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Magnetic and calorimetric studies of double perovskites Ba_2LnReO_6 (Ln = Y, Nd, Sm–Lu)

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The perovskite-type compounds Ba_2LnReO_6 (Ln = Y, Nd, Sm–Lu) have been synthesized. Powder X-ray diffraction measurements and Rietveld analysis show that they are monoclinic with space group $P2_1/n$ and that Ln^{3+} and Re^{5+} ions are structurally ordered. Anomalies are found in their magnetic susceptibility and specific heat measurements, which suggest an antiferromagnetic ordering of Re^{5+} ions for Ba_2LnReO_6 (Ln = Y, Nd, Sm, Gd–Ho, Lu) and that of Tb^{3+} ions for Ba_2TbReO_6.

Introduction

The perovskite-type oxides have the general formula ABO_3, in which A represents a large electropositive cation and B represents a small transition metal ion. The perovskite structure can be described as a framework of corner-shared BO_6 octahedra which contain A cations at 12-coordinate sites. Double perovskite-type oxides have the formula $A_2B'B''O_6$, in which the primes indicate the different ions in different oxidation states, and the cations at the B sites, B' and B'', are regularly ordered, *i.e.*, 1 : 1 arrangement of B' and B'' ions has been observed over the six-coordinate B sites. Since the B cations generally determine the physical properties of perovskites, different kinds of B' and B'' ion should show a variety of the physical properties of double perovskite oxides.

We have been studying preparation, crystal structure and magnetic properties of double perovskite oxides, Ba_2LnNbO_6,[1] Ba_2LnTaO_6,[2,3] Ba_2LnRuO_6[4,5] and Ba_2LnIrO_6,[6,7] where Ln represents a rare earth ion. Through studies on Ba_2LnNbO_6 and Ba_2LnTaO_6 in which both Nb^{5+} and Ta^{5+} ions are diamagnetic, these compounds are paramagnetic down to 4.2 K and their magnetic properties are characterized by the behavior of Ln^{3+} ions in the double perovskites.[1–3] The electronic structure of Ru^{5+} is $[Kr]4d^3$ ([Kr] : krypton electronic core). Such highly oxidized cations from the second or third transition series sometimes show quite unusual magnetic behavior. So, the ordered perovskites Ba_2LnRuO_6 are expected to show interesting magnetic properties at low temperatures. Most of the Ba_2LnRuO_6 compounds show antiferromagnetic transitions at 15–30 K. From the neutron diffraction measurements on Ba_2PrRuO_6[4] and Ba_2NdRuO_6,[5] their magnetic structures are determined to be of Type I. In the above-mentioned Ba_2LnMO_6 (M = Nb, Ta, Ru) compounds, lanthanide and M ions are in the trivalent and pentavalent states, respectively. Magnetic susceptibility and specific heat measurements on iridium compounds Ba_2LnIrO_6 show that they are paramagnetic down to 1.8 K except for the Ce and Pr compounds.[7] Both the Ba_2CeIrO_6 and Ba_2PrIrO_6 show antiferromagnetic transitions at 17 and 71 K, respectively.[6] In these compounds, the Ce and Pr ions are not in the trivalent state, but are rather tetravalent and the Ir ions are also tetravalent, which are quite different from the other Ba_2LnIrO_6 and Ba_2LnMO_6 (M = Nb, Ta, Ru). Now, our attention has been focused on double perovskite oxides containing rhenium, Ba_2LnReO_6. In these compounds, the oxidation state of rhenium ions is expected to be in the pentavalent state. Their electronic configurations are $[Xe]5d^2$ ([Xe] : xenon electronic core), which is different from those for the above transition elements, *i.e.*, the Re^{5+} ion has two unpaired electrons. Therefore, the magnetic properties of Ba_2LnReO_6 are expected to be quite different from those of other double perovskite oxides Ba_2LnMO_6 (M = Nb, Ta, Ru, Ir), because in general, the effect of M^{5+} ions on the magnetic properties of Ba_2LnMO_6 is larger than that of Ln^{3+} ions. However, the magnetic properties of Ba_2LnReO_6 have not been studied in detail.[8]

In this study, we have prepared Ba_2LnReO_6 (Ln = Y, Nd, Sm–Lu), and studied their crystal structures and magnetic properties through X-ray diffraction, magnetic susceptibility, and specific heat measurements.

Experimental

Sample preparation

As starting materials, powders of barium peroxide (BaO_2), lanthanide sesquioxide (Ln_2O_3, except for Ln = Tb), rhenium metal (Re), and rhenium dioxide (ReO_2) were used. For the case of terbium, Tb_4O_7 was used. Their purity is higher than 99.9%. In order to remove any moisture, Nd_2O_3 was preheated in air at 1173 K. The stoichiometric mixtures were ground, pressed into pellets, and sealed in an evacuated silica tube. The pellets were annealed at 1073–1373 K for 6–24 h with several intervening regrinding and repelletizing steps.

