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Synthesis of a new orthorhombic “$SrLaMnO_4$” phase with superstructure via complex precursors

Naoki Kamegashira [a], Hirohisa Satoh [a], Yoshitaka Ito [a], Akira Shimono [b,*]

[a] *Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan*
[b] *Suzuka National College of Technology, Suzuka 510-0294, Japan*

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Abstract

Solid solution of $(Sr, La)_2MnO_4$ with K_2NiF_4 structure was synthesized via decomposition process of organometallic complexes of constituent elements for the composition of La/Sr ratio >1. A new orthorhombic phase with a distorted oxygen octahedron appeared. The preparation under low oxygen partial pressure at high temperature was necessary to form this new orthorhombic phase. Some degree of defect in A-site (site for Sr or La) resulted in the formation of single phases of both tetragonal and orthorhombic compounds for La/Sr ratio >1. The lattice parameters of a new orthorhombic $Sr_{0.5}La_{1.3}MnO_{3.95}$ phase were $a = 5.512(2)$, $b = 5.4863(3)$ and $c = 12.9295(7)$ Å with the space group *Cmca* (No. 64). The unit cell has a dimension with $\sqrt{2}a_t \times \sqrt{2}a_t \times c_t$, where a_t and c_t are the lattice parameters of the fundamental body centered tetragonal cell of K_2NiF_4 structure with $I4/mmm$ space group. In this structure an oxygen octahedron is distorted and tilts each other by angle of 4.5°. This kind of orthorhombic distortion was first found in $(Sr, La)_2MnO_4$ solid solution.

Keywords: New phase; Chemical synthesis; Crystal structure; X-ray diffraction; Strontium lanthanum manganese oxide [$(Sr; La)_2MnO_4$]

1. Introduction

Solid solution of $(Sr, La)_2MnO_4$ has a tetragonal cell with K_2NiF_4 structure, usually in the region of Sr/La ratio $\geqq 1$ [1–13] and also for Sr/La ratio $\leqq 1$ [9,14]. For composition range La/Sr > 1 La_2MnO_4 was prepared by vacuum dry freezing method [9] and $(La_{1-x}Sr_x)_2MnO_4$ $(0.35 \leqq x \leqq 0.65)$ phase was synthesized by solid state reaction method under high vacuum at high temperature [14]. All of these products had a tetragonal structure. Recently tetragonal phase ($I4/mmm$ space group) of various compositions for $(Sr, La)_2MnO_4$ solid solution with La/Sr ratio > 1 was synthesized via complex precursors of each cationic component [15]. The aim of this work is to synthesize $(Sr, La)_2MnO_4$ solid solution with La/Sr ratio >1 and with trivalent manganese ion since many compounds with layered perovskite structure including trivalent manganese ion had various kind of phases by the Jahn-Teller effect [16–18]. In the course of this study we confirmed an existence of a new orthorhombic $Sr_{0.5}La_{1.3}MnO_{3.95}$ phase as described below. The phase behavior appeared in this solid solution was studied to get a synthetic condition of tetragonal and orthorhombic compounds. Although formation of single phase of $(Sr, La)_2MnO_4$ solid solution with La/Sr ratio > 1 is difficult by usual solid state reaction method, it was found that this method via organometallic complex precursors led to a rather easy process to get single phase of these compounds as in other complex oxides [19].

2. Experimental

Metal derivatives of 2-ethylhexanoic acid were used as the precursors [19]. For syntheses of 2-ethylhexanoate complexes of La, Sr and Mn lanthanum sesqui-oxide, manganese acetate and strontium acetate were used as the starting materials and the detailed procedures are described in Refs. [15]. Each amount of metallic composition in each

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[*] Corresponding author. Tel.: +81 593 68 1831; fax: +81 593 68 1820.
E-mail address: shimono@chem.suzuka-ct.ac.jp (A. Shimono).

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2-ethylhexanoate complex was determined by gravimetric analysis. Starting materials of 2-ethylhexanoate solutions of Sr, La and Mn were mixed with an appropriate ratio and completely dissolved into toluene. This solution was heated on the hot plate and the residue obtained by complete drying was heated again up to 873 K to exclude organic constituents. Then the residual powder was pressed into pellet and heated at 1523 K under Ar gas containing 1% H_2 for 2 days. Because the oxygen partial pressure in the atmosphere during heating in this process is considerably low, the valence state of Mn in the products was kept to be trivalent. The valence state of manganese ion in the products was determined by chemical analysis with iodometric titration method.

X-ray powder diffraction data of the sample were collected with Cu Kα radiation using MXP^{18} X-ray powder diffractometer (MAC Science Co. Ltd.) with an equipment of a single-crystal graphite monochromator. For data collection 2θ range was $20^\circ \leqq 2\theta \leqq 120^\circ$ with an increment of 0.04° of step width. The resulting data were analyzed by Rietveld method using RIETAN program [20,21].

