Synthesis and Characterization of Four-Layered Hexagonal \((\text{Sr}_{1-x}\text{Ba}_x)\text{MnO}_3\) \((0.0 \leq x \leq 0.5)\)

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四層構造をとる六方晶系 \((\text{Sr}_{1-x}\text{Ba}_x)\text{MnO}_3\) \((0.0 \leq x \leq 0.5)\) の合成とその性質

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\((\text{Sr}_{1-x}\text{Ba}_x)\text{MnO}_3\) \((0.0 \leq x \leq 0.5)\) は、標準的なセラミック技術を用いる四層六方の晶型を用いて合成が可能であり、導電率の変化を伴う磁気性の変化を示す。

Key-words: Perovskite, Crystal structure, Rietveld, Magnetic property

1. Introduction

Negas and Roth は、SrMnO₃の合成において、気中での固体の分離を報告した。(1) In their study, at temperatures below 1308 K, SrMnO₃ had a four-layered hexagonal \((4H)\) structure in which \(a = 0.5449 \text{ nm}\) and \(c = 0.9078 \text{ nm}\); within the range from 1308 K to 1673 K, SrMnO₃ evolved oxygen and oxygen-deficient SrMnO₃\(_{0.5}\) showed the \(4H\) structure; and above 1673 K, cubic perovskite-type MnO₃\(_{0.5}\) was obtained by rapid quenching of a sample heated above 1673 K. According to Mizutani et al.,(2) the synthesis temperature of cubic perovskite-type MnO₃\(_{0.5}\) was lowered by heating in a flow of CO₂ gas, and the oxygen deficiency of SrMnO₃\(_{0.5}\) vanished with annealing at 573–777 K in air for several hours. In their study, cubic perovskite-type SrMnO₃ had a lattice constant of \(a = 0.38057 \pm 0.00003 \text{ nm}\), in which MnO₃ octahedra shared corners with each other and the Mn⁴⁺–O–Mn⁴⁺ angle was 180°.(2) Takeda and Ohara reported that cubic perovskite-type SrMnO₃ exhibited antiferromagnetism with \(T_N = 260 \text{ K}\).(3)

In two-layered hexagonal \((2H)\) SrMnO₃ with hexagonal closed packing SrO layers, the MnO₆ octahedron links with the neighboring MnO₆ octahedra through face-sharing, and 2H–SrMnO₃ produces a one-dimensional octahedral chain along the c-axis. In 2H–SrMnO₃, an overlap of the atomic orbital between the Mn ions facing each other is expected.(4) Corner-sharing or face-sharing is a basic form of linking of MnO₆ octahedra, and polymorphism of the perovskite structure is introduced by a combination of corner-sharing and face-sharing.(5) The 4H structure is composed of half corner-sharing and half face-sharing.(6–11) Lee and Iguchi have reported the dielectric properties and dc conductivities of 4H–SrMnO₃\(_{0.5}\) and cubic perovskite-type SrMnO₃\(_{0.5}\).(12) In their study, the conductivity of 4H–SrMnO₃\(_{0.5}\) did not change very much even if it was reoxidized, while the conductivity of cubic perovskite-type SrMnO₃\(_{0.5}\) was strongly influenced by oxygen content. Sacchetti et al. investigated the temperature dependence of optical phonons in both 4H–SrMnO₃ and cubic perovskite-type SrMnO₃,(13) finding that changes in the phonon spectrum of 4H–SrMnO₃ observed on decreasing temperature indicated a subtle structural transition between 100 K and 200 K. Ordering and defect in nonstoichiometric 4H–BaMnO₃\(_{0.5}\) has been observed by electron diffraction and high-resolution electron microscopy.(14) The 4H–BaMnO₃\(_{11}\) phase was obtained for \(\delta = 0.25\), and a structural model for the 4H structure showed ordering of vacancies along the cubic layers.

It is expected that the Mn–O distance and the Mn–O–Mn angle of 4H–SrMnO₃ substituting the Ba²⁺ ion for the Sr²⁺ ion vary with increasing Ba²⁺ content. However, there have been few reports on the structural and magnetic properties of 4H–(Sr₁₋ₓBaₓ)MnO₃ in the Sr-rich region.(15,16) The work presented in this paper is the first to synthesize 4H–(Sr₁₋ₓBaₓ)MnO₃ \((0.0 \leq x \leq 0.5)\) in order to study the relationship between its crystal structure and its magnetic properties.

2. Experimental

4H–(Sr₁₋ₓBaₓ)MnO₃ \((0.0 \leq x \leq 0.5)\) was synthesized using a standard ceramic technique. Sr(C₂H₃COO)₂•0.5H₂O, Ba(CH₃COO)₂•2H₂O, and Mn(CH₃COO)₂•4H₂O powders were weighed in appropriate proportions and were ground with acetone. After the mixed powder was calcined at 773 K for 1 h in air, it was reground and heated at 1273–1473 K for 12 h in air. The samples obtained in this manner were then annealed at 673 K for 7 h in a flow of oxygen gas.

