

## Electric and Magnetic Properties of $\text{Eu}_{1-x}\text{Ba}_x\text{MnO}_3$

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We have studied the fundamental properties of the manganites  $\text{Eu}_{1-x}\text{Ba}_x\text{MnO}_3$  as candidates for the light induced ferromagnetic materials. Solid solutions are formed with  $x \leq 0.4$ . The manganites are perovskite-type and the crystal system of them changes successively with increase in  $x$ . The manganites with  $x = 0.0$  and  $0.1$  have orthorhombic cells. The manganites with  $x = 0.3$  and  $0.4$  have rhombohedral cell and cubic cell, respectively. The manganite with  $x = 0.2$  has two perovskite phases, one belongs to orthorhombic system and the other belongs to monoclinic system. All manganites are semiconductors below room temperatures. Magnetic correlation between magnetic moments is antiferromagnetic for the manganite with  $x = 0.0$  and ferromagnetic for the other manganites near room temperature. However, it is found that ferromagnetic clusters are formed at low temperatures for all manganites.

Key words: Light Induced ferromagnetism, Perovskite, Manganite, Eu ion, Magnetism

### 1. INTRODUCTION

Controls of physical properties by stimulation of light have been attempted extensively. Light induced ferromagnetism is one of them. The discovery for thin film of (In, Mn)As, which is a semiconductor and grown on GaSb substrate, has proceed researches of this field [1]. However, the light induced ferromagnetism appears in the film only at very low temperatures below 35 K. The appearance of the light induced ferromagnetism require GaSb substrate, because the ferromagnetism occurs due to injection of hole carriers, which are generated in GaSb substrate by stimulation of light, to (In, Mn)As film. These features make the application of the material difficult. We explore the materials having the light induced ferromagnetism itself, moreover, having higher temperatures at which the ferromagnetism appears. We have selected perovskite-type manganites as the objects of our study.

The perovskite-type manganite is often abbreviated as  $R_{1-x}A_x\text{MnO}_3$ , where  $R$  indicates the trivalent lanthanide ions and  $A$  indicates the divalent alkaline earth ions. The substitution of  $R$  ion by  $A$  ion injects hole carriers to Mn ions and ferromagnetism appears by the double exchange interaction [2]. The hole carriers may be injected to the Mn ions, if the trivalent  $R$  ions change to divalent  $R$  ions by stimulation of light, and the ferromagnetism may appear. The  $R$  ions have trivalent states usually in perovskite-type oxides. However, Eu ion has divalent state in  $\text{EuTiO}_3$ , which was confirmed by Mössbauer spectra [3]. We, thus, selected Eu ion as the  $R$  ion.

Ferromagnetic transition temperature  $T_c$  for the perovskite-type manganites strongly depends on the average ionic radius of  $R$  ion and  $A$  ion and increases with increasing the average ionic radius [4]. Tadokoro *et al.* found that the highest  $T_c$  is 102 K with  $x = 0.3$  in the  $\text{Eu}_{1-x}\text{Sr}_x\text{MnO}_3$  in their pioneering work [5]. Therefore, we selected Ba ion as  $A$  ion because the average ionic radius is increased.

We have prepared the perovskite-type manganites  $\text{Eu}_{1-x}\text{Ba}_x\text{MnO}_3$  and have investigated the properties of

them. We summarize and report the fundamental electric and magnetic properties.

### 2. EXPERIMENTALS

The samples were prepared using the raw materials,  $\text{Eu}_2\text{O}_3$  (99.9 %),  $\text{BaCO}_3$  (99.9%) and  $\text{Mn}_3\text{O}_4$  (99.9%) by solid state reaction. The ignition losses of the materials were determined previously. Stoichiometric mixtures of the materials were calcined twice at 1200 °C in air for 12 h with an intermediate grinding. The calcined samples were pressed into pellets by cold isostatic pressing under pressure of 1 GPa. The pellets were sintered at 1600 °C in air for 2 h at a heating rate of 300 °Ch<sup>-1</sup> and cooling rate of 100 °Ch<sup>-1</sup>.

Crystalline phases were identified using an X-ray diffractometer (RINT2500VHF, Rigaku, Japan) equipped with a graphite monochromator. The lattice constants were calculated by a least square method from diffraction angles which were corrected by the angles of Si as an internal standard. Oxygen contents of the samples were determined by an iodometric titration on the assumption that Eu ions are trivalent in the samples and during the titration.