3. Results and discussion

For all trials to synthesize (Sr, La)$_2$MnO$_4$ phase with La/Sr ratio >1 no single phase was obtained in the case of full occupancy of A-site where La_2O_3 was always included as the second phase, although a new orthorhombic patterns identified by the X-ray diffraction peaks. So a little deficient ratio of La component was tried to form a single phase for the above compound. Finally $Sr_{0.5}La_{1.3}MnO_{3.95}$ was isolated as a single phase with the new orthorhombic structure. Oxygen non-stoichiometry was determined from the results of the chemical analysis, which showed the almost complete trivalent state for Mn in this compound. Phase behavior was studied around this composition, changing La/Sr ratio, oxygen partial pressure and temperature. But all the compounds except this composition showed only tetragonal phase, even if they had single phase [15]. In the published references about (Sr, La)$_2$MnO$_4$ solid solution all the phase with any Sr/La ratio showed only tetragonal structure. So the formation of orthorhombic phase in this solid solution series is the first report. This orthorhombic phase is characterized by a clear split of the second largest peak into double peaks in X-ray diffraction patterns as is shown in Fig. 1. In the tetragonal phase with the space group *I*4/*mmm* such as $SrLaMnO_4$ the main peak is (1 0 3) and the second largest peak is (1 1 0). But it is clearly seen that the second largest peak splits into double peaks and some other peaks such as (1 1 2), etc. show doublets. A general relationship between fundamental tetragonal ($h\,k\,l$) and orthorhombic ($H\,K\,L$) indices except superlattice lines gives the following correspondence,

$$H^2 + K^2 = 2(h^2 + k^2)$$

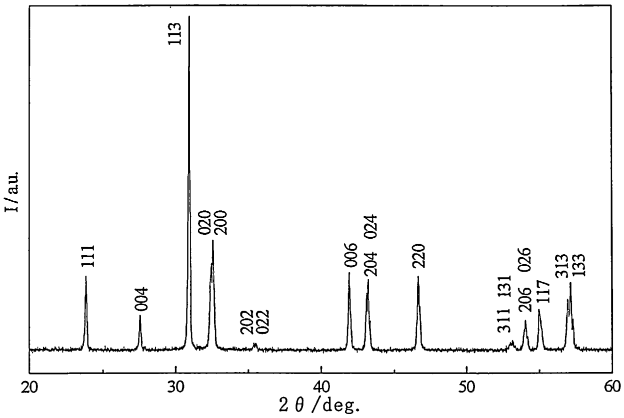

Fig. 1. Powder X-ray diffraction patterns of a new orthorhombic $Sr_{0.5}La_{1.3}MnO_{3.95}$.

and

$$L = l$$

This kind of relation is also seen in a similar compound with the layered structure [17].

For the determination of the space group of this compound CELL program was used [22,23] from which *Fmmm* (No. 69) and *Cmca* (standard setting, No. 64) survived. Then the results from Rietveld analysis were compared for these two candidates, especially on existence of superlattice lines. In Fig. 2(a) and (b) several superlattice lines were compared with the calculated data for these two possible space groups corresponding to some range of diffraction angles. In Figs. (a) and (b) arrows show the superlattice lines obtained from the experimental diffraction data. These small but clear differences proved that: *Cmca* is the most probable space group. The results of the Rietveld analysis is shown in Table 1. From these results the detailed oxygen octahedron is shown in Fig. 3 and each oxygen octahedron has a distortion and tilts with a rotation along *a*-axis by 4.5°. This situation is seen in Fig. 4.

These tilting behavior has been reported in the layered perovskite such as compounds including nickel [24,25], but the first data for layered perovskite with K_2NiF_4 type including rare earth, strontium and manganese ions.

As described in the previous paper [15] any trial to synthesize a pure orthorhombic phase near this composition range resulted in the formation of the fundamental tetragonal phase and only limited region is possible to form a single phase of

Table 1
Fractional atomic coordinates of orthorhombic $Sr_{0.5}La_{1.3}MnO_{3.95}$

Atom	Site	*x*	*y*	*z*	*g*
Sr, La	8f	0	0.3582(3)	0.002(1)	0.900
Mn	4a	0	0	0	1.000
O(1)	8f	0	0.172(2)	0.058(5)	0.975
O(2)	8e	0.25	0.011(3)	0.25	1.000

$a = 5.512(2)$, $b = 5.4863(3)$ and $c = 12.9295(7)$ Å; space group: *Cmca* (No. 64); *R*-factors: $R_{wp} = 0.1776$, $R_p = 0.01401$, $R_e = 0.0658$, $R_I = 0.01031$, $R_F = 0.0606$.

