Synthesis and structural properties of $n = 1$ Ruddlesden–Popper manganites Nd$_{1-x}$Ca$_{1+x}$MnO$_4$

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Abstract

Polycrystalline samples of $n = 1$ Ruddlesden–Popper manganites Nd$_{1-x}$Ca$_{1+x}$MnO$_4$ ($0.55 \leqq x \leqq 1.00$) were synthesized by a solid-state reaction. X-ray diffraction (XRD) and electron diffraction (ED) measurements confirmed that the fundamental crystal structure at room temperature consists of three distorted K$_2$NiF$_4$-types: orthorhombic *Bmab* (64) phase in $0.55 \leqq x < 0.73$, orthorhombic *Acam* (64) phase in $0.73 \leqq x < 0.85$ and tetragonal $I4_1/acd$ (142) phase in $0.85 \leqq x \leqq 1.00$. Furthermore, in a whole range of $0.55 \leqq x \leqq 0.75$, low-temperature magnetic and ED measurements revealed charge-orbital ordering (COO) states, which are accompanied by suppression of magnetization and structural modulations with $\boldsymbol{q} = (1 - x)\boldsymbol{a}^*$. The COO transition temperatures are high with a maximum of ~ 330 K at $x = 0.67$, and then higher than those in non-distorted $n = 1$ Ruddlesden–Popper manganites. The observations suggest that COO states are much stabilized by the distortion in the fundamental structures.
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1. Introduction

A great number of studies have recently been made on various issues in Ruddlesden–Popper manganites (R,A)$_{n+1}$Mn$_n$O$_{3n+1}$ (R = trivalent lanthanides, A = divalent alkaline-earth ions), such as the charge-orbital ordering (COO) and the tunneling magnetoresistance (TMR) [1–5]. In particular, a real-space ordering pattern of charge and orbital of e$_g$ electrons was first directly observed by a resonant X-ray scattering technique for the "$n = 1$" manganite La$_{1-x}$Sr$_{1+x}$MnO$_4$ ($x = 0.5$) [3]. The single-layered K$_2$NiF$_4$-type compound has tetragonal $I4/mmm$ (139) symmetry with non-distorted MnO$_2$ network. In the COO phase, Mn^{3+} stripes and Mn^{4+} stripes are alternately arranged along the diagonal direction in the a–b plane (MnO$_2$ plane) with $3x^2 - r^2/3y^2 - r^2$ orbital ordering of Mn^{3+}. It was also reported that the charge-orbital states are switched by x between $3x^2 - r^2/3y^2 - r^2$ COO state and $3x^2 - r^2$ orbital ordering state in the isostructural Nd$_{1-x}$Sr$_{1+x}$MnO$_4$ ($0.67 \leqq x \leqq 1.0$) [4]. In the

COO phases of the both non-distorted systems, structural modulations based on the MnO$_6$ Jahn–Teller distortions with the modulation vector $\boldsymbol{q} = (1 - x)(\boldsymbol{a}^* \pm \boldsymbol{b}^*)/2$ were clearly observed by electron diffraction (ED) measurements [2,5]. Substitution by isovalent ions in $n = 1$ Ruddlesden–Popper manganites R$_{1-x}$A$_{1+x}$MnO$_4$ is of interest since the different constituent ions can provide different configuration of MnO$_2$ network in which the COO states of e$_g$ electrons are realized. However, there have been only a few reports on the synthesis and the characterization of the A = Ca system R$_{1-x}$Ca$_{1+x}$MnO$_4$ [6,7]. We have synthesized single-layered manganites Nd$_{1-x}$Ca$_{1+x}$MnO$_4$ and investigated them in terms of the structural properties related to the COO states.

