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Synthesis and crystal structure of Sm_2MnTiO_6

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Abstract

A new compound, Sm_2MnTiO_6, with a perovskite-type structure was synthesized. A Rietveld refinement of X-ray diffraction data has been carried out and the refined lattice parameters with the monoclinic space group $P2_1/n$ (No. 14) were $a=0.54463(1)$, $b=0.57104(1)$, $c=0.78048(2)$ nm and $\beta=90.22(2)°$. The oxygen octahedra tilt by several degrees against each other. The antiferromagnetic behavior was observed below 21.0 K. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Synthesis; Perovskite; Crystal structure; Antiferromagnetism; Samarium manganese titanium oxide

1. Introduction

The preparation of La_2MnTiO_6 was reported by Ramanujachary and Swamy [1], but their X-ray data include unassigned peaks and their calculated lattice constants did not correspond to the values cited on their table. In general, $LnMnO_3$ (Ln=rare earth) decomposes at high temperatures under low oxygen partial pressure [2,3], while the formation of $LnTiO_3$ needs much lower oxygen partial pressure to keep a valence state of the Ti ion trivalent [4]. Therefore, the formation of $Ln(Mn,Ti)O_3$ is rather difficult because of difficulty in keeping trivalent Mn and Ti ions in these compounds simultaneously. However, it is more realizable when a combination of divalent Mn and tetravalent Ti ionic states is tried under an appropriate reduced atmosphere at high temperatures during synthesis. In fact, Ramanujachary and Swamy [1] concluded from their magnetic data that these two valence states are included in their sample of La_2MnTiO_6. It is also possible to form $ALaMnTiO_6$ where A is an alkaline earth or their solid solution and the ionic state of Mn and Ti are trivalent and tetravalent [5] and $(La_{0.1}Ca_{0.9})(Mn_{1-x}Ti_x)O_3$ solid solution where tetravalent Ti ion and trivalent and tetravalent Mn ion exist [6]. In this study a single phase of Sm_2MnTiO_6 was successfully synthesized and its crystal structure was determined by Rietveld analysis of X-ray powder diffraction data and its magnetic properties were also measured at low temperatures.

2. Experimental

A polycrystalline sample of Sm_2MnTiO_6 was prepared by the solid-state reaction method. All the starting materials had 99.9% purity (Kanto Chemicals Co. Ltd.) and were pre-treated to adjust the oxygen stoichiometry. Sm_2O_3 was treated as described in other reports [7]. MnO was prepared by reducing Mn_2O_3 under a hydrogen stream at 1273 K. TiO_2 was annealed at 1273 K in air for 1 day. Mixtures of Sm_2O_3, MnO and TiO_2 in an appropriate molar ratio were pressed into pellets and heated at 1473 K for 2 days under a 1% H_2–Ar atmosphere. For the formation of the single phase of Sm_2MnTiO_6, the heat treatment under a reduced atmosphere was necessary, since some other phases, like $Sm_2Ti_2O_7$, were predominantly formed if the ambient oxygen partial pressure was higher. The grinding and heating processes were repeated to get a homogeneous specimen.

X-ray powder diffraction data of the sample were collected with a MAC MXP^{18} powder diffractometer using CuKd radiation equipped with a single crystal graphite monochromator at room temperature. The 2θ range was $10° < 2\theta < 120°$ with increments of 0.04°. The resulting data were analyzed by the Rietveld method using the RIETAN program [8,9]. The overall isotropic thermal parameter $0.629(3) \times 10^{-2}$ nm^2 was used throughout the present calculation.

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Magnetic susceptibility was measured by Faraday and SQUID methods from liquid helium temperature to room temperature.