A diamagnetic material Ba_2LuTaO_6, which is isomorphous with Ba_2LnReO_6, was also prepared. As will be described later, this compound is needed to estimate the lattice contribution of the specific heat to the total specific heat of Ba_2LnReO_6. Starting materials were $BaCO_3$, Lu_2O_3 and Ta_2O_5. These reagents were weighed in appropriate metal ratios and ground thoroughly in an agate mortar. The mixtures were pressed into pellets and were calcined at 1173 K. The calcined materials were reground and sintered in air at 1573 K for several days with intermediate regrinding and repelletizing.

X-Ray diffraction

Powder X-ray diffraction measurements were carried out at room temperature in the range $10 \leqslant 2\theta/^\circ \leqslant 120$, using a 2θ step size of 0.02° with CuKα radiation on a multiflex diffractometer (Rigaku). Rietveld analyses were carried out with the program RIETAN 2000[9] using collected diffraction data.

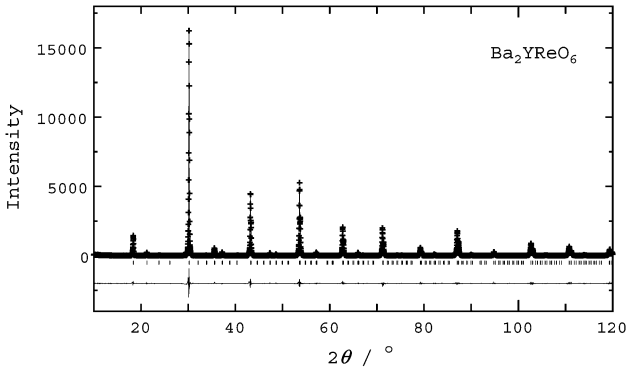

Fig. 1 Powder X-ray diffraction pattern of Ba_2YReO_6.

Magnetic susceptibility

The temperature dependence of the magnetic susceptibilities was measured under both zero-field-cooled condition (ZFC) and field-cooled condition (FC) in the temperature range 2–300 K using a SQUID magnetometer (Quantum Design, MPMS-5S). The ZFC susceptibility measurements were performed under an applied magnetic field of 0.1 T, after the sample was cooled from 300 to 2K in a zero field. For the FC susceptibility measurements, the sample was cooled in the presence of a field of 0.1 T. The magnetization was measured at 5 K by changing the applied magnetic field between −5 and 5 T.

Heat capacity

Heat capacity measurements were carried out using a relaxation technique supplied by commercial heat capacity measurement system (Quantum Design, PPMS) in the temperature range 2–300 K. The sample in the form of pellet was mounted on an alumina plate with Apiezon for better thermal contact.

Results and discussion

Crystal structures

The results of the powder X-ray diffraction measurements show that Ba_2LnReO_6 (Ln = Y, Nd, Sm–Lu) compounds were formed as a single phase with a perovskite-type structure. For the case of Ln = La, Ce and Pr, a single perovskite phase was not formed, which is due to the large size of these lanthanides as the B-site ions. Fig. 1 shows the X-ray diffraction pattern of Ba_2YReO_6. Rietveld analysis was performed with the program RIETAN to obtain powder X-ray diffraction profiles. The structures were refined by applying the space group $P2_1/n$. This space group allows two crystallographically distinct octahedral sites in the perovskite structure, thus permitting 1 : 1 positional ordering between the B site ions, Ln^{3+} and Re^{5+} ions. These ions are arranging alternately and they have a rock salt sublattice. Fig. 2 shows the crystal structure of Ba_2LnReO_6.

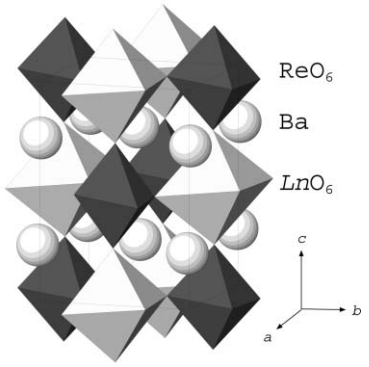

Fig. 2 Crystal structure of Ba_2LnReO_6.

The unit cell parameters and the reliability factors for Ba_2LnReO_6 are listed in Table 1. The atomic positional parameters for Ba_2YReO_6 after refinements are listed in Table 2.