The phase of the samples was identified by powder X-ray diffraction (XRD) with monochromatic Cu Kα radiation. The oxygen content of the samples was determined by the oxidation-reduction method.(17) After a sodium oxalate solution and perchloric acid had been added to dissolve the sample in a flask, the solution was titrated with a standard potassium permanganate solution. Structural refinement was carried out by the Rietveld method with XRD data using the RIETAN 2000 program.(18) XRD data were collected by step scanning over an angular range of 20° ≤ 2θ ≤ 100° at increments of 0.05°.
0.02° (2θ). The magnetic susceptibility of the samples was measured with a SQUID magnetometer (MPMS; Quantum Design, San Diego, CA, USA). A zero-field-cooled (ZFC) run was completed in the temperature range of 5 K ≤ T ≤ 300 K under an applied magnetic field of H = 0.5 T. The magnetic susceptibility of the samples in the temperature range of 300 K ≤ T ≤ 650 K was measured using a magnetic torsion balance.

3. Results and discussion

The XRD pattern of (Sr1-xBa1-x)MnO3 (0.0 ≤ x ≤ 0.5) was completely indexed as the 4H structure. The observed lattice constants of 4H–SrMnO3 are almost equal to the values reported by Negas and Roth.11 The oxygen content calculated from the observed Mn2+/Mn total ratio is 3.000 ± 0.001 for x = 0.0–0.3, 3.000 ± 0.001 for x = 0.4, and 2.972 ± 0.001 for x = 0.5. We heated the samples (x = 0.4 and 0.5) at 1473 K because these samples heated at 1273 K had both the 4H structure and an unknown phase. The samples had oxygen deficiency in spite of annealing at 673 K for 7 h in a flow of oxygen gas. This result indicated that oxygen deficiency was caused by heating at high temperature. It was previously reported that 4H–SrMnO3 has a hexagonal perovskite-type structure with space group P63/mmc.6,7 Structural refinement of 4H–(Sr1-xBa1-x)MnO3 was carried out by the Rietveld method with XRD data. The site occupancy (p) for O(1) and O(2) was fixed as follows: p = 1.000 for 0 ≤ x ≤ 0.3, p = 0.994 for x = 0.4, and p = 0.991 for x = 0.5. Table 1 lists the refined structural parameters, Rwp, R1, and Rf, which are the weighted pattern, the integrated R factor, and the structural factor, respectively. Because Rwp of all samples is less than 11.65%, the present results suggest that the proposed structural model for 4H–(Sr1-xBa1-x)MnO3 is reasonable. Figure 1 shows the observed XRD and the differences between the observation and the calculation of 4H–(Sr1-xBa1-x)MnO3 (x = 0.3).

4H–SrMnO3 with space group P63/mmc consists of four SrO layers in an “ABAC” stacking sequence along the hexagonal c-axis.8,13 The MnO6 octahedra are grouped into face-sharing pairs linked by corner-sharing within the cubically stacked “A” layer. The Sr ions in the “2a” and “2c” sites coordinate with six O(1) ions and six O(2) ions. The Mn ion in the “4f” site coordinates with three O(1) ions and three O(2) ions.6 O(1) ions locate in the “A” layer and take part in the corner-sharing of the MnO6 octahedra, while O(2) ions locate in both the “B” and “C” layers, and take part in the face-sharing of the MnO6 octahedra. Table 2 shows the selected bond lengths and angles of 4H–(Sr1-xBa1-x)MnO3. The average Mn–Mn distance is 0.2488 ± 0.0003 nm and is independent of x. The Mn–O(1) distance increases from 0.1879 ± 0.0001 nm (x = 0.0) to 0.1911 ± 0.0001 nm (x = 0.5), while the Mn–O(2) distance decreases from 0.1911 ± 0.0005 nm (x = 0.0) to 0.1865 ± 0.0004 nm (x = 0.5). The Mn–O(1)–Mn angle involved in corner-sharing is 180.0°, and the Mn–

### Table 1. Refined Structural Parameters of 4H–(Sr1-xBa1-x)MnO3

<table>
<thead>
<tr>
<th>x</th>
<th>Cell data</th>
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<td></td>
<td>a (nm)</td>
<td>c (nm)</td>
<td>Rwp (%)</td>
<td>R1 (%)</td>
<td>Rf (%)</td>
<td>a (nm)</td>
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<td>Rwp (%)</td>
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<tr>
<td>x = 0.0</td>
<td>0.5448(1)</td>
<td>0.90784(1)</td>
<td>11.45</td>
<td>2.11</td>
<td>1.05</td>
<td>0.54660(3)</td>
<td>0.90872(4)</td>
<td>11.54</td>
<td>1.51</td>
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<tr>
<td>x = 0.1</td>
<td>0.5488(6)</td>
<td>0.90999(7)</td>
<td>13.79</td>
<td>0.91</td>
<td>0.91</td>
<td>0.55105(4)</td>
<td>0.91116 (6)</td>
<td>10.48</td>
<td>1.63</td>
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<tr>
<td>x = 0.2</td>
<td>0.55325(3)</td>
<td>0.91262(4)</td>
<td>10.81</td>
<td>1.40</td>
<td>1.09</td>
<td>0.55525(2)</td>
<td>0.91388(2)</td>
<td>11.65</td>
<td>1.60</td>
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<tr>
<td>x = 0.3</td>
<td>0.55506(2)</td>
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<td>x = 0.4</td>
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<td>x = 0.5</td>
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</table>

**Note:** Atomic position: Sr/Ba(1) (2a) 0, 0, 0; Sr/Ba(2) (2c) 1/3, 2/3, 1/4; Mn (4f) 1/3, 2/3, 1/4; O(1) (6g) 1/2, 0, 0; O(2) (6b) x, 2x, 1/4.

