BRIEF COMMUNICATION

The Structure and Magnetic Properties of New Iridium(IV) Perovskites Sr₂LnIrO₆ (Ln = Ce, Tb)

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New compounds with the formula Sr₂LnIrO₆ (Ln = Ce, Sm ~ Lu) were characterized from X-ray diffraction measurements and magnetic susceptibility measurements in the temperatures between 5 and 300 K. They were determined to have ordered monoclinic perovskite structures with space group $P2_1/n$. The oxidation state of iridium is considered to be pentavalent for Sr₂LnIrO₆ (Ln = Sm ~ Gd, Dy ~ Lu), whereas it is tetravalent for Sr₂LnIrO₆ (Ln = Ce, Tb). The compounds in which the iridium is in the tetravalent state show an antiferromagnetic transition. Sr₂CeIrO₆ has a transition temperature at 21 K, and Sr₂TbIrO₆ has two transition temperatures at 25 and 51 K.
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1. INTRODUCTION

Recently, oxides with a perovskite or perovskite-like structure containing iridium have been extensively studied. Barium iridate BaIr(IV)O₃₋δ of which the crystal structure was determined by Powell *et al.* shows a ferromagnetic transition at 180 K (1). The magnetic susceptibility of La₂LiIr(V)O₆ has a unique temperature dependence (2, 3). Sr₂MIr(VI)O₆ (M = Ca, Mg) which is synthesized under high oxygen pressures is antiferromagnetic (4).

These magnetic properties are closely related with the oxidation state of iridium. The most common oxidation state of iridium in solids is tetravalent. The electronic configuration of the Ir⁴⁺ ion is [Xe]$4f^{14}5d^5$, where [Xe] is the xenon core. Magnetic ordering of the third transition series is quite unusual, and these perovskites offer a rare opportunity to study the magnetic behavior of a $5d^5$ electron system. The general aim of this study has been to characterize the electronic properties of the Ir⁴⁺ ion and to determine the extent to which the outer $5d^5$ electrons are characterized. The magnetic behavior is a useful indication of the degree of localization–delocalization in that a localized electron system is expected to show long-range magnetic order-

ing at low temperature, whereas a delocalized system will not.

Perovskite-type oxides, ABO₃, where A is a divalent ion (e.g., Sr, Ba), accommodate tetravalent metal ions at the B site of the crystal. Double perovskites have the formula $A_2B'B''$O₆, in which the primes indicate the possibility of different ions. Because the B cation generally determines the physical properties of perovskites, we focus out attention on the Sr₂LnIrO₆ compounds. In addition to the tetravalent state, the iridium ion has the higher oxidation state such as the pentavalent state. By introducing other metal ions in the lower oxidation state into the B' site of the double perovskites, the iridium ion in the pentavalent or hexavalent state is stabilized at the B'' site.

In our systematic study on the crystallographic and magnetic properties of the series of the double perovskites Sr₂LnIrO₆, we have found the magnetic exchange interactions in Sr₂CeIrO₆ and Sr₂TbIrO₆. Through their crystallographic and magnetic properties, the Ce and Tb ions are both sure to be in the tetravalent state. In this paper, we will report their crystal structures and magnetic properties.

2. EXPERIMENTAL

As starting materials, strontium carbonate SrCO₃, iridium metal powder Ir, and lanthanoids sesquioxide Ln₂O₃ were used. For the case of Ce, Pr, and Tb, CeO₂, Pr₆O₁₁, and Tb₄O₇ were used. These reagents were weighed in the appropriate metal ratios and ground intimately in an agate mortar. The mixtures were pelletized and then calcined in air at 900°C for 12 h. The samples were heated again in air at 1200°C for 79 ~ 81 h with several interval grindings.

Powder X-ray diffraction profiles were recorded in the range $10° ≤ θ ≤ 100$ with Cu$Kα$ radiation on a Rigaku RINT 2000 diffractometer equipped with a curved graphite monochromator. For the samples which were found to have a single phase, the intensity data were collected by step

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scanning in the range between $10°$ and $120°$ at intervals of $0.02°$ for their Rietveld analysis.

The temperature dependence of the magnetic susceptibilities was measured under both zero-field-cooled condition (ZFC) and field-cooled condition (FC). The former was measured on heating the samples to 300 K after zero-field cooling to 5 K. The applied magnetic field was 0.1 T. The latter was measured on cooling the sample from 300 to 5 K at 0.1 T. For the Sr_2CeIrO_6 compound, detailed temperature dependence of the susceptibility was measured in the temperature range between 2 and 40 K, and the magnetization was measured at 10 K by changing the applied magnetic field between -5 and 5 T.

