

Magnetic Properties of Ordered Perovskites Ba_2MUO_6 ($M = Sc, Y, Gd, Yb, Mn$)

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Uranium complex oxides with the ordered perovskite structure Ba_2MUO_6 ($M = Sc, Y, Gd, Yb, Mn$) were prepared, and their magnetic susceptibilities and electron paramagnetic resonance (EPR) spectra were measured. The lattice parameter of the compounds varied linearly with the ionic radius of M^{3+} . The effective magnetic moments of U^{5+} in Ba_2YUO_6 and Ba_2ScUO_6 were very small. The moments of Ba_2GdUO_6 and Ba_2YbUO_6 were 7.74 and 4.69 μ_B , respectively, close to the theoretical values for Gd^{3+} and Yb^{3+} . The electron paramagnetic resonance spectrum was observed for Ba_2GdUO_6 , its g -value was 1.92. In Ba_2MnUO_6 , ferrimagnetic behavior was found below ca. 55 K. The effective magnetic moment was 5.52 μ_B and the g -value of EPR was 2.00. These results show that the manganese ion is divalent at a high spin state and that the uranium ion is in the hexavalent state. © 1993 Academic Press, Inc.

Introduction

Actinide complex oxides with one or more metal ions in addition to an actinide are important because they may be found as fission products in nuclear fuels and because they are models for possible matrices in which nuclear wastes will be stored.

Since the $5f$ electrons which characterize the properties of actinides have energies in close proximity to those of the $6d$ and $7s$ electrons, the actinides may show a great number of oxidation states. Among many oxides, the perovskites ABO_3 ($A = Ba, Sr$) incorporate various kinds of tetravalent actinide ions at the B site of the crystal (1). The solubility of another actinide or lanthanide ion into the B site in the ABO_3 crystal is limited. One interesting feature is that "ordered" perovskites $A_2M^{3+}M^{5+}O_6$ ($A_2M^{2+}M^{6+}O_6$) are obtained by replacing the +4 cations in the $A^{2+}M^{4+}O_3$ perovskite compounds with +3 and +5 cations (+2 and +6 cations). The space group of these $A_2BB'O_6$ compounds belongs to O_h^5 ($Fm3m$)

with four formula units per unit cell. The oxygen atoms are linked to the alkaline earth atom in 12-fold coordination and with B and B' atoms in 6-fold coordination, forming regular octahedra.

We are interested in the $BaUO_3$ compounds, because replacing half of the uranium ions with trivalent rare earth ions (divalent alkaline earth ions) produces the ordered perovskites Ba_2MUO_6 , oxidizing the rest of the uranium ions to the pentavalent state (hexavalent state).

The preparation and characterization of numerous A_2MUO_6 compounds with the ordered perovskite structure have been studied by Sleight and Ward (2). Later, Awasthi *et al.* (3) reported a number of ordered perovskite compounds with $A_2BB'O_6$ where $A = Ba, Sr$, $B = U^{4+}, U^{5+}, U^{6+}$, and B' is a divalent, trivalent, or tetravalent ion. They also examined the formation of ordered perovskites with neptunium and plutonium (4). However, Goodenough and Longo (5) and Keller (6) raise a question about the formation of compounds with the ordered

perovskite structure such as Ba_2ZrUO_6 , Ba_2GeUO_6 , Ba_2TiPuO_6 , and so on.

Magnetic properties of uranium complex oxides with the ordered perovskite structure Ba_2MUO_6 have not yet been studied, except Ba_2MnUO_6 (7). Magnetic studies are effective in elucidating the electronic states of the uranium and M ions in Ba_2MUO_6 . Since the oxygen stoichiometric $BaUO_3$ shows temperature-independent paramagnetism over a wide temperature range (8) and since the hexavalent uranium ion is diamagnetic, the magnetic behavior of U^{5+} in the Ba_2MUO_6 should be quite different from that of U^{4+} and U^{6+} .

In this paper, we prepared cubic Ba_2MUO_6 ($M = Sc, Y, Gd, Yb, Mn$) with the ordered perovskite structure and measured their magnetic susceptibilities and electron paramagnetic resonance (EPR) spectra to elucidate the electronic states of uranium and M in the crystals.

