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# New phase of $BaLaMnO_{4-x}$ formed by annealing in a reducing atmosphere

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**A single crystal of $BaLaMnO_4$ with $I4/mmm$ has been synthesized by a floating zone method. A new phase of $BaLaMnO_{4-x}$ was obtained by annealing the single crystal in a reducing atmosphere at 773 K for 168 h. The structural change was analyzed by four-circle X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The new phase has an orthorhombic unit cell ($Cccm$) of $a=0.5504(7)$ nm, $b=0.5502(5)$ nm, and $c=1.3265(1)$ nm. The structural change from $I4/mmm$ into $Cccm$ was caused by an oxygen deficiency, and a small amount of $Mn^{2+}$ ions was formed by annealing in a reducing atmosphere.**



Key-words: Rare earth manganite, Structure, Transmission electron microscopy, X-ray diffractometry, Nonstoichiometory

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## 1. Introduction

Compounds of $Ba_{1+x}Ln_{1-x}MnO_4$ (Ln = La and Nd) with the $K_2NiF_4$-type structure were first synthesized by Benabad *et al.*.[1] The cell size of the *c*-axis elongates due to the Jahn-Teller effect of the $Mn^{3+}$ ion. Therefore, the cell size of the *c*-axis is the longest when the *x* value is 0. The oxygen non-stichiometry of $BaNdMnO_{4+x}$ was investigated and, consequently, limited to $x=0.17$.[2] A poly-crystalline structure of $BaPrMnO_4$ was first synthesized by Ueno *et al.*.[3] These oxides possess a tetragonal structure with a space group of $I4/mmm$. Single crystals of $BaLnMnO_4$ (Ln = rare earth) were synthesized for the first time in an Ar atmosphere by a floating zone (FZ) method by Kamegashira *et al.*[4] The phases also have a tetragonal structure ($K_2NiF_4$-type) with $I4/mmm$.

Recently, a new phase of $BaNdMnO_4$ with an orthorhombic structure ($Fmmm$) was synthesized by annealing the single crystal in a reducing atmosphere (3%$H_2$–Ar flow) at 523 K.[5] The structural change is related to an oxygen deficiency. In this study, a new phase of $BaLaMnO_4$ was successfully synthesized by annealing in a 1%$H_2$–Ar flow at 723 K. Structural change from a tetragonal to an orthorhombic form was analyzed by using four-circle X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The TEM data revealed that this crystal symmetry was lower than that of $BaNdMnO_4$.

## 2. Experimental procedure

Starting materials of high-purity (99.9%) $BaCO_3$, $La_2O_3$, and $Mn_2O_3$ underwent heat treatment for purification before weighing.[5] These materials were mixed in an agate mortar and pressed. The pellet was heated at 1073 K in Ar for 24 h and subsequently at 1723 K in Ar for 72 h. The obtained product was confirmed by XRD to be a single phase of poly-crystalline $BaLaMnO_4$. The product was placed in a floating zone (FZ) furnace equipped with a bi-ellipsoidal halogen lamp. The detailed procedure is described elsewhere.[4] The single crystal was annealed in a 1% $H_2$–Ar flow at 773 K for 168 h and then quenched.

The chemical ratio of Ba, La and Mn was measured by inductively coupled plasma (ICP). The oxygen deficiency was measured by titration analysis and calculated from the ICP result.

The structure of the crystal was analyzed by four-circle XRD (Rigaku-AFC7R, Tokyo) using the software Shelx 97. The crushed specimen was scooped with carbon-coated copper microgrids for TEM observation. The TEM observation was performed using a high-resolution TEM at 300 kV (JEOL-3000F, Tokyo). Electron energy-loss spectroscopy (EELS) was performed by using a TEM device (JEOL 2000F equipped with GIF).