3. RESULTS AND DISCUSSION

3.1. Structural Properties

The results of the X-ray diffraction measurements are as follows:

Ln = La, Pr: Perovskite phase was not formed,
Ln = Nd: Two perovskite phases were formed,
Ln = Ce, Sm ~ Lu: Single perovskite phase was formed.

For the Sr_2LnIrO_6 compounds with a single perovskite phase, we have performed the Rietveld analysis with the program RIETAN-97 (5) for their diffraction profiles. Figure 1 shows the results of X-ray diffraction pattern fitting for Sr_2CeIrO_6 and Sr_2TbIrO_6. Table 1 lists the lattice parameters and the reliability factor R for the Sr_2LnIrO_6. The diffraction profiles of all the samples with a single perovskite phase showed the existence of the super lattice reflection at $2\theta \approx 19°$ (See Fig. 1). It was concluded that the compounds are ordered perovskites; i.e., the lattice parameters are double those of the single perovskite. The structures were refined by applying the space group $P2_1/n$. This space group $P2_1/n$ allows two crystallographically distinct octahedral sites in the perovskite structure, thus permitting 1:1 positional ordering between the B site ions, Ln^{3+} and Ir^{5+} ions. These ions are arranging alternatively, and they have a rock salt sublattice. For the Sr_2CeIrO_6 sample, some impurity of CeO_2 was contained in the compounds and the R factor is relatively worse compared with those for others. Since the CeO_2 is diamagnetic and its effect on the magnetic susceptibility is negligibly small, we consider that the measured magnetic susceptibility represents the susceptibility of Sr_2CeIrO_6.

To discuss the stability of the perovskite-type compounds ABO_3, Goldshmit introduced the tolerance factor (t) defined by $t = r_A + r_O/\sqrt{2}(r_B + r_O)$, where r_A, r_B, and r_O are the radii of the A and B metal ions and oxygen ions, respectively. For $A_2B'B''O_6$ compounds, it is given by $t = r_A + r_O/\sqrt{2}(r_{B'} + r_{B''}/2) + r_O)$, where $r_{B'}$, $r_{B''}$ are the radii of the B' and B'' metal ions. For tolerance factors less
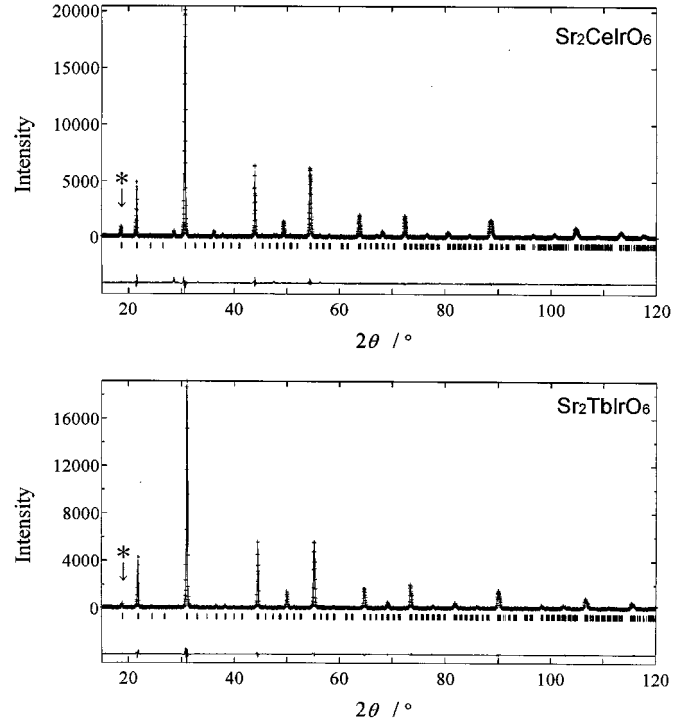

FIG. 1. X-ray diffraction profiles for Sr_2CeIrO_6 and Sr_2TbIrO_6. The calculated and observed diffraction profiles are shown on the top solid line and the cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities. ∗ shows the super lattice reflections.

than unity, the perovskite structure distorts from the ideal cubic symmetry. For larger deviations from the ideal ionic radius ratios, the compound distorts even more from the cubic symmetry.