Experimental

1. Preparation

As starting materials, $BaCO_3$, M_2O_3 (rare earth sesquioxide), MnO_2 , and U_3O_8 were used. Before use, $BaCO_3$ and M_2O_3 were heated in air at $800^\circ C$ to remove any moisture, and U_3O_8 was oxidized in air at $850^\circ C$ to form the stoichiometric compound. $BaCO_3$, M_2O_3 , and U_3O_8 were weighed in the stoichiometric metal ratio $Ba:M:U = 2:1:1$. After being finely ground in an agate mortar, the mixtures were pressed into pellets and then heated in a flowing hydrogen gas atmosphere at $1200^\circ C$. After cooling to room temperature, the samples were crushed into powder, repressed into pellets, and heated in a flowing argon gas atmosphere at $1300^\circ C$. After cooling to room temperature, the samples were recrushed, repressed into pellets, and heated again in an argon gas atmosphere at $1300^\circ C$ to make the reaction complete.

2. Analysis

2.1. X-ray diffraction analysis. The X-ray diffraction analysis was performed with $CuK\alpha$ radiation on a Philips PW 1390 diffractometer equipped with a curved graphite monochromator. The lattice parameters of the samples were determined by a least-squares method.

2.2. Determination of the oxygen content. The oxygen nonstoichiometry in the sample was checked by the back-titration method (9,10). A weighed amount of the sample was dissolved in an excess of cerium(IV) sulfate solution, which was standardized in advance with stoichiometric UO_2 . The remaining cerium(IV) was titrated against a standard iron(II) ammonium sulfate solution with the ferroin indicator. The oxygen amount was evaluated for each predetermined $Ba:M:U$ ratio.

3. Magnetic Susceptibility Measurement

The magnetic susceptibility was measured using a Faraday-type torsion balance in the temperature range between 4.2 K and room temperature. The apparatus was calibrated with a manganese Tutton's salt ($\chi_g = 10,980 \times 10^{-6}/(T + 0.7)$). The temperature of the sample was measured by a "normal" Ag vs Au-0.07 at.% Fe thermocouple (4.2 K ~ 40 K) (11) and an Au-Co vs Cu thermocouple (10 K ~ room temperature). Details of the experimental procedure have been described elsewhere (12).

4. Electron Paramagnetic Resonance Measurement

The EPR measurements were carried out at room temperature using a JEOL RE-2X spectrometer operating at X band frequency (9.1 GHz) with 100 kHz field modulation. The magnetic field was swept from 100 to 13,000 G. Before the specimen was measured, a blank was recorded to eliminate the possibility of interference by the background resonance of the cavity and/or sample tube. The magnetic field was monitored with a proton NMR gaussmeter, and the

TABLE I
LATTICE PARAMETER AND EFFECTIVE MAGNETIC
MOMENT OF Ba_2MUO_6

Compound	a (Å)	μ_{eff} (μ_B)
$Ba_2YUO_{5.892}$	8.682	0.67
$Ba_2ScUO_{5.880}$	8.497	0.49
$Ba_2GdUO_{5.944}$	8.738	7.74
$Ba_2YbUO_{5.944}$	8.647	4.69
Ba_2MnUO_6	8.519	5.52

Note. Estimated error in a is ± 0.001 Å. Estimated error in μ_{eff} is ± 0.01 μ_B .

microwave frequency was measured with a frequency counter.

Results and Discussion

In spite of the report on the successful preparation of some ordered perovskites $Ba_2M^{4+}U^{4+}O_6$ (3), Goodenough and Longo (5) and Keller (6) raise a question about the formation of such ordered perovskites. To clarify this point, we tried to prepare Ba_2TiUO_6 and Ba_2ZrUO_6 by the methods used by Awasthi *et al.* (3), but ordered perovskites were not produced even at still higher temperatures ($\sim 1500^\circ\text{C}$). The product contained at least two phases; for example, Ba_2ZrUO_6 was a mixture of two simple perovskites, $BaUO_3$ and $BaZrO_3$. Although the tolerance factor of Ba_2TiUO_6 would be very close to 1 (13), the formation of the ordered perovskite is difficult due to the large difference in the ionic radius between Ti^{4+} and U^{4+} (14).