Fig. 3 shows the variation of lattice parameters for the Ba_2LnReO_6 with ionic radius of Ln^{3+}.[10] As the ionic radius increases, the lattice parameters a, b and c increase. The variation is nearly linear, so it is thought that the oxidation state of the lanthanide is trivalent and that of rhenium is pentavalent for all Ba_2LnReO_6 (Ln = Nd, Sm, Eu–Lu). Table 1 and Fig. 3 show that in the monoclinic region, the lattice parameter β increases and the differences among a, b and $c/\sqrt{2}$ spread with an increase of the Ln^{3+} ionic radius. This result indicates that the crystal structures of Ba_2LnReO_6 are more distorted from the cubic symmetry as the size of the Ln^{3+} ion becomes larger.

Table 1 Unit cell parameters and R factors of Ba_2LnReO_6 (Ln = Y, Nd, Sm–Lu)

Ln	a/Å	b/Å	c/Å	β/°	R_{wp}	R_I
Y	5.9205(7)	5.9202(7)	8.3750(2)	90.026(5)	14.89	3.34
Nd	6.0064(4)	6.0067(3)	8.5229(1)	90.045(2)	18.24	8.72
Sm	5.9847(7)	5.9868(7)	8.4685(5)	90.043(8)	17.87	6.18
Eu	5.9756(4)	5.9737(4)	8.4685(5)	90.00(2)	14.92	4.43
Gd	5.9602(3)	5.9638(4)	8.4329(3)	90.025(7)	15.87	4.53
Tb	5.944(1)	5.946(1)	8.4075(5)	90.02(1)	13.38	4.95
Dy	5.934(1)	5.933(1)	8.3910(2)	90.00(2)	15.37	3.00
Ho	5.921(1)	5.921(1)	8.3748(4)	90.00(2)	15.23	3.51
Er	5.9118(2)	5.9126(2)	8.3701(2)	90.00(4)	15.63	4.53
Tm	5.898(2)	5.898(2)	8.3417(2)	90.00(2)	11.89	4.44
Yb	5.890(6)	5.890(6)	8.300(1)	90.00(9)	13.91	2.57
Lu	5.880(1)	5.880(1)	8.3171(4)	90.01(5)	14.62	3.11

[a] $R_{wp} = [\sum_k w_k[I_k(obs)-I_k(calc)]^2/\sum_k w_k I_k(obs)^2]^{1/2}$, $R_I = \sum_k|I_k(obs)-I_k(calc)|/\sum_k I_k(obs)$.

Table 2 Structural parameters for Ba_2YReO_6

Atom	Site	x	y	z	B/Å^2
Ba_2YReO_6 space group: $P2_1/n$					
Ba	4e	0.003(4)	0.002(1)	0.243(1)	0.51(6)
La	2d	1/2	0	0	0.1(2)
Re	2c	1/2	0	1/2	0.1(1)
O(1)	4e	0.24(3)	0.26(3)	0.00(4)	0.8(3)
O(2)	4e	0.21(3)	−0.29(3)	0.00(2)	0.8(3)
O(3)	4e	0.01(4)	0.51(1)	0.241(5)	0.8(3)

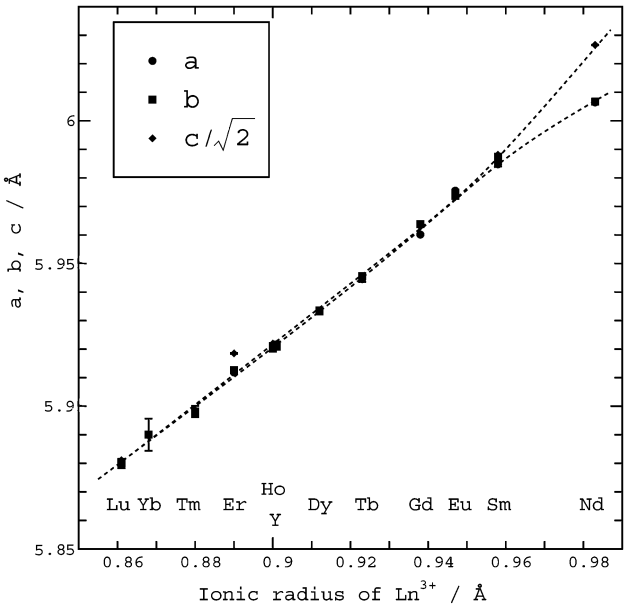

Fig. 3 Variation of lattice parameters for Ba_2LnReO_6 (Ln = Y, Nd, Sm–Lu) with Ln^{3+} radius.