3. Results and discussion

The X-ray diffraction patterns of Sm_2MnTiO_6 are shown in Fig. 1 and were a little different from those of a usual, orthorhombic perovskite like La_2MnTiO_6 reported by Ramanujachary and Swamy [1]. Several diffraction peaks corresponding to an orthorhombic $GdFeO_3$ type perovskite structure became broadening and the peak shape almost begins to split. In fact when the orthorhombic space group was adopted, the value of R_{wp}, the most important parameter to give the degree of fittings, became much higher. All the peaks in the powder X-ray diffraction patterns of Sm_2MnTiO_6 in this study could be completely indexed by a monoclinic crystal system with the aid of the CELL program [10,11].

The magnetization curve is shown in Fig. 2 against the applied magnetic field at 4 K. There are no hysteresis and no saturation phenomenon down to 4 K. The magnetic susceptibility is shown in Fig. 3 as a function of temperature. Antiferromagnetic behavior was observed at 21.0 K and there is no difference between zero field cooling (ZFC) and field cooling (FC) at 1000 Gauss below and above Néel temperature. It is therefore considered that this compound shows a complete antiferromagnetic property and the possibility of a spin glass behavior was denied from the nonhysteresis for ZFC and FC measurements. It was derived from Fig. 3 that a divalent manganese (high spin) ion, tetravalent titanium ion and trivalent samarium ion exist since the effective magnetic moment of $\mu_{eff(exp)}=$ 6.46 Bohr magneton was derived from the temperature dependence of the inverse magnetic susceptibility in the high temperature region, which is in a good agreement with the theoretical value of $\mu_{eff(theo)}=6.28$ Bohr mag-

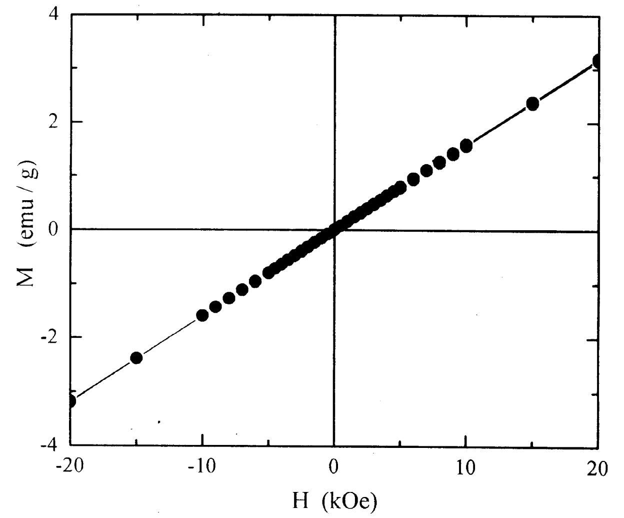

Fig. 2. Magnetization curve against the applied magnetic field at 4.5 K.