The temperature dependence of electric resistivity was measured by dc four-probe method in the temperature range between 10 K and 300 K. The temperature dependence of magnetization and magnetization curve were measured by a vibrating sample magnetometer (BHV-55LHCS Riken-Denshi, Japan).

### 3. RESULTS AND DISCUSSIONS

Figure 1 shows X-ray diffraction profiles of the samples. The crystal system changes with increasing  $x$ . The samples with  $x = 0.0$  and  $0.1$  have orthorhombic cells with  $a \approx b \approx \sqrt{2}a_p$  and  $c \approx 2a_p$ , where  $a_p$  is the lattice parameter of cubic perovskite cell. Orthorhombic and monoclinic cells coexist in the sample with  $x = 0.2$ . The sample with  $x = 0.3$  has a very weak peak at  $2\theta \sim 38.4^\circ$  as shown by an arrow in the figure so that the

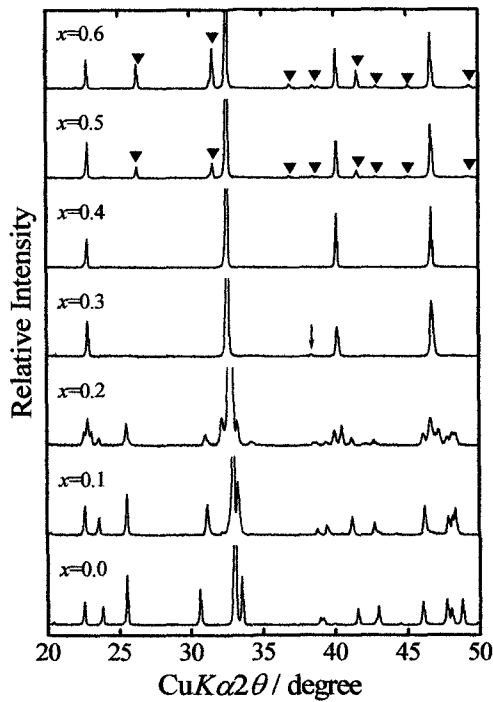


Figure 1 XRD profiles of  $\text{Eu}_{1-x}\text{Ba}_x\text{MnO}_3$ . Triangles indicate  $\text{BaMnO}_{3-x}$ .

sample has slightly rhombohedrally distorted cubic perovskite cell. The weak peak is indexed by 113 of hexagonal cell with  $a \approx \sqrt{2}a_p$  and  $c \approx 2\sqrt{3}a_p$ , which is converted from rhombohedral cell. The crystal system changes to cubic system with  $x$  more than 0.4. The samples with  $x = 0.5$  and  $0.6$  have an additional phase of  $\text{BaMnO}_{3-x}$  (JCPDS, #26-0170).

Lattice constants are listed in Table 1. Reduced cubic perovskite cell volumes were calculated from the cell volumes  $V$  listed in the table. Cubic roots of the cell volumes were calculated as the lattice constants of the reduced cells and plotted in Figure 2(a). The lattice constants of the samples with  $x = 0.2$  and  $0.3$  are smaller than those of the other samples. The lattice constant of the sample with  $x = 0.4$  is 0.13 % larger than that of the sample with  $x = 0.0$ , though Eu ion with radius of 0.1066 nm is substituted by much larger Ba ion with radius of 0.142 nm. The substitution of Ba ion, thus, seems to contribute to relaxation of lattice strain. Figure 2(b) shows the oxygen contents of the samples. Most samples have nearly stoichiometric oxygen content. The

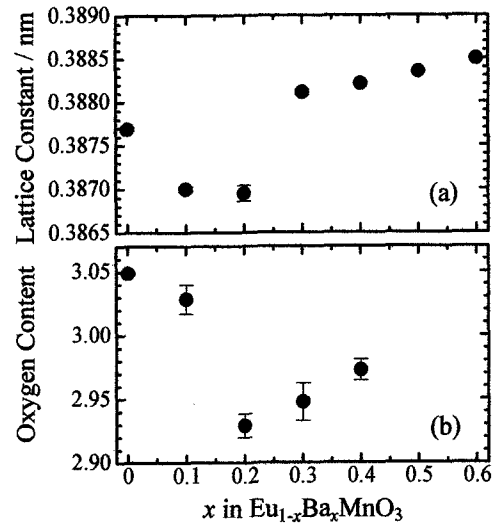


Figure 2 (a) Lattice constant of reduced cubic perovskite cell and (b) oxygen content for the samples.

marked decrease in oxygen content with increasing  $x$  toward 0.2 seems to correspond to the intermediate decrease in the lattice constant found in the samples with  $x = 0.1$  and  $0.2$ . In any case, holes are certainly injected to  $\text{MnO}_6$  octahedron networks by the substitution of Ba ion for all samples containing Ba ion.