Table I lists the ordered perovskites Ba_2MUO_6 prepared in this study. They are all cubic. Sleight and Ward report that Ba_2YUO_6 was slightly distorted (2). This difference is considered to be due to the preparation method. Sleight and Ward prepared the sample in an evacuated silica capsule at 1000°C . On the other hand, our sample was heated at 1300°C and cooled down in a flowing argon atmosphere. We have considered that cubic Ba_2YUO_6 in a high temperature

phase could be quenched and that there is a difference in the oxygen nonstoichiometry between their sample and ours. Unfortunately, Sleight and Ward did not mention any oxygen nonstoichiometry in their sample. From the results of oxygen analysis, we can say that the specimens are nearly oxygen stoichiometric, although some oxygen deficiency is found in Ba_2YUO_6 and Ba_2ScUO_6 . The lattice parameters of Ba_2MUO_6 are plotted against the ionic radius of M^{3+} (14) in Fig. 1. This figure shows that they vary linearly with the ionic radius. This result indicates that the lattice parameter change among Ba_2MUO_6 compounds depends only on the trivalent ion size of the rare earth elements. Similar behavior has been found in the lattice parameter of $M_{0.5}U_{0.5}O_2$ (M = rare earth) compounds (15). For the case of Ba_2MnUO_6 , the situation is complicated; we will discuss this later.

Ba_2YUO_6 and Ba_2ScUO_6

Figure 2 shows the variation of the magnetic susceptibility with temperature for Ba_2YUO_6 and Ba_2ScUO_6 . For comparison, the susceptibility of oxygen-stoichiometric

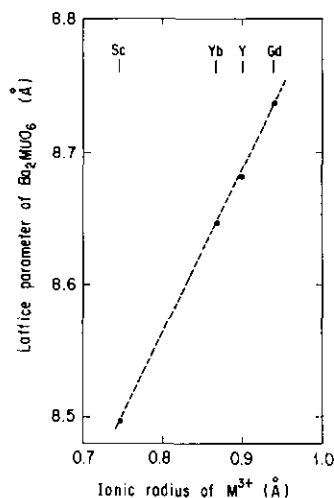


FIG. 1. Lattice parameter of Ba_2MUO_6 vs ionic radius of M^{3+} .

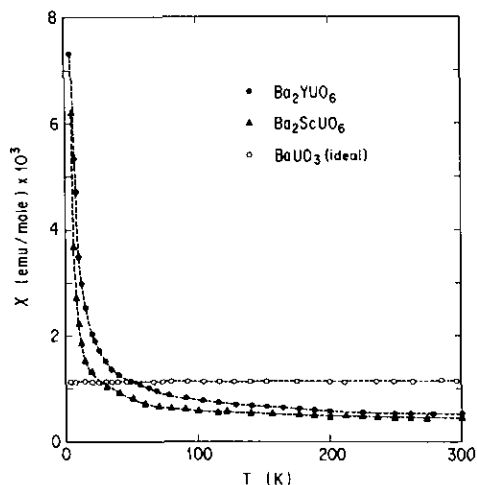


FIG. 2. Temperature dependence of magnetic susceptibilities of Ba_2YUO_6 and Ba_2ScUO_6 . For comparison, the susceptibility of $BaUO_3$ is also shown.

$BaUO_3$ (ideal) is also shown. The susceptibilities of Ba_2YUO_6 and Ba_2ScUO_6 are temperature-dependent, in contrast to the temperature-independent paramagnetism (TIP) of $BaUO_3$. They do not follow the Curie-Weiss law. By extrapolating the reciprocal temperature $1/T$ to 0 for the susceptibility vs reciprocal temperature curve, we obtain the temperature-independent paramagnetic susceptibilities 330×10^{-6} and 340×10^{-6} emu/mole for Ba_2YUO_6 and Ba_2ScUO_6 , respectively. These TIP values are, of course, much smaller than that for $BaUO_3$ (1110×10^{-6} emu/mole) (8). The oxidation state of uranium ions in these nearly oxygen-stoichiometric compounds are considered to be pentavalent from the charge neutrality condition. From the temperature-dependent part of the susceptibility, the effective magnetic moments for Ba_2YUO_6 and Ba_2ScUO_6 are calculated to be 0.67 and $0.49 \mu_B$, respectively. These values are much smaller than the moment for a free f^1 ion ($2.54 \mu_B$), which indicates that the crystal field effect on the magnetic properties of an f electron is large. The effective magnetic moment of Ba_2YUO_6 is a little smaller than the values listed in Ref. (16) as the moments of U^{5+} in an octahedral crystal