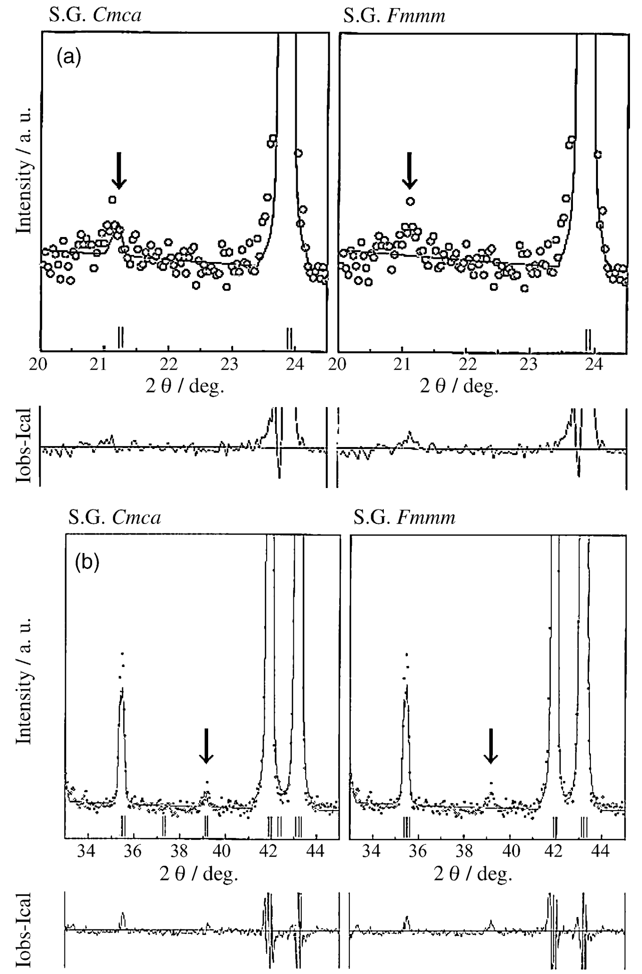

Fig. 2. Comparison of several superlattice lines (arrow) observed in orthorhombic $Sr_{0.5}La_{1.3}MnO_{3.95}$ with the calculated values based on the space group *Fmmm* and *Bmab* (standard: *Cmca*). (a) 2θ near 21° and (b) 2θ near 39°.

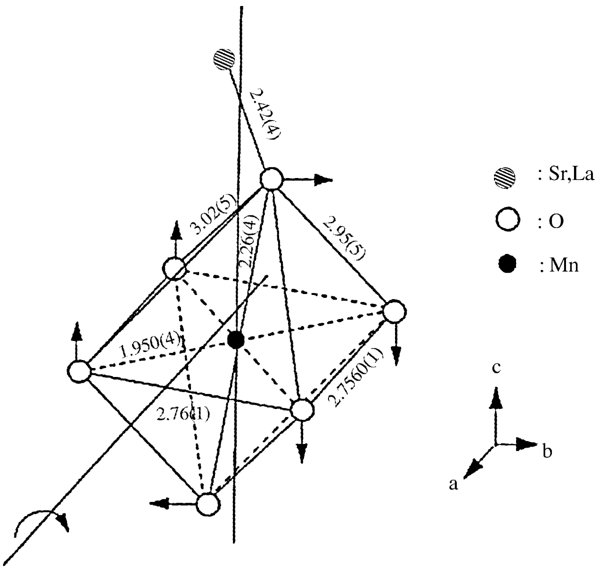

Fig. 3. Oxygen octahedron surrounding a central manganese ion.

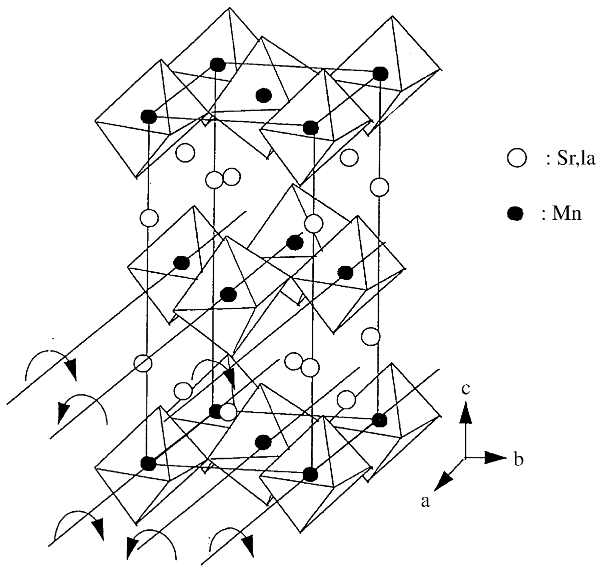

Fig. 4. Overview of the crystal structure of orthorhombic $Sr_{0.5}La_{1.3}MnO_{3.95}$ with *Bmab* (standard: *Cmca*) space group.

an orthorhombic phase for La/Sr ratio >1 and also deficient composition in A-site is characteristic of a formation of single phase since an orthorhombic phase is co-existing with La_2O_3 when it is not single phase.

4. Conclusions

A new orthorhombic phase of $Sr_{0.5}La_{1.3}MnO_{3.95}$ was isolated by a synthesis via organometallic complexes. This orthorhombic phase has a superstructure with a tilting mode of a distorted oxygen octahedron.

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