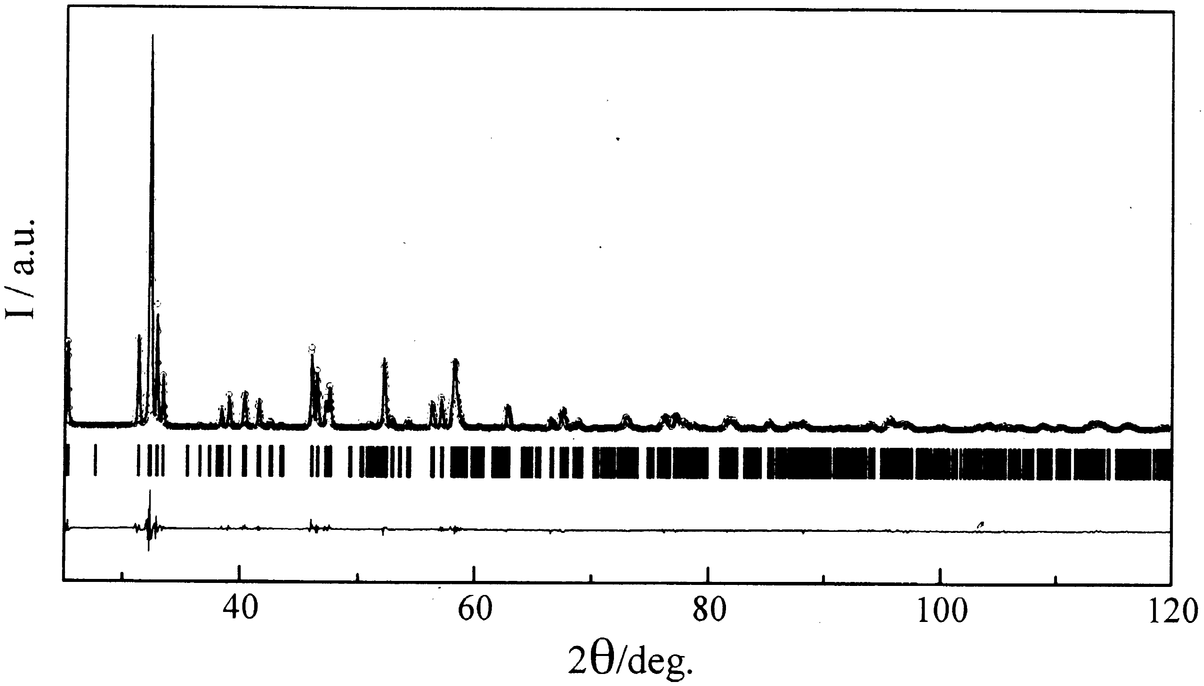

Fig. 1. The observed and calculated profiles of Sm_2MnTiO_6. $P2_1/n$ and B-site ordering are assumed. Experimental points are shown by circles and the calculated profile by a solid line. The bottom curve is the difference pattern, $y_{obs}-y_{calc}$, and the small bars indicate the angular positions of the allowed Bragg reflections.

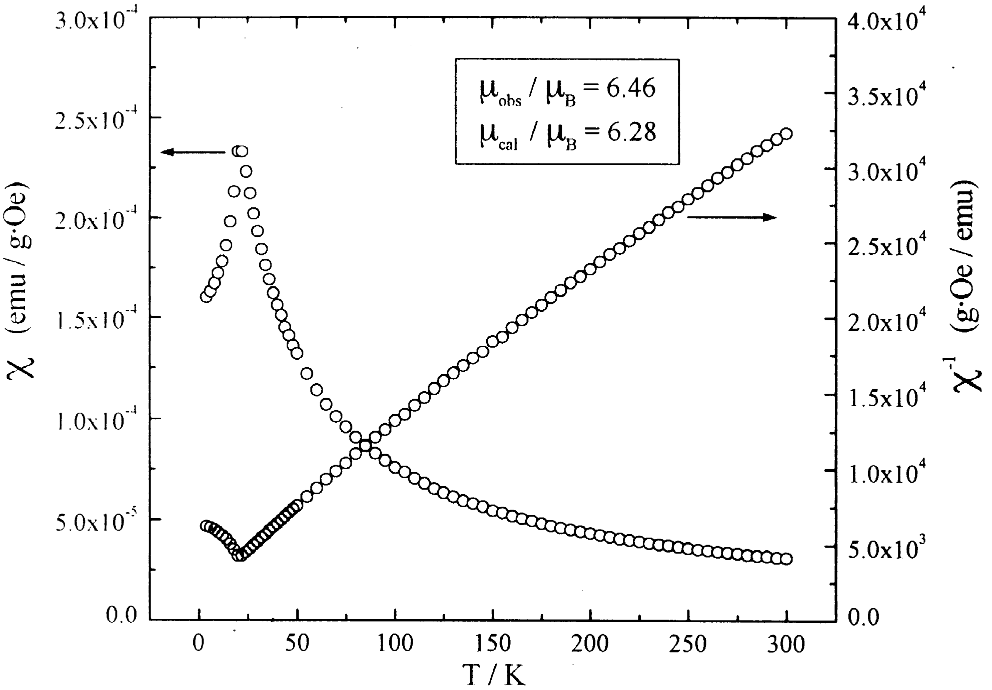

Fig. 3. Magnetic susceptibility as a function of temperature.

neton. But the magnetic interaction should be very weak because there are two oxygen ions and one titanium ion (non-spin) between two manganese ions on an average and so the fact that it is too weak an interaction to induce a magnetic ordering for such a long distance should be considered. So another possibility to evolve magnetic interaction may be considered; for example a role of a f-electron from the samarium ion, although the Néel temperature (20 K) is rather high for the evolution of a role of a 4f electron. A further study on the magnetic properties of Sm_2MnTiO_6 is necessary.