Magnetic properties

The molar magnetic susceptibilities of Ba_2LnReO_6 (Ln = Y, lanthanides) are plotted as a function of temperature in Fig. 4–7(a) and Fig. 8 and 9. A magnetic anomaly is found for Ln = Y, Nd, Sm, Tb and Lu at 31, 6, 103, 2.5 and 33 K, respectively. They seem to be antiferromagnetic. In Ba_2YReO_6, the discrepancy in the observed transition temperatures between magnetic susceptibility and specific heat measurements is found (see Fig. 4), and the reason for this is not clear at present. In this study we adopt 31 K as the transition temperature, because a clear λ-type specific heat anomaly has been observed at 31 K. The Curie–Weiss law is valid for the magnetic susceptibilities of Ba_2LnReO_6 except for those of Ba_2SmReO_6 and Ba_2EuReO_6 in higher temperature ranges ($T > 150$ K). The effective magnetic moments (μ_{eff}) and Weiss constants (θ) of these compounds are listed in Table 3. The effective magnetic moments of Ba_2YReO_6 and Ba_2LuReO_6, in which only the Re^{5+} ion is magnetic, are 2.32 and 2.30 μ_B, respectively. The calculated magnetic moment for a spin-only value (Re^{5+} : $[Xe]5d^2$) is 2.83 μ_B. We consider that due to the effect of the crystal field, the orbital angular momentum has also contributed to the magnetic properties of these compounds, so the effective magnetic moments are smaller than the spin-only value. For other compounds, not only the Re^{5+} ion but also the Ln^{3+} ion is magnetic. When we assume that the magnetic moment of the Re^{5+} ion is 2.30 μ_B (which is close to those of Ba_2LuReO_6 and Ba_2YReO_6), the effective magnetic moments of Ba_2LnReO_6 (μ_{calc}) are calculated from the equation $\mu_{calc}{}^2 = \mu_{eff}(Ln^{3+})^2 + \mu_{eff}(Re^{5+})^2$. They are also listed in Table 3 and agree with the moments experimentally obtained for Ba_2LnReO_6 (μ_{exp}). The negative Weiss constants (θ) indicate that the predominant magnetic interactions in these compounds are antiferromagnetic.

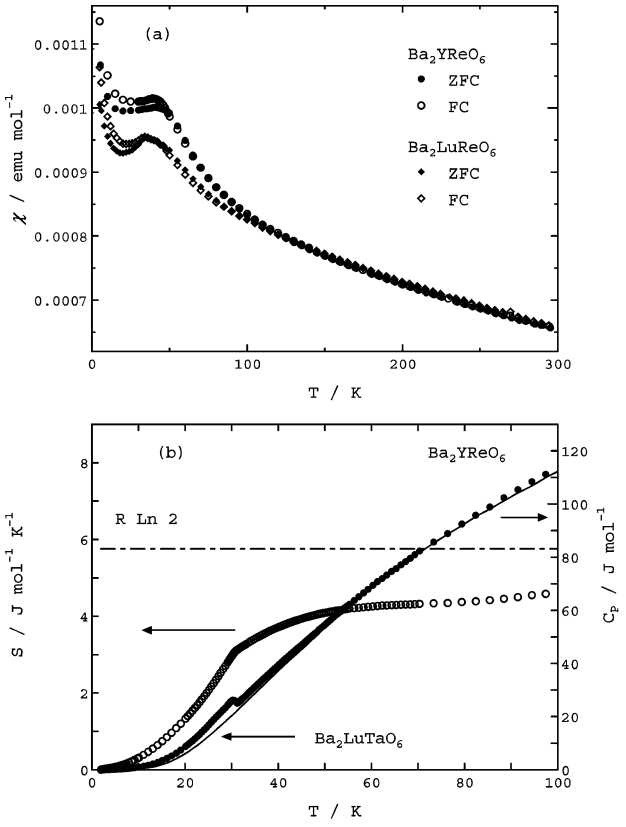

Fig. 4 (a) Temperature dependence of the ZFC (filled symbols) and FC (open symbols) molar magnetic susceptibilities for Ba_2YReO_6 (●,○) and Ba_2LuReO_6 (◆,◇). (b) Temperature dependence of specific heat (filled circle) and magnetic entropy (open circle) for Ba_2YReO_6.The solid line shows temperature dependence of specific heat for Ba_2LuTaO_6.

