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The Crystal Structure of α-SrMnO$_3$

KOJI KURODA, NOBUO ISHIZAWA, NOBUYASU MIZUTANI, AND MASANORI KATO

The Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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α-SrMnO$_3$ crystallizes in the hexagonal system with unit-cell dimensions $a = 5.454(1)$ Å, $c = 9.092(2)$ Å, space group $P6_3/mmc$, Z = 4. The structure was solved by the heavy-atom method; of 404 unique reflections measured by counter method, 203 that obeyed the condition $|F_0| \geq 3\sigma(|F_0|)$ were used in the refinement to a conventional R value of 0.043. The structure consists of four close-packed SrO$_3$ layers in an *ABAC* stacking sequence along the hexagonal c axis. Oxygen octahedra containing Mn^{4+} are grouped into face-sharing pairs linked by corner sharing within the cubically stacked "*A*" layer.

Alkaline-earth metal–manganese double oxides (*1–10*) are very interesting materials because of their large oxygen deficiency, which is largely dependent on the partial pressure of oxygen and temperature of preparation, and which significantly affects their crystal structure and electrical properties. Synthesis (*1*), thermal behavior (*2*), phase relation (*8*), nonstoichiometry, and electrical properties (*10*) have been reported. These studies, however, were performed on polycrystalline samples. To obtain further precise information on these materials, single crystals suitable for X-ray experiments and electrical property measurements were needed. In this paper, the crystal growth and crystal structure of α-SrMnO$_3$ are reported.

A crystallographic description of the α-SrMnO$_3$ crystal was first given by Syono (*11*) and Negas (*3*) on the basis of X-ray powder diffraction studies, reporting that the crystal had hexagonal structure with $P6_3/mmc$ and is isostructural with the high-temperature form of BaMnO$_3$ (hexagonal, $a = 5.669$ Å, $c = 9.38$ Å, space group $P6_3/mmc$) given by Hardy (*12*). Single crystals of α-SrMnO$_3$ were grown from SrCl$_2$ solvents by the slow-cooling flux method. α-SrMnO$_3$ powder was prepared by heating a mixture of SrCO$_3$ and MnCO$_3$ at 1000°C in air. A mixture of SrCl$_2$ and α-SrMnO$_3$ powder (molar ration 10 : 1) was put in an alumina crucible, soaked for 3 hr at 1250°C, and then cooled to 800°C at the rate of 4°C/hr. Hot-pouring techniques were used to separate crystals from the molten flux, and dark violet hexagonal crystals up to 5 × 1 mm were obtained. A spherical crystal, 0.14 mm in diameter, was used for data collection on an automatic Philips four-circle diffractometer PW 1100, using the ω-2θ scan technique ($2\theta_{\max} = 80$) with graphite-monochromatized Mo$K\alpha$ radiation. The scan speed was 4° min^{-1} in ω, and scanning was repeated up to three times when the total counts were less than 20,000. The scan width was determined

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TABLE I

POSITIONAL PARAMETERS AND CRYSTAL DATA

α-$SrMnO_3$						High-temperature $BaMnO_3$ (Hardy)				
	Site	x	y	z	B		Site	x	y	z
Sr(1)[a]	4*e*	0.0	0.0	0.0120(4)	0.80(4)	Ba(1)	2*a*	0	0	0
Sr(2)	2*c*	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.71(4)	Ba(2)	2*c*	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
Mn	4*f*	$\frac{1}{3}$	$\frac{2}{3}$	0.6127(2)	0.57(4)	Mn	4*f*	$\frac{1}{3}$	$\frac{2}{3}$	0.61
O(1)	6*g*	$\frac{1}{2}$	0.0	0.0	1.42(13)	O(1)	6*g*	$\frac{1}{2}$	0	0
O(2)	6*h*	−0.8179(11)	0.8179(11)	$\frac{3}{4}$	0.80(11)	O(2)	6*h*	$\frac{5}{6}$	$\frac{5}{6}$	$\frac{3}{4}$

Hexagonal $P6_3/mmc$, $a = 5.454(1)$ Å, $c = 9.092(2)$ Å, $Z = 4$, $Dx = 5.40$ g · cm^{-3}

Hexagonal $P6_3/mmc$, $a = 5.669$ Å, $c = 9.38$ Å, $Z = 4$.