![Fig. 1. Observed XRD and differences between the observation and the calculation of 4H–(Sr1-xBa1-x)MnO3 (x = 0.3).](image)
increases slightly from 81.0 of the ordered moment at additional magnetic transition occurred, leading to a canting and 0.1 through face-sharing, temperature is shown in 2H–BaCoO

0.5

found that the magnetic susceptibility of 4H–MnO

Sr/Ba(1)–O(1) 0.2724(0) 0.2733(0) 0.2745(0) 0.2755(0) 0.2767(0) 0.2775(0) 
Sr/Ba(1)–O(2) 0.2831(4) 0.2841(4) 0.2860(4) 0.2876(5) 0.2896(3) 0.2917(3) 
Sr/Ba(2)–O(1) 0.2761(0) 0.2766(0) 0.2772(0) 0.2778(0) 0.2785(0) 0.2791(0) 
Sr/Ba(2)–O(2) 0.2727(0) 0.2736(0) 0.2749(0) 0.2760(1) 0.2773(0) 0.2783(0) 
Mn–Mn 0.2483(4) 0.2488(4) 0.2492(4) 0.2489(5) 0.2490(4) 0.2487(4) 
Mn–O(1) 0.1879(1) 0.1883(1) 0.1890(1) 0.1897(1) 0.1904(1) 0.1911(1) 
Mn–O(2) 0.1911(5) 0.1911(5) 0.190(5) 0.1893(6) 0.1882(4) 0.1865(4) 
Mn–O(1)–Mn 180.0 180.0 180.0 180.0 180.0 180.0 
Mn–O(2)–Mn 81.0(3) 81.2(3) 81.9(3) 82.2(3) 82.8(2) 83.6(3) 

Table 2. Selected Bond Lengths (nm) and Angles (°) of 4H–(Sr1−xBa)xMnO3

4H–(Sr1−xBa)xMnO3 above T_N. 4H–SrMnO3 had subtle structural phase transition from the hexagonal symmetry (space group P63/mmc) to the orthorhombic symmetry (space group C2221) at \( T_N \approx 350 \text{ K} \). A small bending of the Mn–O–Mn angle was induced at some corner-sharing octahedra, and the electron transfer between Mn pairs was reduced. The distortion accordingly enhanced correlation associated to the direct exchange interaction inside each pair below 380 K, before the magnetic ordering was established below 286 K. Battle et al. proposed a model of 4H–SrMnO3 in which the interaction between two Mn ions in face-sharing octahedra would be stronger than the interaction between the Mn ions in corner-sharing octahedra. According to Goodenough, the 90° superexchange interaction for Mn\(^{2+}\)–O–Mn\(^{2+}\) is strong and antiferromagnetic at \( T_N \approx 300 \text{ K} \). Although to the best of our knowledge there have been no reports on the relationship between the superexchange interaction and the Mn–O–Mn angle in the 4H structure, it is expected that the superexchange interaction involved in face-sharing is influenced by the Mn–O–Mn angle. In 4H–(Sr1−xBa)xMnO3, therefore, it is assumed that slight increase in the Mn–O–Mn angle play an important role in the variation in \( T_N \). Peaks at \( x = 0.0 \) and \( x = 0.1 \) might have been caused by the cationic ordering in the ordered moment. Further investigation is necessary to explain the variation in \( T_N \) and the peaks found at low temperatures.

4. Summary

4H–(Sr1−xBa)xMnO3 was synthesized in the range of 0.0 ≤ x ≤ 0.5. The oxygen content is 3.000 ± 0.001 for \( x = 0.0 \), 3.000 ± 0.001 for \( x = 0.4 \), and 3.000 ± 0.001 for \( x = 0.5 \). The increase in the lattice constants is explained by the difference in the ionic radius between the Sr\(^{2+}\) and Ba\(^{2+}\) ions. Rietveld analysis at room temperature indicates that the Mn–Mn distance is independent of \( x \). Both the Mn–O(1) distance and the Mn–O(2)–Mn angle increase with increasing \( x \), while the Mn–O(2) distance decreases with increasing \( x \). 4H–(Sr1−xBa)xMnO3 exhibits antiferromagnetism, and \( T_N \) decreases slightly from \( \approx 276 \text{ K} \) (for \( x = 0.0 \)) to \( \approx 264 \text{ K} \) (for \( x = 0.5 \)). It is assumed that the variation in \( T_N \) is influenced by the Mn–O(2)–Mn angle.

References