## 3. Results and discussion

The structure of the annealed crystal $BaLaMnO_4$ was analyzed by TEM. **Figure 1** shows selected area electron diffraction (SAED) patterns taken from the [001] zone axis for as-grown crystal in (a) and annealed crystal in (b). We found a difference in those SAED patterns, as shown by the extra reflections detected in the annealed crystal in (b). The cell parameter of $a \approx b = 0.550$ nm for annealed crystal is larger by 1.41 times than that of as-grown crystal. Typical

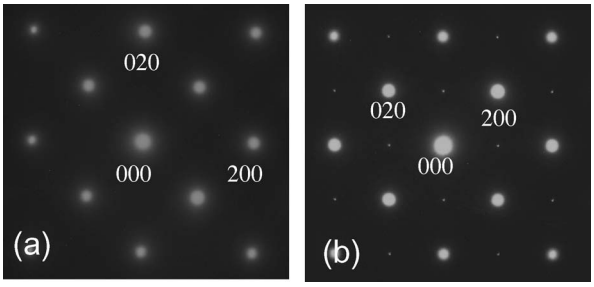


Fig. 1. SAED patterns of $BaLaMnO_4$ (a) as-grown crystal and (b) annealed crystal.

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SAED patterns of the annealed crystal are shown in **Fig. 2** (a)–(c), which were taken from the [101], [121] and [301] zone axes, respectively. The reflections with strong intensities satisfy a condition for *Fmmm* symmetry as reported for $BaNdMnO_4$.[5] However, the SAED pattern in Fig. 1 (b) indicates the presence of 110 reflections with weak intensities, and this does not conform to the *Fmmm* symmetry that excludes the *hk*0 reflections with *h*, *k* odd. The 100, 010 $10\bar{1}$, $01\bar{2}$ reflections were not observed in Fig. 1(b) and 2. These results disagree with the $P4_2/ncm$ symmetry reported for $La_{0.875}Ba_{0.125}CuO_4$,[6] *Cmca* symmetry for $La_{1.91}Sr_{0.09}CuO_{4.12}$,[7] *Pccm* symmetry for $SrGdMnO_4$[8] and $La_{0.9}Ba_{0.1}CuO_4$,[9] and *Pccn* symmetry for $La_2CuO_{3.98}$.[10] These extinction rules uniquely lead to *Cccm* as a possible space group for annealed crystal of $BaLaMnO_4$. The orthorhombicity of the crystal was measured by four-circle XRD. The refinement was carried out using crystal structures with some possible space groups. The XRD result shows that the crystal structure with *Fmmm* symmetry had a lowest value (4.98%) of the reliability factor based on the integrated intensity $R_I$. The reason for this is that the weak reflections caused by *Cccm* symmetry could not be detected by XRD measurement. The refined atomic parameters based on *Ccmm* symmetry are shown in **Table 1**. Ba and La ions randomly occupied the 8*k* site in the orthorhombic structure with *Cccm* symmetry. The reliability factor $R_I$ is 7.06%, and the goodness of fit *S* is 1.371 but anisotropic displacement parameters were not reasonable values. The crystal symmetry is related to the octahedral distortion of layered perovskite $K_2MgF_4$, found by Alksandrov.[11] The relationship between $I4/mmm$ and *Cccm* was described by the distortion of (Mn, Ti)$O_6$ octahedra as 000 and $\phi\phi$0, respectively. The rotations of $\phi$ type are characterized by alternating signs of the rotations around the rotation axis.[11]

**Figure 3** shows high-resolution TEM (HRTEM) images taken from the [110] and [001] axes. The periodic distance of 0.67 nm is the (002) spacing along the *c*-axis. In Fig. 3 (b), weak periodicity of about 0.4 nm was observed, which is (110) spacing. This periodicity clearly shows that the phase has a new structure.