Figure 3 shows the temperature dependence of electric resistivity. The resistivity decreases with increasing  $x$  and all samples are semiconductive. The activation energies were evaluated on the assumption of thermally activating conduction process and are plotted in the inset of the figure. The activation energy decreases monotonously with increasing  $x$  to 0.4 and constant with  $x$  larger than 0.4. Trukhanov *et al.* have been succeeded to reduce steeply the electric resistivity of perovskite-type  $\text{EuBaMn}_2\text{O}_{6-y}$  by two-step annealing of reduction and reoxidation [6]. They have thought that the electric conductivity is improved because the lattice strain due to disordering of Eu ions and Ba ions at  $A$ -sites of perovskite structure are released by ordering of these ions through the annealing. The improvement of the electronic conduction for our samples is supposed to be due to hole doping and the relaxation of the lattice strain by Ba substitution, however, the semiconduction means that considerable lattice strain remains in our sample with  $x = 0.4$ .

Table 1 Lattice constants of the samples.

$x$	System	$a$ / nm	$b$ / nm	$c$ / nm	$V$ / nm <sup>3</sup>
0.0	Orthorhombic	0.53394(3)	0.58582(4)	0.74520(4)	0.23309(3)
0.1	Orthorhombic	0.53772(8)	0.57355(9)	0.75174(11)	0.23185(6)
0.2*	Orho. + Monoclinic	0.53771(23)	0.57294(25)	0.75229(31)	0.23176(17)
0.3 <sup>+</sup>	Rhombohedral	0.54800(5)		1.3487(2)	0.35077(7)
0.4	Cubic	0.38821(1)			0.058506(2)
0.5	Cubic	0.38835(1)			0.058570(2)
0.6	Cubic	0.38850(1)			0.058636(2)

\*The lattice constants are of the orthorhombic cell.

<sup>+</sup>The lattice constants of hexagonal cell converted from rhombohedral cell are shown.

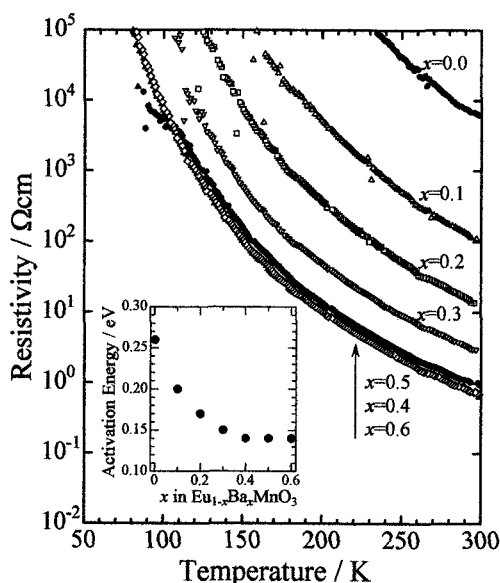


Figure 3 Temperature dependence of electric resistivity. The inset shows the activation energy evaluated by the Arrhenius plot.

Figure 4 shows the temperature dependence of magnetic susceptibility. The temperature dependences obey Curie-Weiss law in the higher temperature range. Magnetic parameters were evaluated from Curie-Weiss fitting and are summarized in Table 2. The negative Weiss temperature  $\theta$  for the sample with  $x = 0.0$

Table 2 Magnetic parameters.