TABLE 1
Lattice Parameters and R Factors of Sr_2LnIrO_6

Compounds	a	b	c	β	V	R_{wp}	R_I	R_F
Sr_2CeIrO_6	5.835	5.846	8.260	90.21	281.74	12.09	2.48	2.35
Sr_2SmIrO_6	5.830	5.872	8.268	90.36	283.05	8.89	1.60	1.61
Sr_2EuIrO_6	5.821	5.858	8.252	90.32	281.41	9.35	1.60	1.64
Sr_2GdIrO_6	5.813	5.847	8.239	90.30	280.00	9.09	1.43	1.48
Sr_2TbIrO_6	5.751	5.760	8.137	90.09	269.55	9.74	1.76	2.20
Sr_2DyIrO_6	5.790	5.811	8.201	90.26	275.96	11.86	2.02	2.48
Sr_2HoIrO_6	5.785	5.794	8.187	90.21	274.44	10.63	1.67	1.93
Sr_2ErIrO_6	5.777	5.781	8.171	90.17	272.87	11.22	1.72	2.35
Sr_2TmIrO_6	5.767	5.767	8.153	90.16	271.16	10.23	1.53	2.26
Sr_2YbIrO_6	5.756	5.757	8.138	90.14	269.67	10.95	1.54	2.36
Sr_2LuIrO_6	5.747	5.750	8.126	90.12	268.53	9.60	1.04	1.47

Note. $R_{wp} = [\sum w(|F(o)| - |F(c)|^2/\sum w(|F(o)|^2]^{1/2}$, $R_I = \sum |I_k(o) - I_k(c)|/\sum I_k(o)$, and $R_F = \sum |[I_k(o)]^{1/2} - [I_k(c)]^{1/2}|/\sum [I_k(o)]^{1/2}$.

The ionic radius of the Ln^{3+} ion decreases with an increasing atomic number of lanthanoid elements. Therefore, the tolerance factors (t) of Sr_2LnIrO_6 increase with the atomic number of Ln from $t = 0.919$ for Sr_2LaIrO_6 to $t = 0.956$ for Sr_2LuIrO_6. This trend is in accordance with the variation of the β value with the ionic radius of the Ln^{3+} ion, which is shown in Fig. 2. The β value decreases with an decreasing ionic radius of the Ln^{3+} ion and that of the Sr_2LuIrO_6 approaches 90° most, which means that the distortion from the cubic symmetry is the least for Sr_2LuIrO_6. Figure 2 shows that the lattice parameters for Sr_2LnIrO_6 increase smoothly with the ionic radius of the Ln^{3+} ion. However, those for Sr_2CeIrO_6 and Sr_2TbIrO_6 deviate greatly from this trend. We consider that the Ce and Tb ions are in the tetravalent state and that the Ir ions are also in the tetravalent state, although in the other Sr_2LnIrO_6, the lanthanoid and iridium ions are in the trivalent and pentavalent states, respectively. From the Rietveld analysis for Sr_2LnIrO_6, the average bond lengths of Ln–O and those of Ir–O are calculated and their variation with the ionic radius of Ln^{3+} is shown in Fig. 3. Both Ln–O and Ir–O bond lengths increase smoothly with the ionic radius of Ln^{3+}. However, those for Sr_2CeIrO_6 and Sr_2TbIrO_6 deviate from this smooth increase of bond lengths against the ionic radius of the Ln^{3+} ion.
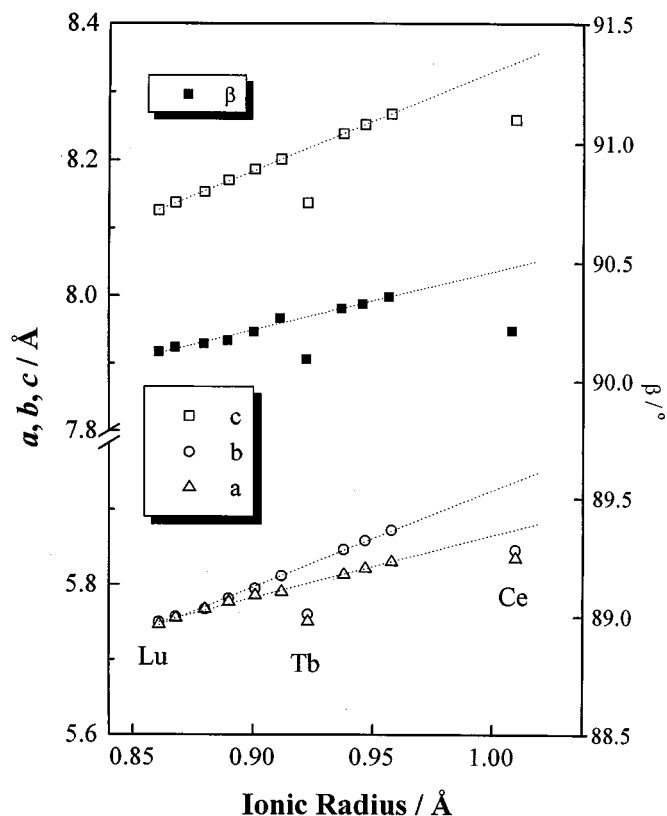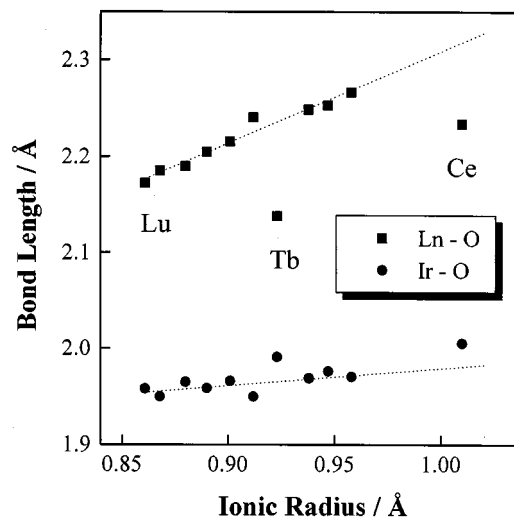