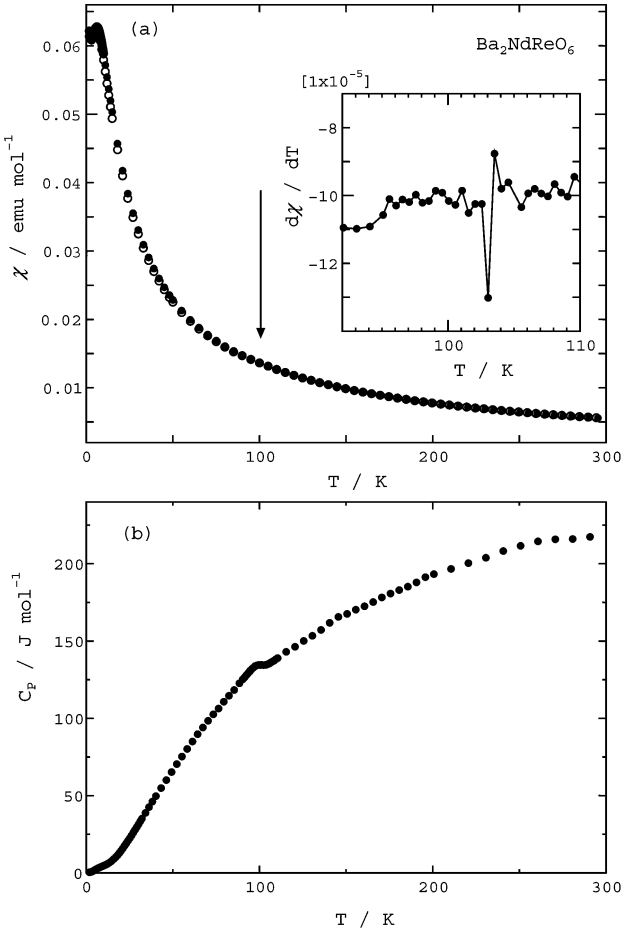

Fig. 5 (a) Temperature dependence of the ZFC (filled circle) and FC (open circle) molar magnetic susceptibilities for Ba_2NdReO_6. The arrow shows the magnetic anomaly temperature. The inset displays the temperature derivative of molar magnetic susceptibilities. (b) Temperature dependence of specific heat (filled circle) for Ba_2NdReO_6.

The divergence between the FC and ZFC susceptibilities has been observed for Ba_2LnReO_6 (Ln = Y, Sm, Lu) (see Fig. 4 and 6). Fig. 10 shows the variation of magnetization as a function of magnetic field for Ba_2LuReO_6 at 5 K. Small magnetic hysteresis has been found. These results indicate that the above Ba_2LnReO_6 compounds are not ideal antiferromagnets. We consider that this is due to the results of a low crystal symmetry of these compounds (*i.e.*, monoclinic symmetry). That is, the Dzyaloshinsky–Moriya (D–M) interaction can exist between the magnetically ordered elements, which results in the existence of a weak ferromagnetic component in their susceptibilities. The Ba_2EuReO_6 and Ba_2SmReO_6 shows that the temperature dependence of magnetic susceptibility does not obey the Curie–Weiss law. The ground state $^7F_0$ of Eu^{3+} is nonmagnetic, and the excited states ^7F_J (J = 1, 2, ..., 6) are close enough to give energy differences comparable to k_BT at room temperature. The excitation to the upper states affects sufficiently the magnetic susceptibility at room temperature. Thus, the molar magnetic susceptibility for Eu^{3+} can be expressed by the following equation[11]:

$$\chi_M(Eu^{3+}) = \frac{N_A\mu_B{}^2/3k_B}{\gamma T} \times \frac{24+(13.5\gamma-1.5)e^{-\gamma}+(67.5\gamma-2.5)e^{-3\gamma}+(189\gamma-3.5)e^{-6\gamma}}{1+3e^{-\gamma}+5e^{-3\gamma}+7e^{-6\gamma}} \quad (1)$$

where the parameter $\gamma = \lambda/k_BT$ is the ratio of the multiplet

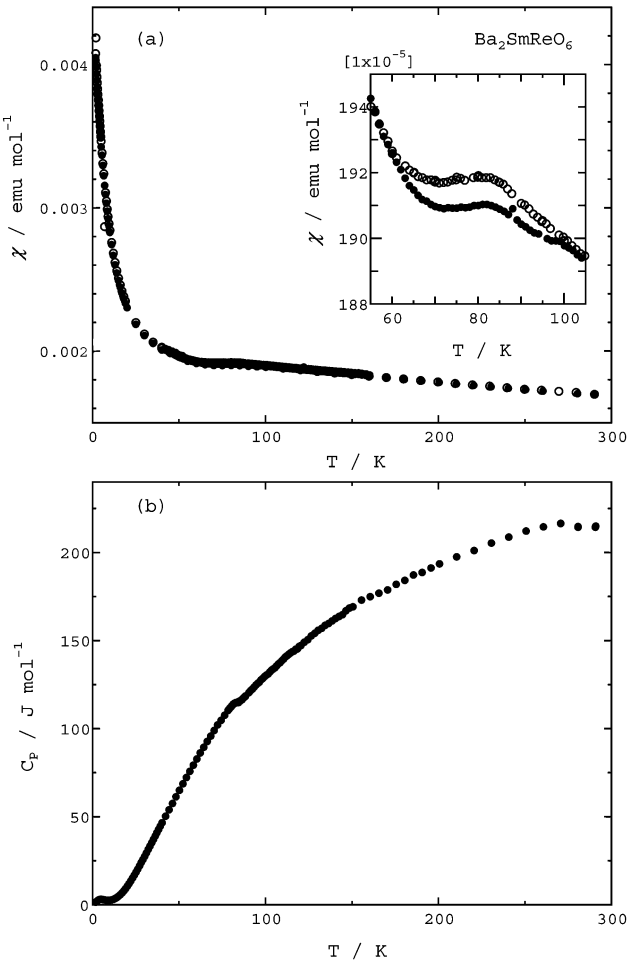

Fig. 6 (a) Temperature dependence of the ZFC (filled circle) and FC (open circle) molar magnetic susceptibilities for Ba_2SmReO_6. The inset shows the detailed susceptibilities in the temperature range of 55–105 K. (b) Temperature dependence of specific heat (filled circle) for Ba_2SmReO_6.