$x$	$C / \text{emu mol}^{-1}\text{K}^{-1}$	$\theta / \text{K}$	$p / \mu_B$
0.0	4.58	-79.2	6.05
0.1	3.33	45.7	5.16
0.2	7.61	57.1	7.80
0.3	12.8	55.0	10.1
0.4	10.0	39.1	8.94

indicates that the magnetic correlation between magnetic moments is antiferromagnetic and the positive values of  $\theta$  for the samples with  $x$  except 0.0 indicate that the correlation is ferromagnetic. The effective numbers of Bohr magneton  $p$ , which are derived from Curie constants  $C$ , are very large for all samples, considering that  $\text{Eu}^{3+}$  ion has no magnetic moment theoretically. These large numbers of  $p$  may be due to the small energy between magnetic ground state and magnetic excited state in the samples.

The magnetic susceptibility of the sample with  $x = 0.0$  jumps at 47 K. The jump suggests that magnetic, structural, or both transitions occur. There are differences between the magnetic susceptibility on field cooling mode and on zero field cooling mode for the samples with  $x = 0.2, 0.3$ , and  $0.4$  in the low temperature range. The features indicate that magnetic clusters are formed at lower temperature in the samples. The positive values of  $\theta$  also suggest that the ferromagnetic clusters exist. It has been reported that  $A$ -site ions disordered  $\text{EuBaMn}_2\text{O}_{6-\gamma}$ , as prepared in air atmosphere shows spin glass state below 40 K and the  $A$ -site ions ordered  $\text{EuBaMn}_2\text{O}_{6-\gamma}$  after the two-step annealing shows ferromagnetism with ferromagnetic transition

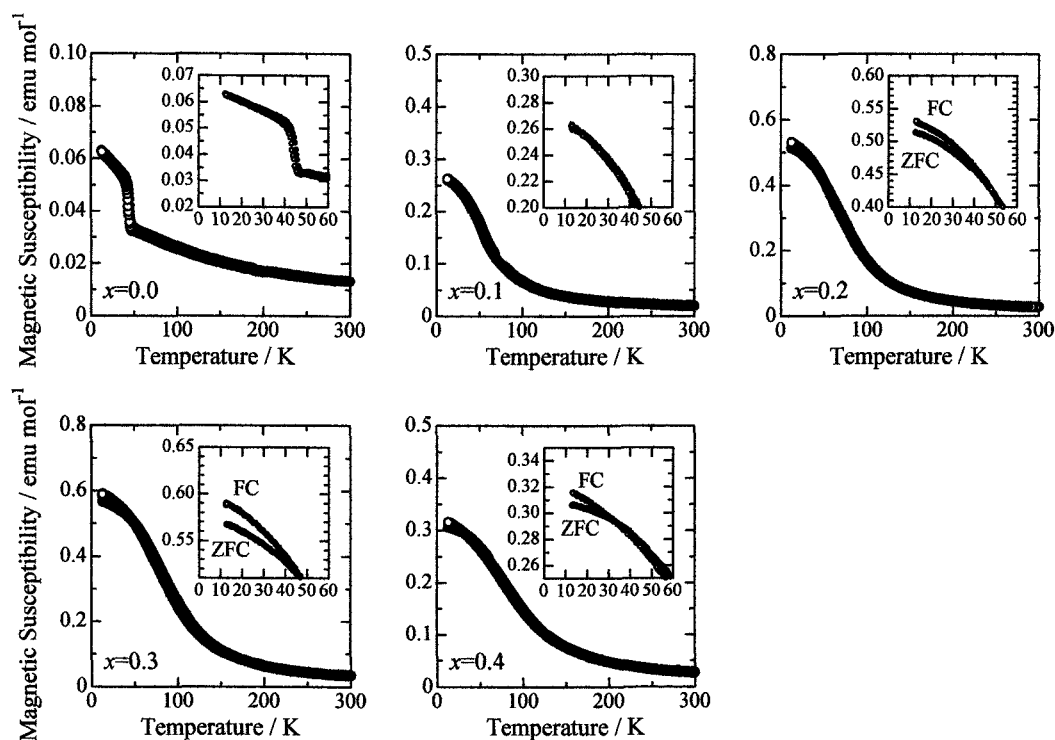


Figure 4 Temperature dependence of magnetic susceptibility measured under 15 kOe. The abbreviations 'FC' and 'ZFC' in the insets indicate the results measured on field cooling and zero field cooling mode, respectively.