FIG. 3. Variation of average bond lengths of Ln–O and Ir–O with ionic radius of Ln^{3+}.

From Shannon's ionic radius (6), Ce^{3+}–O^{2-} and Ce^{4+}–O^{2-} bond lengths are calculated to be 2.41 and 2.27 Å, respectively, and the Tb^{3+}–O^{2-} and Tb^{4+}–O^{2-} bond lengths are 2.32 and 2.10 Å, respectively. The observed Ce–O and Tb–O bond lengths are 2.234 and 2.138 Å, respectively. These values exactly accord with the corresponding Ln^{4+}–O^{2-} bond lengths, which indicates that the cerium and terbium ions are both in the tetravalent state in Sr_2CeIrO_6 and Sr_2TbIrO_6, respectively.

We have calculated the tolerance factors for two models, i.e., $Sr_2Ce^{4+}(Tb^{4+})Ir^{4+}O_6$ and $Sr_2Ce^{3+}(Tb^{3+})Ir^{5+}O_6$, and they are listed in Table 2. The values for $Sr_2Ce^{4+}(Tb^{4+})Ir^{4+}O_6$ are nearer 1 than those for $Sr_2Ce^{3+}(Tb^{3+})Ir^{5+}O_6$, which means the ionic model $Sr_2Ce^{4+}(Tb^{4+})Ir^{4+}O_6$ is more plausible. The results of the magnetic properties of Sr_2LnIrO_6 also indicate that both cerium and terbium ions are in the tetravalent state, which will be described in the following section.

3.2. Magnetic Properties

Magnetic susceptibility measurements have been performed for Sr_2LnIrO_6 (Ln = Ce, Sm ~ Lu). Among them, only Sr_2CeIrO_6 and Sr_2TbIrO_6 show the antiferromagnetic

FIG. 2. Variation of lattice parameters with ionic radius of Ln^{3+}.

TABLE 2
Tolerance Factors for Sr_2CeIrO_6 and Sr_2TbIrO_6

Compounds	$t(Sr_2Ln^{3+}Ir^{5+}O_6)$	$t(Sr_2Ln^{4+}Ir^{4+}O_6)$
Sr_2CeIrO_6	0.917	0.935
Sr_2TbIrO_6	0.935	0.959

FIG. 4. Molar magnetic susceptibility of Sr_2CeIrO_6 as a function of temperature.

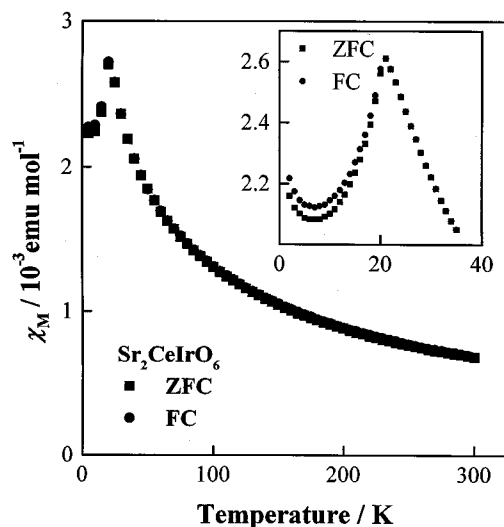**FIG. 5.** Molar magnetic susceptibility of Sr_2TbIrO_6 as a function of temperature.

transition at low temperatures. This fact also indicates that the iridium ions are in the tetravalent state ($5d^5$ electronic configuration). Several compounds such as Sr_4IrO_6 and La_2MgIrO_6 show antiferromagnetic transitions at low temperatures and the oxidation state of iridium ions are tetravalent in any such compounds (2). As far as we know, no compounds containing pentavalent iridium ions show magnetic ordering at low temperatures.