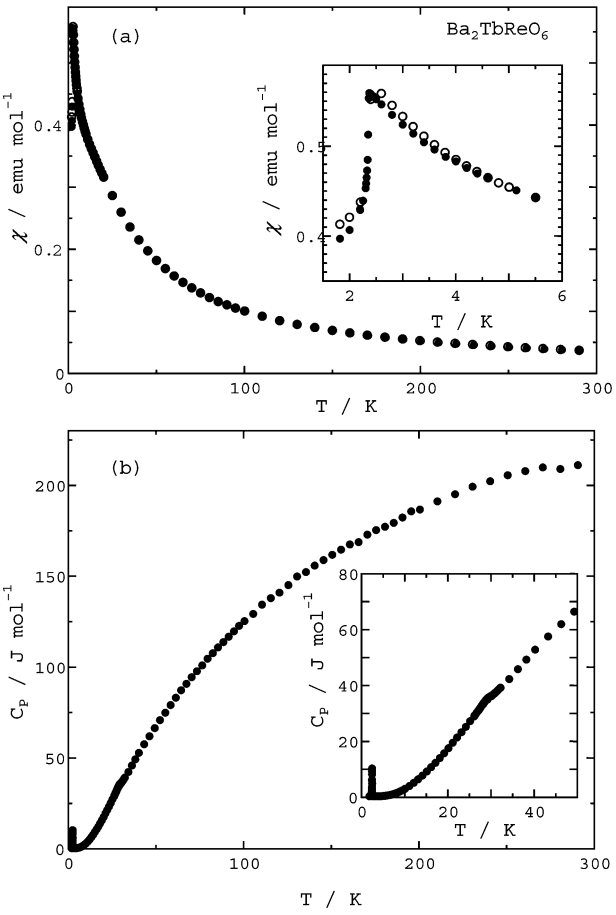

Fig. 7 (a) Temperature dependence of the ZFC (filled circle) and FC (open circle) molar magnetic susceptibilities for Ba_2TbReO_6. The inset shows the detailed susceptibilities in the temperature range 1.8–5.5 K. (b) Temperature dependence of specific heat (solid circle) for Ba_2TbReO_6. The inset shows the detailed specific heat in the temperature range of 1.8–50 K.

width (the spin-orbit coupling constant, λ) and the thermal energy (k_BT), and γ is 1/21 for the Eu^{3+} ion. We consider that in the paramagnetic region, the magnetic behavior of the Eu^{3+} ion and Re^{5+} ion are independent of each other and that the susceptibility of Ba_2EuReO_6 will be given by the sum of the susceptibilities of each paramagnetic ion. If we assume that the susceptibility of Re^{5+} follows the Curie–Weiss law, the total magnetic susceptibility of Ba_2EuReO_6 will be given by

$$\chi_M = \chi_M(Eu^{3+}) + \frac{C}{T-\theta} + \chi_{TIP} \quad (2)$$

where C is the Curie constant for Re^{5+} and χ_{TIP} is the temperature-independent susceptibility of Ba_2EuReO_6. In order to explain the behavior of magnetic susceptibility and to estimate the effective magnetic moment and Weiss constant of Re^{5+}, we attempted to fit this equation to experimental susceptibilities. To prevent the parameters from converging to meaningless values, we fixed the Curie constant values to 0.66, which is close to the values for Ba_2YReO_6 and Ba_2LuReO_6. By fitting, we have obtained $\lambda = 349\ cm^{-1}$ and $\theta = -289.5$ K. This λ value is close to the values reported in other ordered perovskites, for example, 339 cm^{-1} (Ba_2EuNbO_6)[1], 364 cm^{-1} (Ba_2EuIrO_6)[6] and 332 cm^{-1} (Ba_2EuTaO_6).[2] We attempted the same fitting for the susceptibilities of Ba_2SmReO_6, but the calculation did not converge. This is because of magnetic anomaly found at a relatively high temperature.