This structural change from tetragonal ($I4/mmm$) to orthorhombic (*Cccm*) form might have been caused by the oxygen deficiency during annealing for a long time in a reducing atmosphere. The nonstichiometry of the as-grown crystal and the annealed crystal were measured by chemical analysis. The chemical compositions are $Ba_{0.966}La_{1.005}Mn_{1.000}O_{3.9774}$ and $Ba_{0.966}La_{1.005}Mn_{1.000}O_{3.898}$ for as-grown crystal and annealed crystal, respectively. The oxygen deficiency is relat-

Table 1. Atomic Parameters of Annealed Crystal $BaLaMnO_4$

| atom | site | *x* | *y* | *z* |
|---|---|---|---|---|
| Ba/La | 8*k* | 0.25 | 0.25 | 0.35725(1) |
| Mn | 4*e* | 0.25 | 0.25 | 0 |
| O1 | 4*c* | 0 | 0 | 0 |
| O2 | 4*d* | 0 | 0.5 | 0 |
| O3 | 8*k* | 0.25 | 0.25 | 0.17046(7) |

*Space group*: *Cccm* $R_I$ 7.06 % *S* 1.371

Lattice parameters : $a = 0.5504(7)$ nm, $b = 0.5502(5)$ nm, $c = 1.3265(1)$ nm

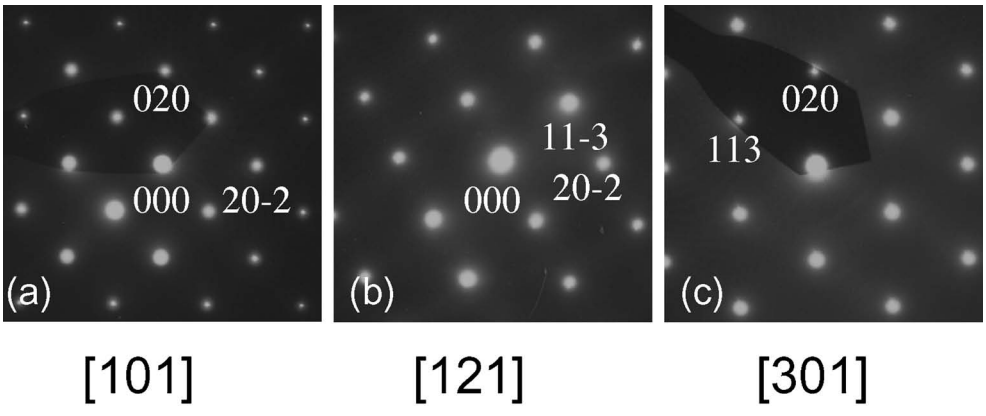


Fig. 2. SAED patterns of annealed crystal of $BaLaMnO_4$ taken from (a) [101], (b) [121], and (c) [301].