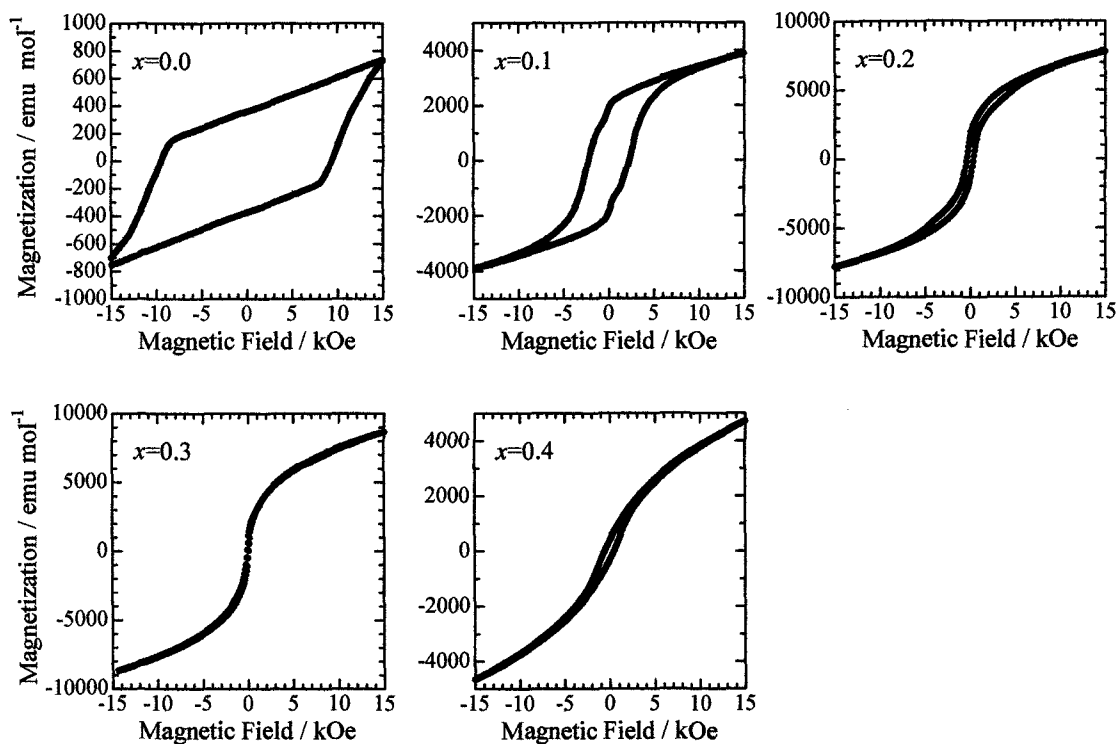


Figure 5 Hysteresis loop measured at 20 K.

temperature  $T_c$  of 260 K [6]. Reduction of lattice strain will be a key for making our sample have higher  $T_c$ .

Figure 5 shows hysteresis loops measured at 20 K. The magnetizations of all samples are not saturated under high magnetic field of 15 kOe. Large loop of the sample with  $x = 0.0$  is conspicuous so that the sample has phases showing ferromagnetism with high coercive force and paramagnetism. Therefore, the jump of magnetic susceptibility at 47 K of the sample is suggested to be related to the ferromagnetic transition of the fraction of the sample. The samples with  $x = 0.1$  also shows hysteresis loop and its coercive force is smaller than the sample with  $x = 0.0$ . The hysteresis loops of the samples with  $x = 0.2 \sim 0.4$  and the differences in the magnetic susceptibility on field cooling mode and on zero field cooling mode support the formation of ferromagnetic clusters in the samples.

#### 4. SUMMARY

Products, electric properties, and magnetic properties have been found for  $\text{Eu}_{1-x}\text{Ba}_x\text{MnO}_3$  in the present study. The substitutive range of Ba, at which only perovskite phase is formed, is from  $x = 0.0$  to 0.4. Crystal system of the perovskite phase successively changes with increasing  $x$ , i.e., orthorhombic system for  $x = 0.0$  and 0.1, coexistence of orthorhombic and monoclinic systems for  $x = 0.2$ , rhombohedral system for  $x = 0.3$  and cubic system for  $x = 0.4$ .

The substitution of Eu by Ba reduces the resistivity of the sample, but all samples show semiconductive properties. Holes doped by the substitution do not

contribute to the electric conduction effectively in the samples.

The substitution also makes the magnetic correlation between magnetic moments to be ferromagnetic and the ferromagnetism has short range order rather than long range order.

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