Figure 4 shows the temperature dependence of the magnetic susceptibility of Sr_2CeIrO_6. This compound transforms to the antiferromagnetic state below 21 K. There is no divergence between the FC and the ZFC magnetic susceptibilities, and no magnetic hysteresis is observed in the magnetization vs magnetic field curve. The magnetic behavior of Sr_2CeIrO_6 is typical of the antiferromagnetic substance. In the case that cerium ion is in the tetravalent state (it is diamagnetic), the Ir^{4+} ion is the only paramagnetic ion in the Sr_2CeIrO_6. The effective magnetic moment is calculated to be $\mu_{eff} = 1.02\mu_B$ at 100 K and $\mu_{eff} = 1.28\mu_B$ at 300 K from the formula $\chi_M = N\mu_{eff}^2/3k_BT$. These values are very low. In solids, the Ir^{4+} ion is usually in the strong crystal field, so the total spin quantum number is $S = 1/2$ and the effective magnetic moment is calculated to be $1.73\mu_B$. The moment obtained experimentally is still smaller than this value, suggesting the large octahedral crystal field effect on the Ir^{4+} ion.

Figure 5 shows the temperature dependence of magnetic susceptibilities for Sr_2TbIrO_6, indicating the existence of two magnetic transitions. Their transition temperatures are 25 and 51 K. The magnetic susceptibilities for Sr_2TbIrO_6 are about two orders of magnitude larger than those for Sr_2CeIrO_6. This is due to the fact that the theoretical
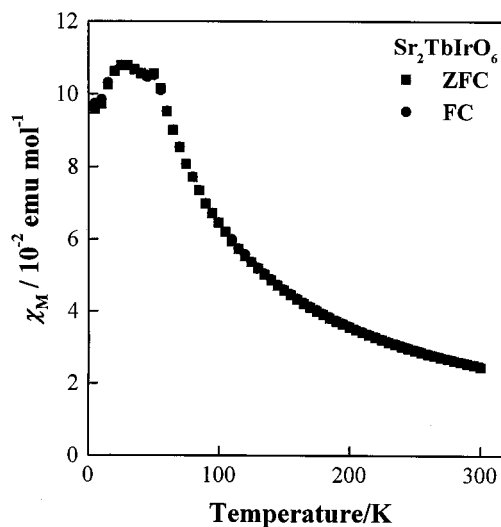
effective magnetic moment of the Tb^{4+} ion is $7.94\mu_B$ and the magnetic susceptibility is proportional to the square of the effective magnetic moment. The effective magnetic moment of Sr_2TbIrO_6 is obtained to be $7.97\mu_B$ in the temperature range in which the Curie–Wiess law holds. This value is close to the theoretical moment for the Tb^{4+} ion. The small difference between them is probably due to the contribution of the magnetic moment of the Ir^{4+} ion. These results also strongly indicate that both terbium and iridium ions are in the tetravalent state in Sr_2TbIrO_6.

We consider that in Sr_2TbIrO_6, the magnetic exchange interactions between Tb^{4+} ions and those between Ir^{4+} ions occur independently and that the magnetic transition at a lower temperature is due to the interactions between Ir^{4+} ions, because the transition temperature 25 K is close to the Néel temperature for Sr_2CeIrO_6. So we consider that the higher transition temperature corresponds to the magnetic transition between Tb^{4+} ions. It is known that some perovskite compounds ABO_3 having Tb^{4+} ion at the B site show antiferromagnetic transitions as high as the transition temperature for Sr_2TbIrO_6 (7, 8). However, such an antiferromagnetic compounds (i.e., $BaTbO_3$ and $SrTbO_3$) show complicated magnetic behavior below Néel temperatures, i.e., magnetic susceptibilities again increase with decreasing temperature below Néel temperature (8). To ascertain our discussion, it is necessary to carry out more detailed experiments such as neutron diffraction measurements between the transition temperatures and determine its magnetic structure.

The detailed magnetic investigations on other samples, Sr_2LnIrO_6 (Ln = Sm ∼ Gd, Dy ∼ Lu), will be reported elsewhere.

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