2. Experimental

Polycrystalline Nd$_{1-x}$Ca$_{1+x}$MnO$_4$ were synthesized by a solid-state reaction similar to that used by Daoudi and Flem [8]. Neodymium oxide powder (Nd$_2$O$_3$, 99.9%, Kojundo Chemical Laboratory Co. Ltd., Japan) was fired at 1273 K for 24 h in air so that the included water and carbonate ions were eliminated. The fired Nd$_2$O$_3$ powder, dried calcium carbonate powder (CaCO$_3$, 99.99%, Kanto Chemical Co. Inc., Japan) and dried manganese (III) oxide powder (Mn$_2$O$_3$, 99.9%, Kojundo Chemical Laboratory Co. Ltd.) were mixed in the atomic ratios of Nd:Ca:Mn = $1 - x$:$1 + x$:1 ($0.40 \leqq x \leqq 1.00$). The mixtures were calcined in air at 1273 and 1523 K, each for 24 h with an intermediate grinding. The reacted

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powders were pressed into pellets, which were fired in air at 1573 K for 48 h and subsequently cooled slowly over a span of another 10 h to room temperature. X-ray diffraction (XRD) data were collected with Cu Kα radiation using a powder X-ray diffractometer (Rint 2000, Rigaku Corporation, Japan). Electron diffraction (ED) patterns were obtained using a field-emission transmission electron microscope (FE-TEM, HF-3000S, Hitachi High-Technologies Corporation, Japan) operated at an accelerating voltage of 300 kV, and equipped with a liquid-nitrogen type low-temperature sample holder. The TEM specimens were prepared by crushing the synthesized samples into fine fragments, which were transferred to carbon microgrids. Rietveld refinements of XRD data were conducted with Rietan 2000 program [9]. The atomic ratios of the constituent metallic ions were analyzed by inductively-coupled plasma atomic emission spectroscopy (ICP, SPS4000, Seiko Instruments Inc., Japan) and the oxygen contents were determined with a redox titration proposed by Mizutani et al. [10]. Magnetization measurements were carried out with a superconducting quantum interference device magnetometer (MPMS, Quantum Design Inc., USA).

3. Results and discussion

By the XRD measurements, we confirmed that the samples in $0.55 \leqq x \leqq 1.00$ are free from the starting materials, whereas a small amount of Nd_2O_3 was detected in the composition range of $x < 0.55$. The positions of the reflections which originate in $n = 1$ single-layered manganite did not shift in $x < 0.55$, indicating that the solution limit is $x = 0.55$. Fig. 1 shows XRD patterns which were measured at room temperature for $x = $ (a) 0.67, (b) 0.75 and (c) 1.00. ICP analyses showed that the Nd:Ca:Mn ratio of the obtained samples is almost the same as the nominal one in the mixing of the starting materials. In terms of the oxygen content, the chemical analyses revealed that the ratio of O to Mn is constant ∼4.0 in $0.55 \leqq x \leqq 1.00$.

Moreover, the ED measurements showed the fundamental crystal structure at room temperature consists of three distorted K_2NiF_4-types corresponding to the composition x. Fig. 2 shows ED patterns taken along $[0\,0\,-1]$ at room temperature for $x = $ (a) 0.67, (b) 0.75 and (c) 1.00. The ED patterns taken along other main zone-axis are shown in Fig. 3. In $0.55 \leqq x < 0.73$, the fundamental reflection conditions are $h\,k\,0{:}h = 2n$ and $k = 2n$,
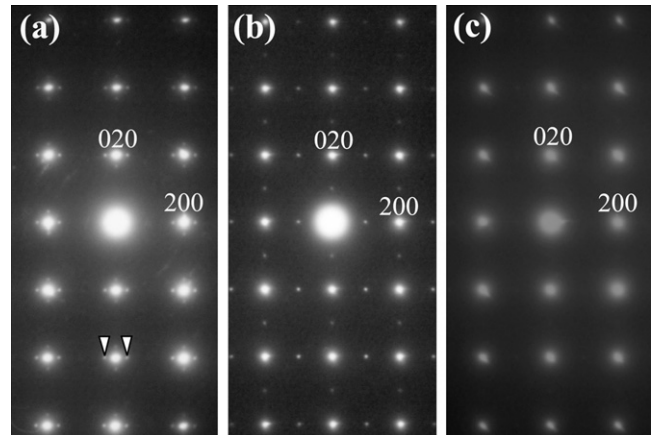
Fig. 2. ED patterns taken along $[0\,0\,-1]$ at room temperature for $Nd_{1-x}Ca_{1+x}MnO_4$ samples with $x = $ (a) 0.67, (b) 0.75 and (c) 1.00.