field, and is comparable to the moment of, for example, Li_7UO_6 ($0.87 \mu_B$). The moment of Ba_2ScUO_6 is very small. The TIP values are larger than the values calculated for an f^1 electron in an octahedral crystal field on the basis of the crystal field model developed by Eisenstein and Pryce (17) and Hinatsu *et al.* (18) ($110 \sim 220$ emu/mole). In this case, we have no spectroscopic data to determine the crystal field level, so we cannot calculate the TIP values for Ba_2YUO_6 or Ba_2ScUO_6 . The excess TIP values might be responsible for a U^{4+} ion produced by the oxygen deficiency found in Ba_2YUO_6 and Ba_2ScUO_6 (see Table I), because the U^{4+} ion in an octahedral field shows large TIP (19). In fact, ideal $BaUO_3$ shows TIP (1110×10^{-6} emu/mole) over the temperature range from 4.2 K to room temperature. No EPR spectrum was observed for the U^{5+} ion in Ba_2YUO_6 and Ba_2ScUO_6 even at 4.2 K.

Ba_2GdUO_6 and Ba_2YbUO_6

Figure 3 shows the temperature dependence of the reciprocal susceptibility of

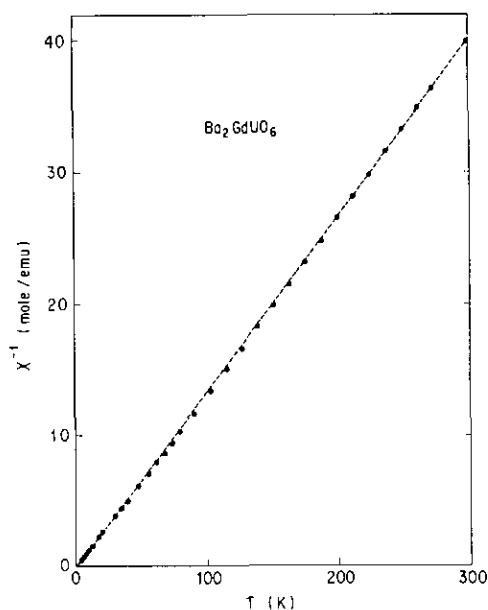


FIG. 3. Temperature dependence of reciprocal magnetic susceptibility of Ba_2GdUO_6 .

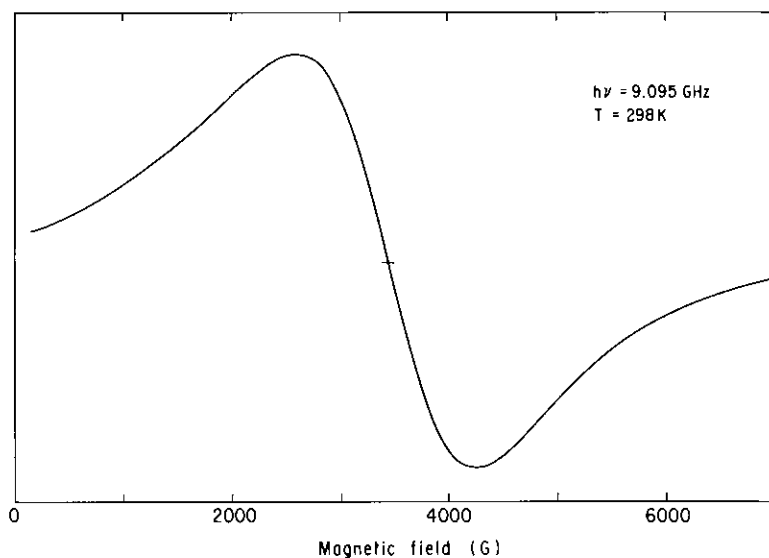


FIG. 4. EPR spectrum of Ba_2GdUO_6 at room temperature.

Ba_2GdUO_6 . A linear relationship is found in this χ^{-1} vs T curve, from which it can be determined that the effective magnetic moment is $7.74 \mu_B$. This value is very close to the theoretical moment of a Gd^{3+} ion, indicating that the magnetic properties of this compound are attributable entirely to the moment of the Gd^{3+} ion. This result is consistent with the very small magnetic moment of U^{5+} in Ba_2YUO_6 and Ba_2ScUO_6 .