[a] Sr(1) is placed in 4*e* as a half-atom.

according to the formula $(1.6 + 0.3 \tan \theta)°$. Intensities were corrected for Lorentz polarization and absorption effects. The intensities of 404 crystallographically independent reflections were measured; 203 of these had $|F_0| \geq 3\sigma(|F_0|)$ and were used in the subsequent refinement. The systematic absences were $l = 2n + 1$ for $00l$, indicating that the possible space groups are $P6_3$, $P6_3/m$, or $P6_322$. The *hhl* reflections were very weak and the intensities were smaller than three times of the background intensity even for the most strong one. If those reflections are omitted, the possible space groups are restricted to be centrosymmetric $P6_3/mmc$, and noncentrosymmetric $P\bar{6}2c$ and $P6_3mc$. Considering that the prototype of the α-$SrMnO_3$ structure has the symmetries of $P6_3/mmc$, the refinements were undertaken on the basis of four structural models assuming $P6_3/mmc$, $P6_3$, $P6_3/m$, and $P6_322$, respectively. The full-matrix least-squares program LINUS (Coppens and Hamilton (*13*)) was used. Extinction correction was carried out in an isotropic mode. The atomic scattering factors and dispersion correction coefficients were taken from the International Tables for X-Ray Crystallography (*14*). The conventional *R* values of the refinements based on the four models gave no significant differences. On the other hand, some unreasonable temperature factors and high correlations between the parameters were obtained in the models assuming $P6_3$, $P6_3/m$, and $P6_322$. Thus, we adopted $P6_3/mmc$ for the space group of the α-$SrMnO_3$ structure. When the Sr(1) atom was fixed at the origin in the $P6_3/mmc$ model as in the case of Ba atoms in the $BaMnO_3$ structure, a very large thermal parameter of Sr(1) along the *c* axis was obtained and relatively high peaks still remained at $(00z)$ with $z \simeq 0.04$ on the difference Fourier maps. This indicated that the Sr(1) was disordered along the *c* axis. Refinements were, then, carried out assum-

TABLE II

INTERATOMIC DISTANCES (Å)

α-$SrMnO_3$		$BaMnO_3$	
Sr(1)–O(1)	2.73(1)	Ba(1)–O(1)	2.83
Sr(2)–O(1)	2.76(1)	Ba(2)–O(1)	2.86
Sr(1)–O(2)	2.85(1)	Ba(1)–O(2)	2.86
Sr(2)–O(2)	2.73(1)	Ba(2)–O(2)	2.83
Mn–O(1)	1.87(0)	Mn–O(1)	1.94
Mn–O(2)	1.89(1)	Mn–O(2)	2.10
Mn–Mn	2.49(0)	Mn–Mn	2.62
Mn–Mn′	3.74(0)	Mn–Mn′	3.88

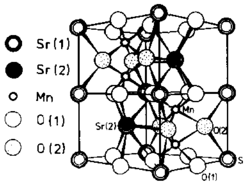

FIG. 1. Crystal structure of α-SrMnO$_3$.

ing that the Sr(1) atoms are distributed statistically at (00z) with $z = 0.0120$ as a half-atom. Thus, this structural model was adopted for the α-SrMnO$_3$ structure. The isotropic thermal parameters of Sr(1) became an ordinary value, 0.80(4) and there remained no significant peaks on the difference Fourier maps. Satisfactory results were obtained by distributing Sr(1) atoms statistically at (00z) with $z = 0.0120$. The final R value became 0.043. Final positional parameters and crystal data are given in Table I. Interatomic distances are given in Table II.

The structure of α-SrMnO$_3$ is shown in Fig. 1. The structure is almost the same as BaMnO$_3$ (high-temperature form). Both α-SrMnO$_3$ and high-temperature BaMnO$_3$ consist of four close-packed AO$_3$ (A; Sr or Ba) layers in an $ABAC$ stacking sequence along the hexagonal c axis. Tetravalent Mn assumes interlayer octahedral sites. Oxygen octahedra containing Mn^{4+} ions are grouped into face-sharing pairs linked by corner sharing within the cubically stacked "A" layer. The Mn–O(1) and Mn–O(2) bond distances are 1.87(0) and 1.89(1) Å, respectively, and the Mn–Mn bond distance of 2.49(0) Å are short, resulting in metal–metal interactions through overlap of d orbitals. The Mn–Mn bond distance between the octahedra which share corners is 3.74(0) Å. The Sr^{2+} ion is surrounded by 12 O^{2-} ions. The Sr–O bond distances, shown in Table II, were compared to Ba–O bond distances of high-temperature BaMnO$_3$. Hardy reported that Ba–O bond distances were almost equal. On the other hand, in α-SrMnO$_3$ the Sr(1)–O(2) bond distance is larger than the other Sr–O bond distance. This indicates that the free space around Sr(1) is expanded along the c axis in comparison with Sr(2) in the α-SrMnO$_3$ structure and Ba atoms in the high-temperature BaMnO$_3$ structure. Thus, it is reasonable that the structural model in which Sr(1) atoms are statistically distributed at two sites (0, 0, ±0.0120) in close vicinity to the origin, gave a satisfactory result in the refinement.

Acknowledgments

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