$h\,0\,l{:}h = 2n$ and $l = 2n$, $0\,k\,l{:}l = 2n$ and $h\,k\,l{:}h + l = 2n$, using an orthorhombic unit cell with $a \approx b \approx \sqrt{2}a_p$ and $c = c_p$ as shown in Figs. 2(a) and 3(a) (a_p and c_p represent the a- and c-axis parameters of non-distorted K_2NiF_4-type unit cell with tetragonal $I4/mmm$ (139) symmetry). The reflections in Fig. 1(a) are indexed on the cell. We display in Fig. 4(a) an enlarged portion of the XRD pattern showing reflection splitting due to orthorhombic distortion. On the basis of the reflection conditions, we proposed the model of the fundamental structure at room temperature in $0.55 \leqq x < 0.73$, which is shown in Fig. 5(a). The model accompanying rotations of the MnO_6 octahedra about the a-axis has orthorhombic $Bmab$ (64) symmetry. It has been reported that the equivalent structure was confirmed for $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ ($0 \leqq x \leqq 0.25$), $Sm_{1-x}Ca_{1+x}CrO_4$ ($0 \leqq x \leqq 0.5$), etc. [11,12]. Additionally, sharp superlattice reflections due to the COO state were observed around $x = 0.67$ as indicated by white arrows in Fig. 2(a). The superlattice reflections also appear in the 90°-rotated positions because of the twin domain structure. We could not detect the superlattice reflections in the XRD pattern, indicating that the intensity is enhanced by dynamical effect in the ED experiment. In order to support the fundamental structure model, we performed the Rietveld refinement of the XRD data. Table 1(a) lists the structural parameters and the reliability factors, which indicate the good fitting. The experimental, calculated and difference patterns are displayed in Fig. 6(a).

In $0.73 \leqq x < 0.85$, the fundamental reflection conditions are $h\,k\,0{:}k = 2n$, $h\,0\,l{:}h = 2n$ and $l = 2n$, $0\,k\,l{:}k = 2n$ and $l = 2n$ and $h\,k\,l{:}k + l = 2n$, using an orthorhombic unit cell with $a \approx b \approx \sqrt{2}a_p$ and $c = c_p$ as shown in Figs. 2(b) and 3(b). In Fig. 2(b), the $h\,k\,0$ reflections with $h = 2n + 1$ and $k = 2n$ also appear in the 90°-rotated positions because of the twin domain structure. Based on the conditions, we proposed the fundamental structure model in $0.73 \leqq x < 0.85$ as shown in Fig. 5(b). In the model, the MnO_6 octahedra are rotated about the c-axis, giving rise to orthorhombic $Acam$ (64) symmetry. The equivalent structure was confirmed for $LaCaFeO_4$, etc. [13]. The results of the Rietveld refinement using the model are displayed in Table 1(b) and Fig. 6(b). These support the $Acam$ structure model.
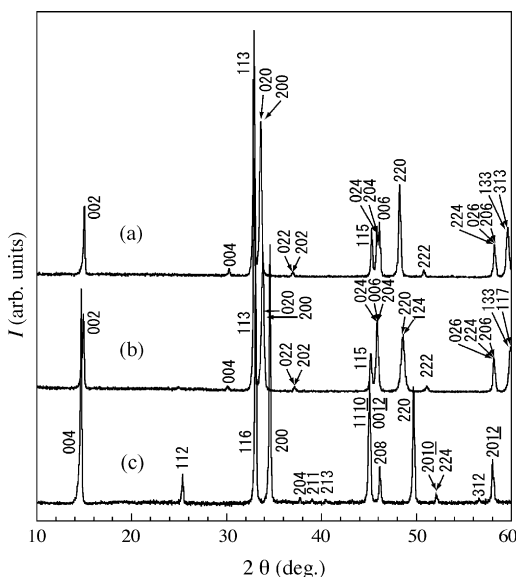

Fig. 1. XRD patterns measured at room temperature for $Nd_{1-x}Ca_{1+x}MnO_4$ samples with $x = $ (a) 0.67, (b) 0.75 and (c) 1.00.