Table 1
Crystallographic data for Sm_2MnTiO_6 from Rietveld refinement at room temperature

Space group	$P2_1/n$[a]
a (nm)	0.54463(1)
b (nm)	0.57104(1)
c (nm)	0.78048(2)
β (°)	90.22(2)
Volume (nm^3)	0.2427
Z	2
Calculated density (g cm^{-3})	6.8347
No. of reflections	752
No. of profile parameters refined	14
No. of structure parameters refined	17
No. atoms/asymmetric unit	6
Reliability factor (%)	
R_{WP}	9.56
R_P	7.16
R_E	5.90
R_I	2.06
R_F	1.51
R_{WP}/R_E	1.62

[a] The standard deviation of last digit is given in parenthesis.

It was considered that the sites for the divalent Mn ion in the B-site in the perovskite structure should be definite from the results of the antiferromagnetic property of this compound. Actually the ionic radii of the divalent Mn and tetravalent Ti ions are a little different. Taking into consideration this point, the Riedvelt analysis was carried out for an ordered model of Mn and Ti ions in the B-site, although it is very difficult to observe extra superlattice lines in the X-ray diffraction patterns from the ordering of Mn and Ti ions. Lattice parameters obtained by a least-squares refinement for reflections were used as initial ones for the Rietveld analysis. Initial fractional coordinates of each atom were estimated from other perovskites like $SrLaMnTaO_6$ [12]. In the structure refined by $P21/n$, the assigned occupation sites for the model with an ordered distribution of the B-site cation are 4e for Sm, O1, O2 and O3, 2d for Mn and 2c for Ti, respectively. Crystallographic

Table 2
Fractional atomic coordinates of Sm_2MnTiO_6 at room temperature

Atom	Position	x[a]	y[a]	z[a]
Sm	4e	0.5152(3)	0.5610(2)	0.2487(5)
Mn	2d	0.5	0	0
Ti	2c	0	0.5	0
O(1)	4e	0.1787(5)	0.2044(5)	−0.0654(3)
O(2)	4e	0.2934(5)	0.6862(5)	−0.0478(3)
O(3)	4e	0.3937(3)	0.9600(2)	0.2634(4)

[a] The standard deviation of last digit is given in parentheses.

Table 3
Interatomic distances of Sm_2MnTiO_6

Distances (nm)[a]								
Sm–O(1)	Sm–O(2)	Sm–O(3)	Mn–O(1)	Mn–O(2)	Mn–O(3)	Ti–O(1)	Ti–O(2)	Ti–O(3)
0.367(3)	0.236(3)	0.230(3)	0.216(2)×2	0.215(3)×2	0.215(3)×2	0.201(3)×2	0.196(2)×2	0.195(3)×2
0.258(3)	0.270(3)	0.283(1)						
0.281(3)	0.262(3)	0.327(3)						
0.228(3)	0.359(3)	0.350(1)						

[a] The standard deviation of the last digit is given in parentheses.

data, R factors and refined structure parameters are given in Table 1. The positional parameters obtained in this refinement are listed in Table 2. Selected interatomic distances and bond angles between atoms are summarized in Tables 3 and 4. When Mn and Ti ions were assumed to be randomly distributed in the B-site of the perovskite structure, the resulting R_{wp} value was only slightly different from that of the ordered model.