It is well known that the EPR spectra for rare earth ions can be measured only at very low temperatures because of the rapid spin-lattice relaxation. However, the situation is different for the rare earth ions with a half-filled f shell such as the Gd^{3+} ion, because the ground state is the $^8S_{7/2}$ state. Figure 4 shows the EPR spectrum measured at room temperature. The g -value is 1.92, and the peak-to-peak line width is about 1700 G. At 4.2 K, there was little change in the resonance spectrum other than an increased intensity. The large deviation of the g -value from 2.00 indicates that there is a significant amount of intermediate coupling, which results in the ground state of $4f^7$ including the $^6P_{7/2}$ state. On the other hand, the g -value for an f^1 electron in an octahedral

crystal field should be in the range $-1.43 \leq g \leq 2.00$ (18). However, even at 4.2 K no EPR signal corresponding to the U^{5+} ion was detected up to 13,000 G. This result is consistent with the result that no EPR spectrum was found for the Ba_2YUO_6 and Ba_2ScUO_6 in which the only paramagnetic ion is U^{5+} .

In Ba_2YbUO_6 , the paramagnetic ions are Yb^{3+} and U^{5+} . Figure 5 shows the recipro-

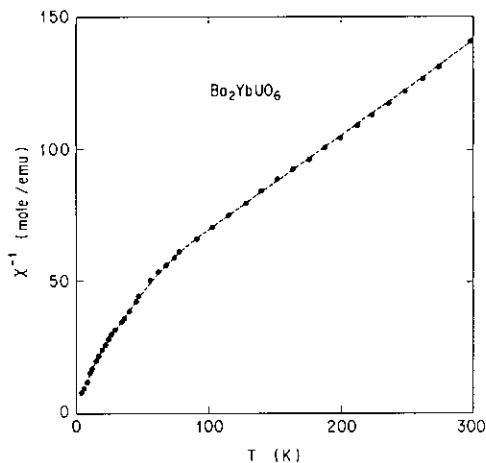


FIG. 5. Temperature dependence of reciprocal magnetic susceptibility of Ba_2YbUO_6 .

cal susceptibility vs temperature curve for Ba_2YbUO_6 . The effective magnetic moment derived from this figure is $4.69 \mu_B$. This value is a little larger than the theoretical moment of Yb^{3+} ($4.54 \mu_B$). Assuming that both Yb^{3+} and U^{5+} contribute to the susceptibility of this compound, the effective magnetic moment of U^{5+} is calculated to be $1.18 \mu_B$. This is a small value for the moment of the U^{5+} ion. No EPR spectrum for U^{5+} or Yb^{3+} was observed even at 4.2 K.

Ba_2MnUO_6

In this compound, both uranium and manganese have two or more oxidation states. Therefore, there exist several combinations for which different oxidation states of uranium and manganese are possible. Awasthi *et al.* (3) claimed that they prepared both $Ba_2Mn^{4+}U^{4+}O_6$ and $Ba_2Mn^{2+}U^{6+}O_6$, but did not show any experimental evidence for the oxidation states of uranium and manganese. Kemmler-Sack (7) also prepared Ba_2MnUO_6 and considered that the charge distribution in her sample was $Ba_2(Mn^{3+}_{0.4}$,

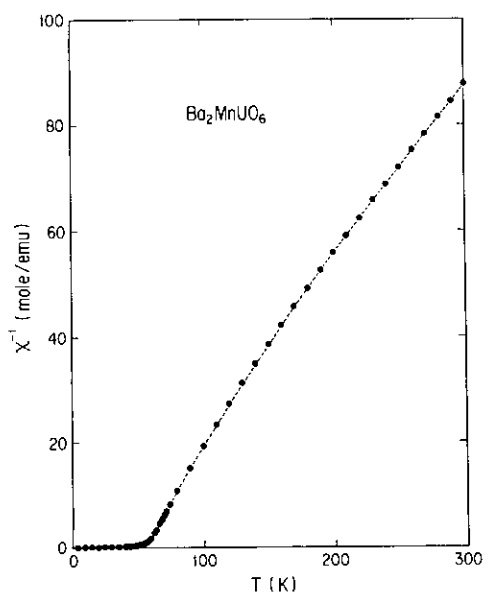


FIG. 6. Temperature dependence of reciprocal magnetic susceptibility of Ba_2MnUO_6 .

