μV K^{-1} at 100 K and 175 μV K^{-1} at 280 K. Similar to the behavior of the electrical resistivity, there was no anomaly of the Seebeck coefficient at the magnetic transition temperature around 240 K.

In this study, the solid-solution system $Sr_{2-x}A_xIrO_4$ (A =Ca and Ba) was synthesized and the properties were investigated. The solubility limits were found to be $x=0.10$ for A =Ca and $x=0.20$ for A =Ba. From the powder x-ray-diffraction analysis, monotonous decreases of lattice parameters and unit-cell volume with Ca substitution and increases of them with Ba substitution were confirmed. Rietveld refinement for the powder neutron-diffraction data revealed the change in bond length and bond angle with substitution. On the other hand, in spite of the structural change with substitution, there is no shift in the magnetic transition temperature from 240 K or change in the magnetic behavior above 240 K. A semiconducting temperature dependence of resistivities for $Sr_{2-x}A_xIrO_4$ (A =Ca and Ba) was observed, but no remarkable change was observed with substitution. The sign of the Seebeck coefficient for Sr_2IrO_4 was positive.

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