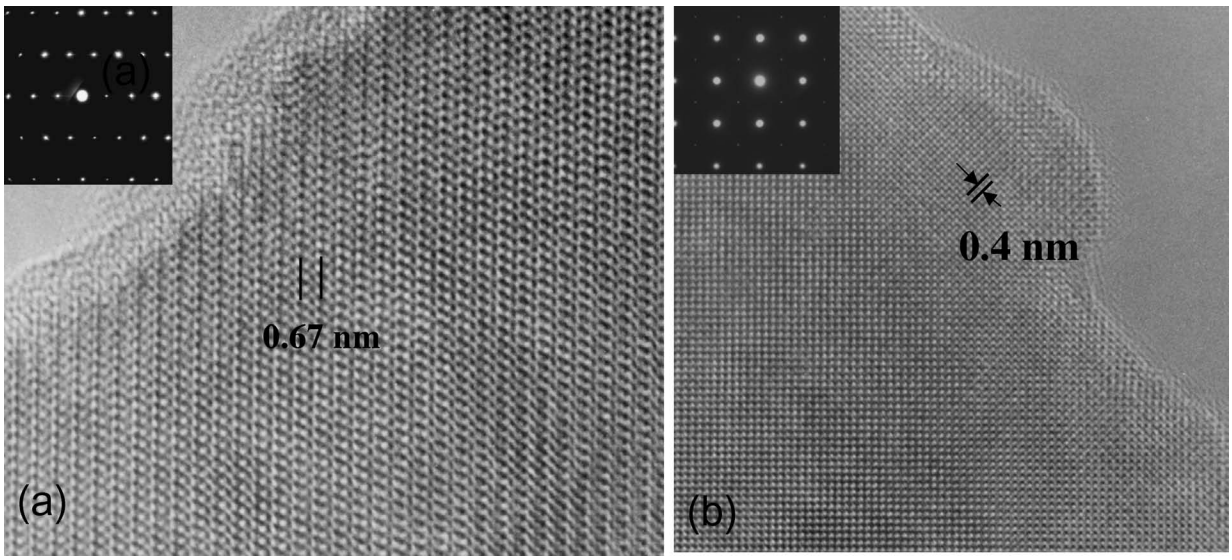


Fig. 3. High-resolution TEM images of annealed crystal $BaLaMnO_4$ taken from [110] zone axis in (a) and [001] in (b).

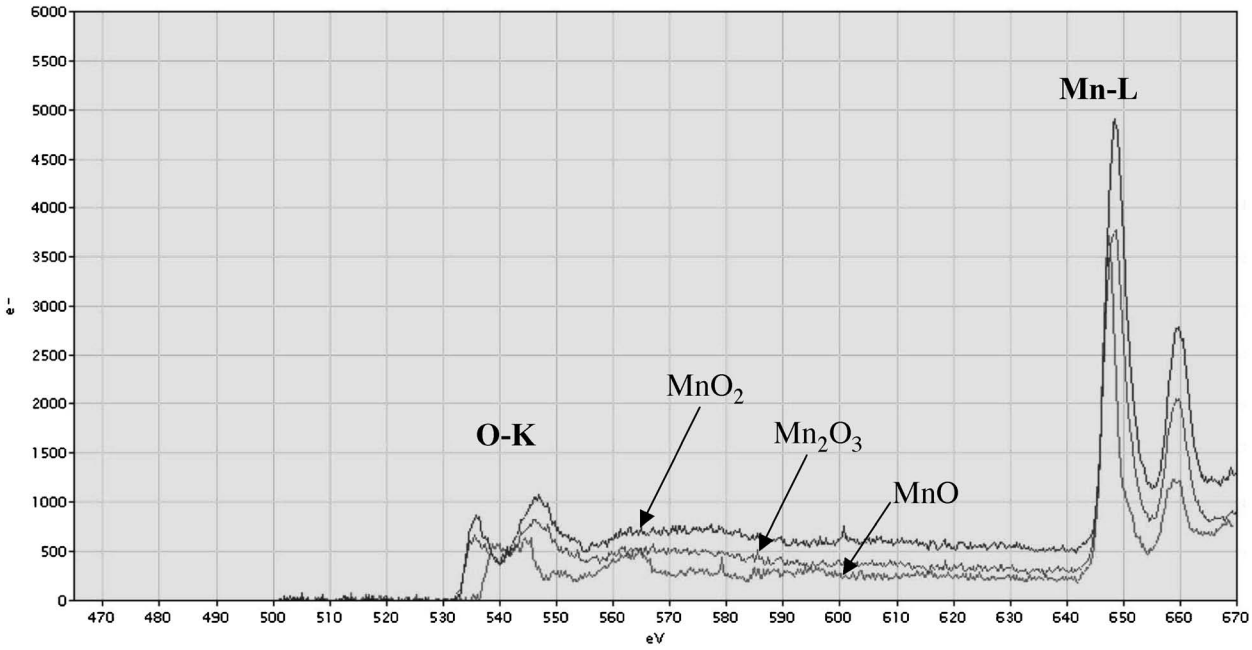


Fig. 4. EELS peaks of standard materials MnO, $Mn_2O_3$ and $MnO_2$.

