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In-situ observation of phase transformations in layered perovskite $BaEu_2Mn_2O_7$

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Abstract

The layered perovskite $BaLn_2Mn_2O_7$ (Ln = rare earth) has a $Sr_3Ti_2O_7$-type structure with double-block oxygen octahedra belonging to the Ruddlesden–Popper-type homologous series $AO(ABO_3)_2$. The $BaEu_2Mn_2O_7$ shows multiple phase transformations upon heating by high-temperature TEM, from tetragonal phase I ($P4_2/mnm$) to monoclinic phase III via phase II ($I4/mmm$). Weak reflections from phase III started to appear on the selected area diffraction pattern along the c-direction above 277 °C and became stronger gradually with increasing temperature. Finally, all of the reflections were from only phase III above 750 °C. This shows a first-order phase transformation, and the coexistence of low- and high-temperature phases was also observed clearly in a quenched specimen. The differences in those structures are the periodicity along the *c*-axis and the high-temperature phase's 1.5% longer *c* length than that of the low-temperature phase.

Keywords: Electron microscopy; Microstructure; Perovskites; Phase transformation; Manganite

1. Introduction

The rare-earth manganite $BaLn_2Mn_2O_7$ (Ln = rare-earth element) has a $Sr_3Ti_2O_7$-type layered perovskite structure with double-block oxygen octahedra belonging to the Ruddlesden–Popper-type homologous series $AO(ABO_3)_2$.[1] Deshizeaux Cheruy and Joubert were the first to synthesize those manganites (Ln = Nd–Gd) in an N_2 atmosphere.[2] Subsequently, many phases were reported for the oxides, depending on the synthesis or annealing conditions.[3–9] Those annealing conditions were based on the phase transformation of the $BaLn_2Mn_2O_7$. The phase transformations of the oxides have been investigated by high-temperature X-ray diffraction (XRD), electrical conductivity, and thermal analyses.[3,10,11] The transformation temperatures tend to increase with decreasing ionic radii of the Ln cations.[10] These results showed that the transformation occurring is the successive phase transition series common in perovskite-related families, whose symmetries are expected to change from lower to higher with increasing temperature. As a result, it was reported that the tetragonal $I4/mmm$ structure of $BaLn_2Mn_2O_7$ is stable at high temperatures.[12]

Recently, however, we have found first-order phase transformations in the $BaGd_2Mn_2O_7$ and $BaPr_2Mn_2O_7$ by using a high-temperature transmission electron microscope (TEM).[13,14] These findings are contradictory to the conventional understanding of the successive phase transformation. We believe that the first-order phase transformation may uniquely occur in layered perovskite with double-block oxygen octahedra. In the case of $BaPr_2Mn_2O_7$, it occurred for only 10 min without change in the crystal symmetry.[14] On the other hand, the first-order phase transformation in $BaGd_2Mn_2O_7$ was observed slowly with increasing temperature. It was found that the time of phase transformation was related to the ionic radius of rare earth and its structural distortion. It is expected that similar phase transformations should occur in other rare-earth manganites. In order to observe such *in-situ* structural change, high-temperature TEM is the most suitable technique, even though it requires a high-level technique for observation.

In the present study, we report phase transformation of $BaEu_2Mn_2O_7$ observed mainly by a high-temperature TEM. Furthermore, the high-temperature phase appearing in the phase

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transformation was analyzed using a quenched specimen, which was heated to 700 °C and then cooled down.

2. Experimental procedure

The starting powders of $BaCO_3$, Eu_2O_3, and Mn_2O_3 were mixed together and calcined at 1350 °C in Ar atmosphere for 2 days. The product was confirmed as a single phase of $BaEu_2Mn_2O_7$ by the powder XRD analysis. The product was then pulverized and hydrostatically pressed into a rod. Single crystals were grown by the floating zone (FZ) method in Ar atmosphere. The procedure of crystal growth is detailed in the previous paper.[5] The crystals were examined by the four-circle single-crystal diffractometer Rigaku-AFC7R. The quenched specimen was annealed at 700 °C and then cooled down.