Fig. 4–7(b) show the variation of the heat capacity for Ba_2LnReO_6 as a function of temperature. The data for Ba_2LnReO_6 (Ln = Y, Nd, Sm, Gd, Dy, Ho and Lu) show a heat capacity anomaly at low temperatures, and Ba_2TbReO_6 shows two heat capacity anomalies. The anomaly temperatures are consistent with the magnetic transition temperatures in magnetic susceptibility curves and they are listed in Table 3. No specific heat capacity anomaly has been observed down to 2.0 K

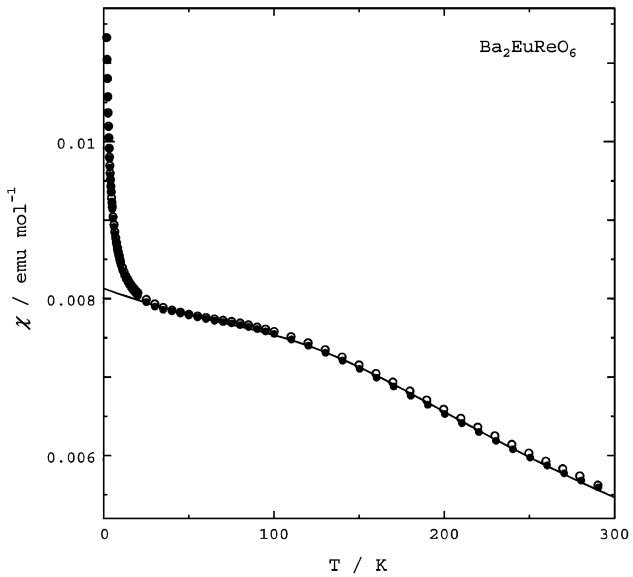

Fig. 8 Temperature dependence of the magnetic susceptibility of Ba_2EuReO_6. A solid line is calculated with eqn. (2).

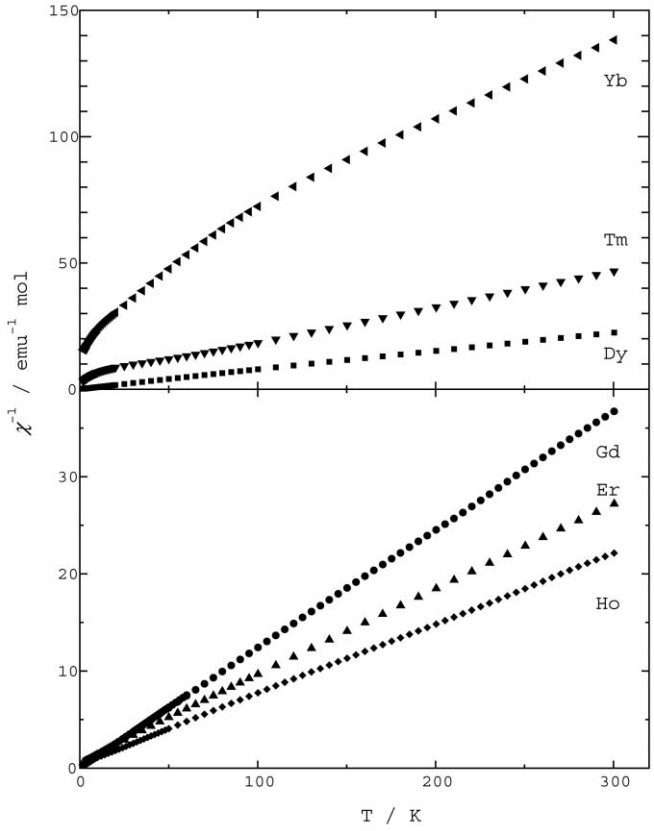

Fig. 9 Temperature dependence of the inverse magnetic susceptibilities of Ba_2LnReO_6 (Ln = Gd, Dy, Ho, Er, Tm and Yb).

for Ba_2LnReO_6 with Ln = Eu, Er, Tm and Yb, which is consistent with the results of the magnetic susceptibility measurements. In Fig. 4(b), the results of the specific heat measurements for Ba_2LuTaO_6, which has no paramagnetic ion, are also shown by the solid line. If we assume that the electronic and lattice contributions to the specific heat are equal between Ba_2LnReO_6 and Ba_2LuTaO_6, the magnetic specific heat for Ba_2LnReO_6 is obtained by subtracting the specific heat of Ba_2LuTaO_6 from that of Ba_2LnReO_6. From the temperature dependence of the magnetic specific heat, the magnetic entropy change of Ba_2YReO_6 is calculated as shown in Fig. 4(b). The magnetic entropy changes of Ba_2YReO_6 and Ba_2LuReO_6 at 100 K are 4.6 and 4.7 J (mol K)$^{-1}$, respectively. It is expected that the magnetic entropy change of Re^{5+} is $R\ln(2S + 1)$ = 9.13 J (mol K)$^{-1}$, where R and S are the molar gas constant and the spin quantum number, respectively. It is thought that due to the effect of the crystal field, the magnetic entropy decreases. In an octahedral crystal field environment, the ground state of the Re^{5+} ion ($5d^2$, the state $^3F_2$) degenerate to five-fold ($\Gamma_3 + \Gamma_5$). In the case of lower symmetry, the degeneracy is lifted and the ground state becomes doublet (Γ_3). Thus the magnetic entropy change is $R\ln 2$ = 5.76 J (mol K)$^{-1}$. Although this assumption is correct, the magnetic entropy change is still lower. It might be ascribed to the beginning of magnetic transition at higher temperature.