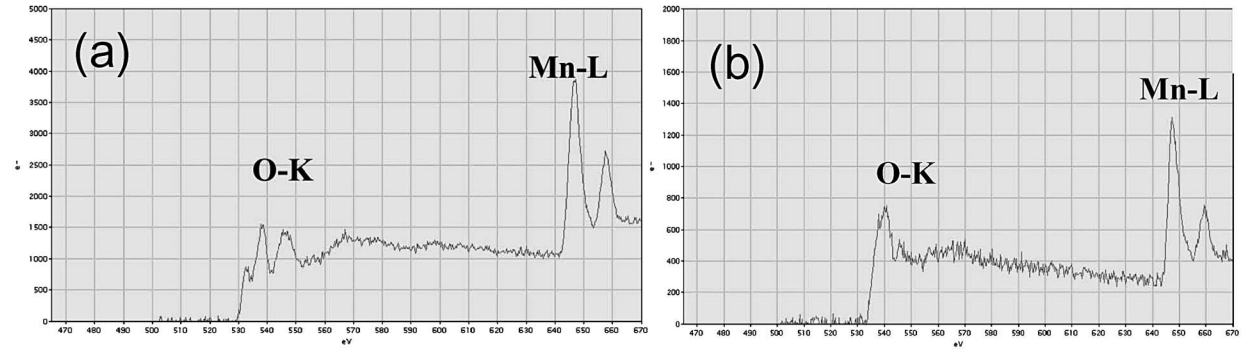


Fig. 5. EELS peaks of $BaLaMnO_4$ (a) As-grown crystal and (b) annealed crystal.

ed to the valence of the Mn ion. When the Mn oxidation state changes from trivalent to divalent, an oxygen defect would occur during the annealing. It was calculated that 15% of $Mn^{3+}$ ions changed into $Mn^{2+}$ ions by annealing. **Figure 4** shows EELS peaks of standard materials MnO, $Mn_2O_3$, and $MnO_2$. The two peaks of the O–K line at 535 eV and 545 eV were detected for $Mn_2O_3$ and $MnO_2$, respectively, and no difference in the oxidation state between $Mn^{3+}$ and $Mn^{4+}$ could be observed. On the other hand, one broad peak of O–K was detected at around 540 eV for MnO, and the oxidation state of $Mn^{2+}$ was confirmed. **Figure 5** shows EELS peaks of as-grown crystal and annealed crystal of $BaLaMnO_4$. The O–K line peak was affected by Ba–O and La–O bonding in $BaLaMnO_4$. However, the difference between (a) and (b) for EELS peak of O–K line was caused by the oxidation state of Mn ion. We found the existence of $Mn^{2+}$ ion in the partially grain of $BaLaMnO_4$. Our findings also indicate that the nonstoichiometry of the annealed crystal was caused by a reduction in Mn ions to some extent.

Finally, the structural change from $I4/mmm$ to *Cccm* was related to the nonstoichiometry of $BaLaMnO_{4-x}$ due to oxygen deficiency. In addition to the octahedral tilting, the Jahn–Teller (J–T) distortion occurred in the case of $Mn^{3+}O_6$. This effect manifested itself in the changes in unit cell size and $c/a$ ratio of $Sr_{1+x}La_{1-x}MnO_4$ ($0<x<1$).[1] This sort of J–T distortion may contribute slightly to the symmetry changes from tetragonal to orthorhombic. Therefore, the appearance of weak reflections on the $a^*$–$b^*$ plane is assumed to be related to the tilting of $MnO_6$ octahedra.[11]

## 4. Conclusion

We successfully synthesized a new phase of $BaLaMnO_{4-x}$ by annealing in a reducing atmosphere. A structural characterization was performed using four-circle X-ray diffractometry (XRD) and transmission electron microscopy (TEM) equipped with electron energy-loss spectroscopy (EELS). The presence of extra reflections with weak intensities was detected on the $a^*$–$b^*$ plane, and the extinction rule led to *Cccm* as a possible space group. The orthorhombicity was measured by XRD analysis, where the cell parameters were $a = 0.5504(7)$ nm, $b = 0.5502(5)$ nm, and $c = 1.3265(1)$ nm. The structural change from $I4/mmm$ to *Cccm* was related to the nonstoichiometry of $BaLaMnO_{4-x}$ due to oxygen deficiency. This nonstoichiometry was caused by a reduction in Mn ions during annealing in the reducing atmosphere. Furthermore, the EELS data revealed the existence of $Mn^{2+}$ ion in the annealed crystal of $BaLaMnO_4$.

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