A fragment of the crystal was crushed and scooped onto a copper mesh with carbon-coated microgrids. The *in-situ* TEM observation was performed on a thermal stage in the temperature range from 20 to 800 °C (JEM-2000EX, EM-SHU2 specimen holder, JEOL). The temperature was controlled manually. The heating rate was approximately 600 °C/h. High

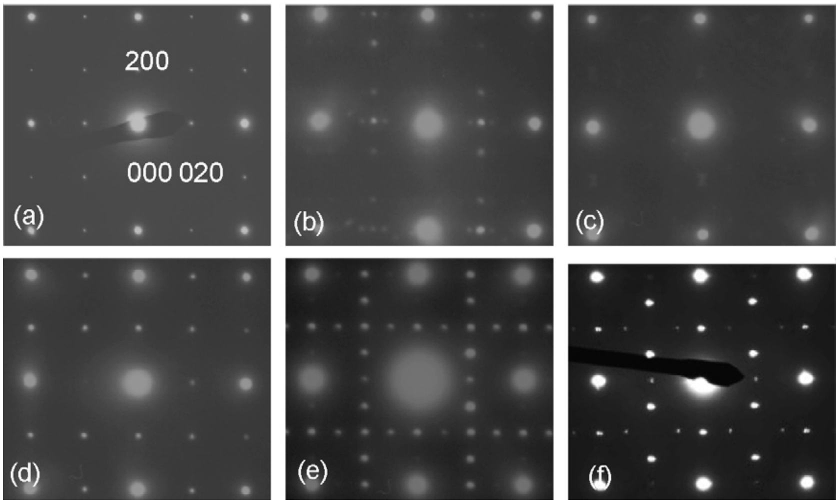

Fig. 1. SAED patterns of $BaEu_2Mn_2O_7$ along the [0 0 1] zone axis taken at various temperatures: (a) RT for phase I, (b) 100 °C, (c) 160 °C for phase II, (d) 227 °C, (e) 277 °C, and (f) 500 °C for phase III.

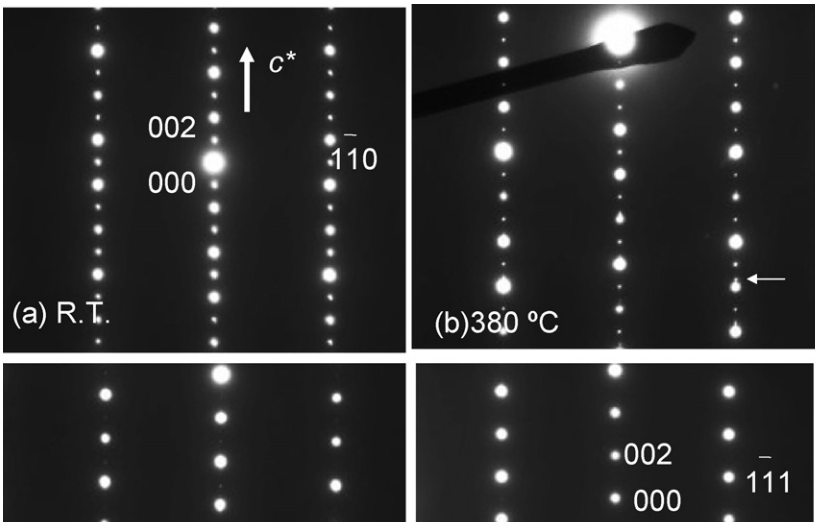

Fig. 2. Changes in SAED patterns taken from [1 1 0] zone axis. (a) RT, (b) at 380 °C, (c) at 714 °C, and (d) at 750 °C.

resolution image observation was using a TEM (JEM 3000F, JEOL).

3. Results and discussion

The as-grown crystal of BaEu$_2$Mn$_2$O$_7$ showed the tetragonal $P4_2/mnm$ symmetry by four-circle single-crystal diffractometer.[5] Fig. 1 uses high-temperature TEM to show the SAED patterns along the [0 0 1] zone axis at various temperatures. At around 100 °C, the tetragonal phase I ($P4_2/mnm$) started to transform into an intermediate phase with a rather complex diffraction pattern as shown in Fig. 1(b). Then, the intermediate phase transformed into the tetragonal phase II at approximately 160 °C in (c). The space group of phase II was assumed to be $I4/mmm$. However, the transformation temperature was lower than that of phase transition (277 °C) measured by DSC.[11] With increasing temperature, we found the phase transformation in the next step. The $I4/mmm$ phase was stable in a narrow temperature region. Pattern (c) changed into pattern (d), which was assumed to be $P4_2/mnm$. Then, a new phase III started to nucleate in the low-temperature phase matrix at 277 °C, and the temperature agreed with the DSC and electrical conductivity results.[10,11] The complex pattern (e) can be interpreted as a mixture of the low-temperature phase (d) and the high-temperature phase (f). At around 500 °C, the intensity of 1 1 0 reflection became very weak, which indicated that the low-temperature phase nearly disappeared in (f).

