Preparation and Magnetic and Electrical Properties of EuBaMn$_2$O$_6$ (γ = 0, 1)
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Abstract—The EuBaMn$_2$O$_6$ composition prepared in air at $T = 1500^\circ$C is shown to be a cubic perovskite exhibiting spin-glass properties below $T_f = 40$ K. The reduced composition, EuBaMn$_2$O$_5$, crystallizes in a perovskite-like, YBaCuFeO$_2$-type layered structure with a tetragonal unit cell. EuBaMn$_2$O$_5$ with crystallographically ordered Eu$^{3+}$ and Ba$^{2+}$ ions is a ferromagnet with $T_N = 160$ K. The anomalous behavior of the paramagnetic susceptibility is assumed to be due to a partial ordering of the Mn$^{2+}$ and Mn$^{3+}$ ions. EuBaMn$_2$O$_5$ oxidized in air at 900$^\circ$C to EuBaMn$_2$O$_6$ has a magnetic ordering temperature $T_M = 260$ K near which the magnetoresistance reaches a peak value. X-ray diffraction measurements show the long-range order in the Eu$^{3+}$ and Ba$^{2+}$ ion arrangement to persist in the oxidized EuBaMn$_2$O$_6$ sample. © 2003 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The discovery of the colossal magnetoresistance phenomenon in the Ln$_{1-x}$D$_x$MnO$_2$-type manganites (Ln stands for the lanthanide, and D, for an alkaline-earth metal) [1–3] initiated intense study of their physicochemical properties aimed at establishing the nature of the relation connecting the magnetic and electrical characteristics of these systems. It is well known that the magnetic and electrical states of the manganites are determined to a great extent by the relative concentrations of the tri- and quadrivalent manganese. This relation is usually varied by properly doping the compound by an alkaline-earth metal. There is, however, another way in which the oxygen content can be varied in the sample. It was found, for instance, that oxidation of the magnetic-ordering temperature $T_c = 250$ K [10], whereas Tb$_{0.7}$Ca$_{0.3}$MnO$_3$ is a spin glass with $T_f = 40$ K [11]. This stimulated our study of the properties of the Eu$_{0.50}$Ba$_{0.50}$MnO$_3$-γ system as functions of the oxygen content. The europium ion was chosen because the Eu$^{3+}$ ions reside, as a rule, in the ground diamagnetic state and do not contribute noticeably to the sample magnetization.

2. EXPERIMENT

Polycrystalline Eu$_{0.50}$Ba$_{0.50}$MnO$_3$ was prepared using the usual ceramic technology. The OSCh-grade Eu$_2$O$_3$ and Mn$_2$O$_3$ oxides and the BaCO$_3$ carbonate were weighed in the required molar ratio and mixed thoroughly in an agate mortar with addition of a small amount of ethyl alcohol. The mixture thus prepared was pressed into a pellet and calcined in air at 1150$^\circ$C for 4 h with subsequent grinding. The final synthesis was carried out in air at 1560$^\circ$C for 2 h. The sample was spread on a platinum substrate. To obtain a composition with a close-to-stoichiometric oxygen content, the samples were maintained at 900$^\circ$C in air for 100 h and...
cooled afterwards to room temperature at a rate of 100°C/h.

X-ray diffraction measurements on the product of the chemical reaction were performed on a DRON-3 diffractometer in Cr-Kα radiation at room temperature within the angular interval 30° ≤ 2θ ≤ 100°. The oxygen content was deduced from thermal gravimetry data (TGA). Our studies suggest that the sample synthesized in air was stoichiometric in oxygen. According to [12], the oxygen content in manganites prepared in air and substituted strongly (x ~ 0.50) by calcium and strontium ions is close to its stoichiometric value.

A reduced EuBaMn
2 O
5 sample was prepared using a topotactic reaction. The sample was placed in an evacuated quartz ampule containing a predetermined amount of metallic tantalum employed as an oxygen absorber. The quartz ampule was maintained at 900°C for 10 h, followed by cooling to room temperature at a rate of 100°C/h.

The oxygen content in the reduced sample was derived from the change in sample mass by weighing the sample before and after the reduction. The sample chosen for reduction had a mass of ~3 g. In this case, the error in the oxygen concentration measurements did not exceed 0.03%.

The reduced sample was reoxidized in air at 900°C for 5 h. The weighing made after the reoxidation showed that the oxygen content increased and corresponded to the chemical formula EuBaMn
2 O
6.

The magnetization was studied on a commercial OI-3001 vibrating-sample magnetometer in the temperature range 4–300 K. The magnetic transition temperature was determined in a weak magnetic field of 100 Oe. Electrical-resistivity measurements were performed on samples 8 × 2 × 2 mm in size, following the standard four-probe technique at temperatures of 77–350 K. The magnetoresistance was calculated from the expression

\[ MR(\%) = \left( \frac{(p(H) - p(0))}{p(H)} \right) \times 100\%, \]

where \( p(H) \) is the electrical resistivity in a magnetic field of 9 kOe and \( p(0) \) is that in a zero magnetic field. The magnetic field was applied parallel to the electrical current flowing through the sample.

3. RESULTS AND DISCUSSION

X-ray diffraction measurements show the Eu
0.50 Ba
0.50 MnO
3 perovskite prepared in air to have cubic structure with the unit-cell parameter \( a = 3.881 \text{ Å} \) (\( V = 58.47 \text{ Å}^3 \)) (Fig. 1a). The EuBaMn
2 O
5 sample reduced in the quartz ampule produces the same reflections as YBaCuFeO
5; therefore, these two compounds are isostructural. The reduced compound EuBaMn
2 O
5 has a tetragonal unit cell with the parameters \( a = 3.945 \text{ Å} \) and \( c = 7.712 \text{ Å} \) (\( V = 120.03 \text{ Å}^3 \); Fig. 1b). The doubling of the unit-cell parameter along one direction is due to the Y and Ba ions ordering in alternate planes. A similar structure was observed in HoBaCo
2 O
5 cobaltites in [13]. TGA data suggest that the oxidation of the EuBaMn
2 O
5 sample in air starts at 250°C and comes to an end at approximately 500°C. The change in mass corresponds to an increased oxygen content and the chemical formula EuBaMn
2 O
6. The samples annealed at 1300°C and prepared from reagents at 1560°C have identical diffractograms. In this case, both samples are cubic perovskites. However, if the annealing was performed at temperatures below 1200°C, strong deviations from cubic symmetry are observed. For instance, the unit cell of the EuBaMn
2 O
6 sample annealed at 900°C for 5 h exhibits pronounced orthorhombic distortions (Fig. 1c). The unit-cell parameters are \( a = 3.917 \text{ Å}, b = 3.835 \text{ Å}, \) and \( c = 7.764 \text{ Å} \) (\( V = 116.63 \text{ Å}^3 \)).