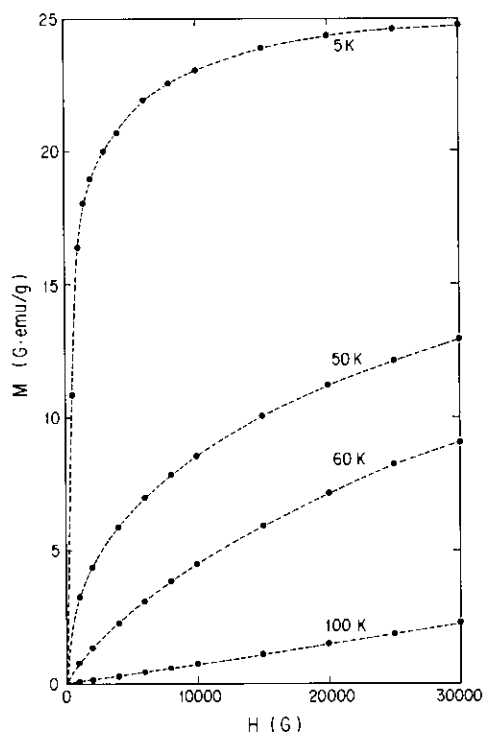


FIG. 7. Magnetization curves of Ba_2MnUO_6 at 5, 50, 60, and 100 K.

$Mn^{2+}_{0.6})(U^{5+}_{0.4}, U^{6+}_{0.6})O_6$ from the results of spectroscopic and magnetic measurements. The lattice parameter of our sample is 8.519 \AA , which is near that reported by Sleight and Ward (2), but larger than those of Awasthi *et al.* (3) and Kemmler-Sack (7). As will be discussed later, the oxidation states of Mn and U in the Ba_2MnUO_6 prepared in this study are divalent and hexavalent, respectively; i.e., the $Ba_2Mn^{2+}U^{6+}O_6$ model is valid. Grenet *et al.* stated that the lattice parameter for the $Ba_2Mn^{2+}U^{6+}O_6$ model is larger than that for the $Ba_2Mn^{3+}U^{5+}O_6$ model and still larger than that for the $Ba_2Mn^{4+}U^{4+}O_6$ model (20). So, if the lattice parameter of Ba_2MnUO_6 reported by Kemmler-Sack is correct (8.465 \AA), the lattice parameter for pure $Ba_2Mn^{2+}U^{6+}O_6$ should be larger than this value, because her sample was $0.6Ba_2Mn^{2+}U^{6+}O_6 + 0.4Ba_2Mn^{3+}U^{5+}O_6$ (7). The lattice parameter of $Ba_2Mn^{2+}U^{6+}O_6$ reported by Awasthi

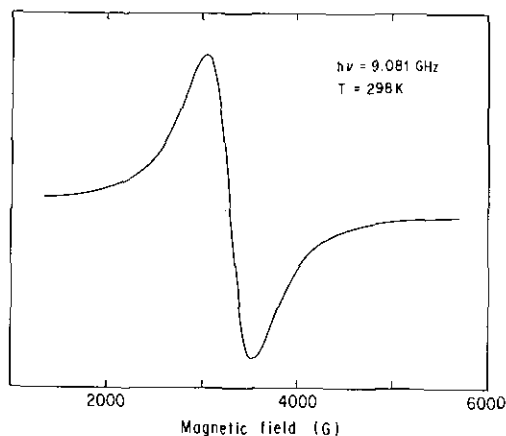


FIG. 8. EPR spectrum of Ba_2MnUO_6 at room temperature.

et al. (8.36 Å) is smaller than that of $\text{Ba}_2\text{Mn}^{4+}\text{U}^{4+}\text{O}_6$ reported by the same researchers (8.47 Å); i.e., their data are unreliable. Figure 6 shows the temperature dependence of the reciprocal susceptibility (χ^{-1}) of Ba_2MnUO_6 prepared in this study. This compound shows ferrimagnetic behavior below ca. 55 K. Figure 7 shows its magnetization curves at various temperatures, clearly indicating a large field dependence of the susceptibility at 5 K. Above 160 K, a linear relationship is found in the χ^{-1} vs T curve (Fig. 6). The effective magnetic moment is calculated to be $5.52 \mu_B$. This value is close to the moment of Mn^{2+} at a high spin state ($3d^5$), which indicates that the magnetic properties of Ba_2MnUO_6 are mostly attributable to the behavior of the manganese ion at a high spin state. If the electronic state of the manganese ion in the compound were an S -state (d^5 configuration at the high spin state), the EPR spectrum should be measurable even at room temperature. We measured the EPR spectrum at room temperature; the g -value is 2.00 as expected, and is shown in Fig. 8. From the charge balance in the Ba_2MnUO_6 , the oxidation state of uranium is +6. The U^{6+} ion is diamagnetic and

shows no contribution to the magnetism of the compound, which is in accordance with the results of magnetic susceptibility and EPR measurements.

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