Structural change was *in-situ* observed clearly along the [1 1 0] zone axis, as shown in Fig. 2. Above 277 °C, weak reflections started to appear, as indicated by the arrow in (b), and the intensities grew stronger at 714 °C. The split reflections indicate that the c length of phase III is 1.5% longer than that of the low-temperature phase, as with BaGd$_2$Mn$_2$O$_7$.[13] With increasing temperature, the intensities of the reflections at $1\,\bar{1}\,0$ became weaker. Finally, the low-temperature phase disappeared above 750 °C. The repeated *in-situ* experiments revealed that the transformation speed is temperature-dependent. The results show that the transformation from the low-temperature phase into phase III was of first order due to the coexistence of low- and high-temperature phases.

A structure of coexisting phases was also observed using a quenched specimen, which was heated to 700 °C and quenched, as shown in Fig. 3. The lamellar structure was observed along the c-axis, which was composed of the low-temperature phase and the high-temperature phase with a lattice mismatch of 1.5%. The SAED pattern corresponded to Fig. 3. In the enlarged TEM image enclosed by the rectangle in (a), we can clearly observe the low-temperature phase region and the high-temperature phase region due to the difference in periodicity along the c-axis. These results show that phase III was nucleated in the low-temperature phase matrix.

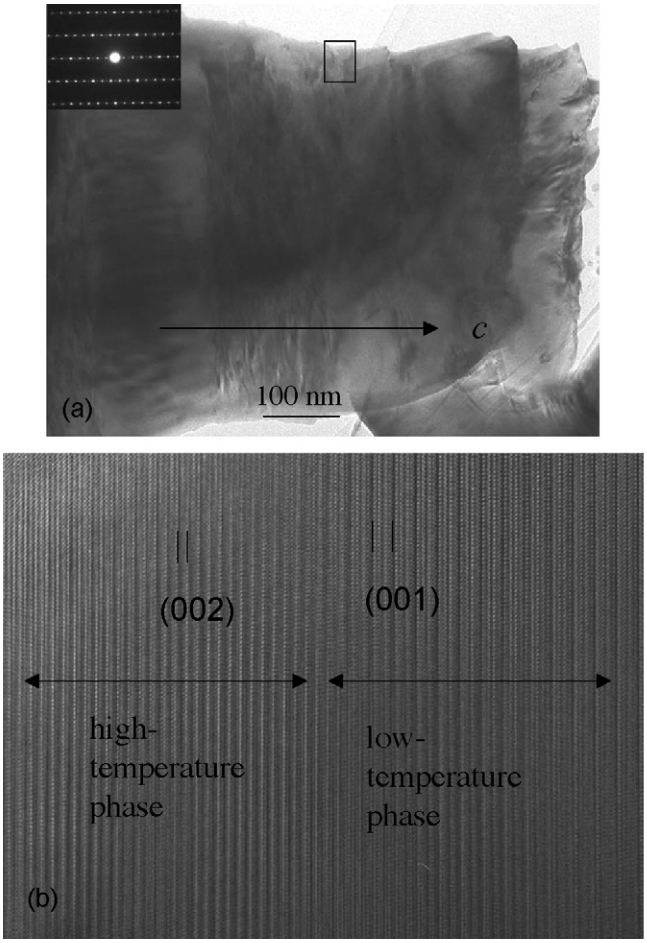

Fig. 3. TEM images of quenched specimen of BaEu$_2$Mn$_2$O$_7$ taken from the [1 1 0] zone axis. (a) Low-magnification image and (b) enlarged image from area enclosed by the rectangle in (a).

Fig. 4 shows a TEM image and SAED pattern of the quenched specimen along the [0 2 1] zone axis. The lamellar structure formed by twinning at about 40-nm sizes was observed in (a). This structure of the phase is not a tetragonal because the angle formed by the planes of (2 0 0) and $(0\,\bar{2}\,4)$ is not 90°. Extra reflections were detected as $1/2,\ 1/2,\ \bar{1}$. This result agrees with the SAED pattern shown in Fig. 1(f). Phase III seems to have a close relation with the monoclinic $B112/m$ structure, which was observed in annealed BaTb$_2$Mn$_2$O$_7$.[9] The complex diffraction pattern was caused by the twinning structure of the monoclinic cell.