For Ln = Sm and Nd, heat capacity anomalies, corresponding to magnetic anomalies found in the magnetic susceptibility curve, were also observed. It is suggested that the anomalies are based on the magnetic transition of Re^{5+}.

For Ln = Gd, Tb, Dy and Ho, heat capacity anomalies are also observed at 65, 29, 70 and 27 K, respectively, as is the case with Ba_2SmReO_6 and Ba_2NdReO_6. However, no magnetic

Table 3 Experimental effective magnetic moments (μ_{exp}), calculated magnetic moments ($\mu_{calc}{}^2 = \mu_{eff}(Ln^{3+})^2 + \mu_{eff}(Re^{5+})^2$), Weiss constants ($\theta$) and magnetic transition temperatures (T_N) for Ba_2LnReO_6 (Ln = Y, Nd, Sm–Lu)

Ln	μ_{exp}/μ_B	μ_{calc}/μ_B	θ	T_N
Y	2.32	—	−726	31
Nd	3.86	4.29	−35.2	100
Sm	—	2.45	—	82
Eu	—	2.30	—	—
Gd	8.10	8.27	−1.9	65
Tb	9.48	9.99	−14.1	2.4, 29
Dy	10.51	10.88	−10.0	70
Ho	10.52	10.83	−7.4	27
Er	9.56	9.86	−10.9	—
Tm	7.49	7.89	−26.9	—
Yb	5.04	5.09	−138	—
Lu	2.30	—	−703	33

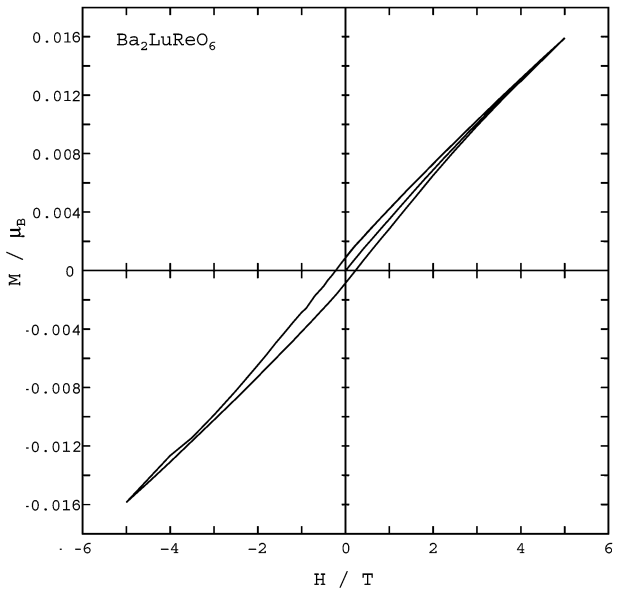

Fig. 10 Field-dependence of the magnetization for Ba_2LuReO_6 at 5 K.

anomaly is observed in the magnetic susceptibility curve since the contribution of the magnetic moment of the Re^{5+} ion to the behavior of Ba_2LnReO_6 (Ln = Gd, Tb, Dy and Ho) is smaller compared with that of the Ln^{3+} ion. The heat capacity anomalies might be based on magnetic transition of Re^{5+}.

Ba_2TbReO_6 shows a heat capacity anomaly also at 2.5 K, corresponding to the magnetic anomaly found in the magnetic susceptibility curve. It is thought that this anomaly is based on the magnetic transition of Tb^{3+}.

In conclusion, we have found that Ba_2ReLnO_6 (Ln = Y, Nd, Sm, Gd, Tb, Dy, Ho, Lu) show magnetic transitions at low temperatures which vary with the Ln^{3+} ion. They might be the antiferromagnetic transition of the Re^{5+} ion. Ba_2TbReO_6 shows the magnetic transition due to the antiferromagnetic transition of the Tb^{3+} ion. On the other hand, Ba_2LnReO_6 (Ln = Eu, Er, Tm and Yb) are paramagnetic down to 1.8 K.

It should be noticed that the magnetic transition temperatures for the compounds with Ln = Nd, Sm, Gd, Dy are much higher than those for the compounds with Ln = Y, Lu, although these magnetic transitions could be due to antiferromagnetic interactions between the same Re^{5+} ions. To fully understand the nature of the transition, it is necessary to perform single crystal growth and microscopic measurements such as neutron diffraction and NMR.

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