Table 4
Bond angles of Sm_2MnTiO_6

	Angles (°)[a]
Mn–O(1)–Ti	142(1)
Mn–O(2)–Ti	148(1)
Mn–O(3)–Ti	145(1)
O(1)–Mn–O(2)	89(1)
O(1)–Mn–O(3)	86(1)
O(2)–Mn–O(3)	86(1)
O(1)–Ti–O(2)	89(2)
O(1)–Ti–O(3)	90(1)
O(2)–Ti–O(3)	90(1)

[a] The standard deviation of last digit is given in parentheses.

Three Mn–O distances in the oxygen octahedron surrounding the divalent manganese ion (MnO_6) are almost same as is seen from Table 3. The mean distance of Mn (divalent)–O is 0.215 nm and is comparable with the distance of 0.223 nm calculated from the ionic radii of Shannon [13]. Similarly the mean distance of Ti (tetravalent)–O being 0.197 nm in the TiO_6 octahedron is comparable with 0.201 nm from Shannon's radii. The MnO_6 and TiO_6 octahedra in the structure of Sm_2MnTiO_6 are shown in Fig. 4. Both of the oxygen octahedra around the Mn and Ti ions are only slightly distorted in this compound and each oxygen octahedron is orderly arranged in turn and tilted against each other like zig-zag chains in each direction as is seen from Table 3. On the other hand there are eight oxygen ions with shorter distances and four with further distances among the twelve oxygen ions surrounding the Sm ion. The overview of Sm_2MnTiO_6 is shown in

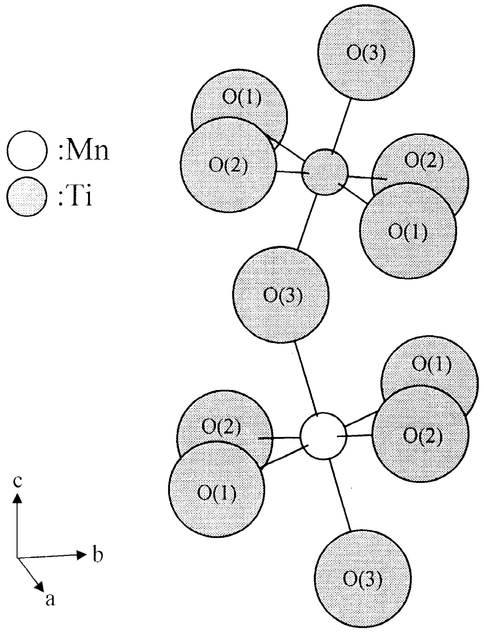

Fig. 4. Distorted octahedron of Sm_2MnTiO_6 around Mn and Ti ions.

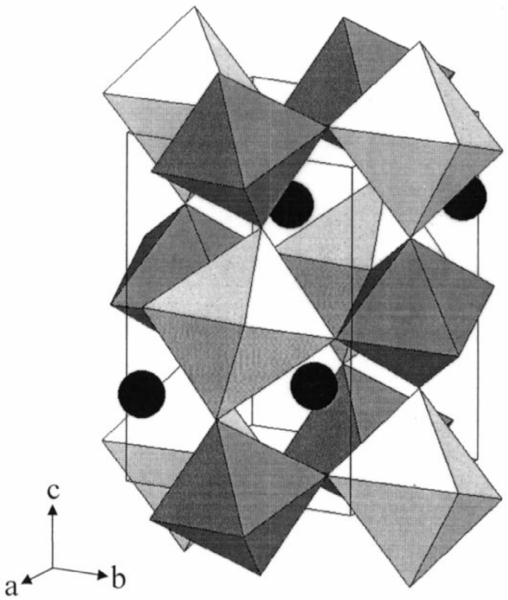

Fig. 5. Overview of the structure of Sm_2MnTiO_6. The MnO_6 octahedra are shaded, the TiO_6 octahedra are unshaded and the spheres show the Sm site.

Fig. 5. The mean tilting angle is approximately 18° toward each zig-zag connection.

Acknowledgements

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