The I–II transformation may accompany tilts of the MnO$_6$ octahedra because the symmetries suggest a change in the octahedral tilt system from (0 0 0)(0 0 0) for $I4/mmm$ to $(\Phi\,0\,0)(0\,\Phi\,0)$ for $P4_2/mnm$.[15] A previous paper, by using high-temperature XRD, reported that the tetragonal $I4/mmm$ structure is stable at high temperatures.[12] In our experiment, we confirmed that the $I4/mmm$ phase is stable in a narrow temperature range during the phase transformation. In the case of BaGd$_2$Mn$_2$O$_7$, however, the $I4/mmm$ phase did not appear during the phase transformation. This seems to be related to the structural distortion and ionic radius of rare earth. On the other hand, later transformation of phase III suggested that the transformation is of the first order. We believe that the first-order phase transformation may uniquely occur in layered perovskite with double-block oxygen octahedra.[10,14] The multiple transformations are related to the distortion of the structure. In the repeated trial, the transformation occurred slowly via the $I4/mmm$ phase as a meta-stable phase. It is expected that Tb–manganite will require a longer

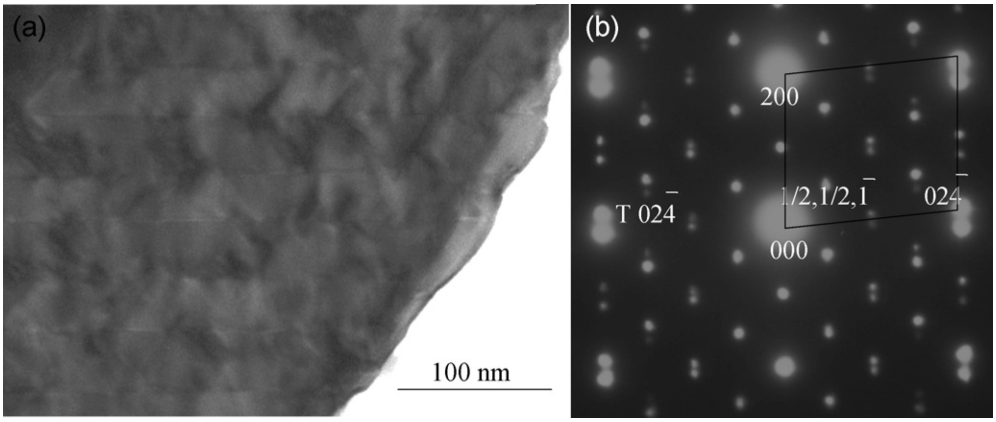

Fig. 4. Lamellar structure by twinning in quenched specimen of $BaEu_2Mn_2O_7$. (a) TEM image, and (b) SAED pattern taken from the [0 2 1] zone axis.

time for phase transformation because, like Gd–manganite, it has a small ionic radius. On the other hand, it is also assumed that the transformation for Nd–manganite, via the *I*4/*mmm* phase as a stable phase, will take a shorter time because, like Pr–manganite, it has a large ionic radius. Although we can make these assumptions based on the known experimental data for Pr–manganite and Gd–manganite, an *in-situ* experiment using high-temperature TEM should be conducted to more systematically clarify such issues as phase transformation. In the future, we are going to use high-temperature TEM to more systematically clarify such issues as *in-situ* phase transformation in order to understand the nature of layered perovskite structure.

4. Conclusion

Phase transformation in $BaEu_2Mn_2O_7$ has been studied by *in-situ* high-temperature TEM observation. The tetragonal phase I (*P*4$_2$/*mnm*) transformed into the tetragonal phase II (*I*4/*mmmm*) at a temperature roughly above 160 °C. The *I*4/*mmm* phase is stable at narrow temperature region. Then, phase III nucleated in the matrix at 277 °C and grew to cover the entire region under inspection at 500 °C. Phase III has an approximately 1.5% larger cell size along the *c*-axis compared with phase II. Phase III seems to have a close relation with the monoclinic structure. The transformation into phase III was considered a first-order transformation due to the coexistence of low-temperature and high-temperature phases. A structure of coexisting phases was observed in a quenched specimen, which was heated to 700 °C and then cooled down. The first-order phase transformation should occur uniquely in the layered structure with double-block oxygen octahedra.

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