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Superstructure of tetragonal $BaGd_2Mn_2O_7$

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Abstract

The crystal structure of a layered perovskite compound, $BaGd_2Mn_2O_7$, was analyzed for the powder X-ray diffraction data by Rietveld method. The tetragonal $BaGd_2Mn_2O_7$ phase has superlattice lines so that the space group of $P4_2/mnm$ (No. 136) was determined with the unit cell dimensions $a=0.55024(1)$ and $c=2.02457(5)$ nm. The MnO_6 octahedron was distorted and tilts by 6° apart from the c axis mutually in the reverse direction.

Keywords: Crystal structure; Oxygen octahedron; Barium gadolinium manganese oxide

1. Introduction

The layered perovskites $BaLn_2Mn_2O_7$ (Ln=rare earth) were synthesized by Deschizeaux Cheruy and Joubert [1] for Ln=Pr–Gd and by Kamegashira and Umeno [2] for Ln=Tb. These compounds have the $Sr_3Ti_2O_7$-type structures which belong to a Ruddlesden–Popper type homologous series $AO\cdot(ABO_3)_n$ where $n=2$ [3]. According to Deschizeaux Cheruy and Joubert [1], these compounds for Ln=Nd, Sm and Eu orthorhombically distort when they are prepared in a N_2 atmosphere.

The orthorhombic distortion is related to the tetragonal phase as follows [1,4]. $a_o \doteq b_o \doteq \sqrt{2}a_t$ and $c_o \doteq c_t$ where a_o, b_o and c_o are lattice constants of the orthorhombic phase, while a_t and c_t are those of tetragonal phase. So in the X-ray diffraction patterns, orthorhombic (HKL) indices obey the following relations to tetragonal (*hkl*): $H^2+K^2=2\ (h^2+k^2)$ and $L^2=l^2$.

The existence of another type of orthorhombic phase was reported for Ln=Tb [2] and Ln=Gd [4,5]. In these compounds the relationships between orthorhombic and tetragonal phases are as follows. $a_o \doteq b_o \doteq a_t$ and $c_o \doteq c_t$. So in this family the relation $H^2+K^2=h^2+k^2$ and $L^2=l^2$ are derived. The formation of both phases of orthorhombic distortion depends on the preparative conditions and oxygen nonstoichiometry. The former type of orthorhombic $BaGd_2Mn_2O_7$ was also prepared after thermal cycles [6].

It has been considered that the tetragonal phase has the $I4/mmm$ space group for all of Ln in this family [1]. The detailed crystal structure for tetragonal $BaTb_2Mn_2O_7$ was also refined by Meng et al. [7] with this space group.

In this study tetragonal $BaGd_2Mn_2O_7$ with a superstructure was found and the refinement of the crystal structure was determined by X-ray powder diffraction using the Rietveld method.

2. Experimental

A polycrystalline specimen of the tetragonal $BaGd_2Mn_2O_7$ was prepared by the solid state reaction method. The starting materials, Gd_2O_3, Mn_2O_3 and $BaCO_3$ were pre-treated before the reaction as described previously [5]. Mixtures of $BaCO_3$, Gd_2O_3 and Mn_2O_3 with an appropriate molar ratio were pressed into pellets, heated at 1423 K for 24 h and subsequently at 1623 K for 72 h in a purified Ar atmosphere and then slowly cooled to room temperature.

X-ray powder diffraction data of the sample were collected with a MACMXP^{18} powder diffractometer using Cu Kα radiation. The 2θ range was $20° \leq 2\theta \leq 120°$ with increments of 0.04°. The resulting data were analyzed by the Rietveld method using the RIETAN program [8,9].

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3. Results and discussion

X-ray diffraction patterns of $BaGd_2Mn_2O_7$ prepared in this study are similar to those of the tetragonal phase [1,2] as is shown in Fig. 1, but several superlattice lines with small intensity are clearly observed. From the results of the CELL program [10,11] for the fundamental lines the space group $I4/mmm$ (No. 139) was derived, while $P4_2nm$ and its related space groups were derived using the diffraction lines including superlattice lines. There are three kinds of candidates for these space groups, $P4_2nm$ (No. 102), $P\text{-}4n2$ (No. 118) and $P4_2/mnm$ (No. 136). All the calculation using these space groups lead to almost same values for R_{wp}. In order to compare these space groups some superlattice lines of X-ray diffraction patterns were examined for fitting to the calculated lines profile as is shown in Fig. 2 where the space group $I4/mmm$ is also included for comparison. There remain two candidates for the space group from this figure, $P4_2nm$ and $P4_2/mnm$. The degree of fitting between the observed and calculated patterns for these space groups is best. Since the $BaLn_2Mn_2O_7$ family has semiconducting properties with rather high electrical conductivity [12], no possibility of ferroelectricity could be considered and this compound should be centrosymmetric. Therefore $P4_2/mnm$ was chosen as the most probable space group for $BaGd_2Mn_2O_7$ with a superstructure. This space group was adopted for $SrTb_2Fe_2O_7$ by Samaras et al. [13] and $Sr_2HoMn_2O_7$ and $Sr_2YMn_2O_7$ by Battle et al. [14], which are isostructural with $BaGd_2Mn_2O_7$. So the model of the structure for the Rietveld refinement in this study was built by reference to these compounds. In this refinement a model for a random distribution of Ba and Gd ions in the A-sites is carried out and so a virtual atom (1/3 Ba + 2/3 Gd) was used, which is designated by (Ba/Gd) in the following description

In the refined structure the assigned occupation sites for the model are 8j for (Ba/Gd)2, Mn and 05, 8 h for O2, 4 g for O1, 4f for (Ba/Gd)1 and 4e for O3 and O4, respectively. The crystallographic data are given in Table 1 and a plot of the observed and calculated profiles are shown in Fig. 1 where the degree of agreement between them is also shown in the difference curve. The positional parameters obtained in this refinement are listed in Table 2. The bond distances and bond angles between atoms are given in Tables 3 and 4.

A considerably distorted octahedral arrangement around the Mn ion exists in this compound as is shown in Fig. 3. In the plane perpendicular to the c-axis, four oxygen ions,

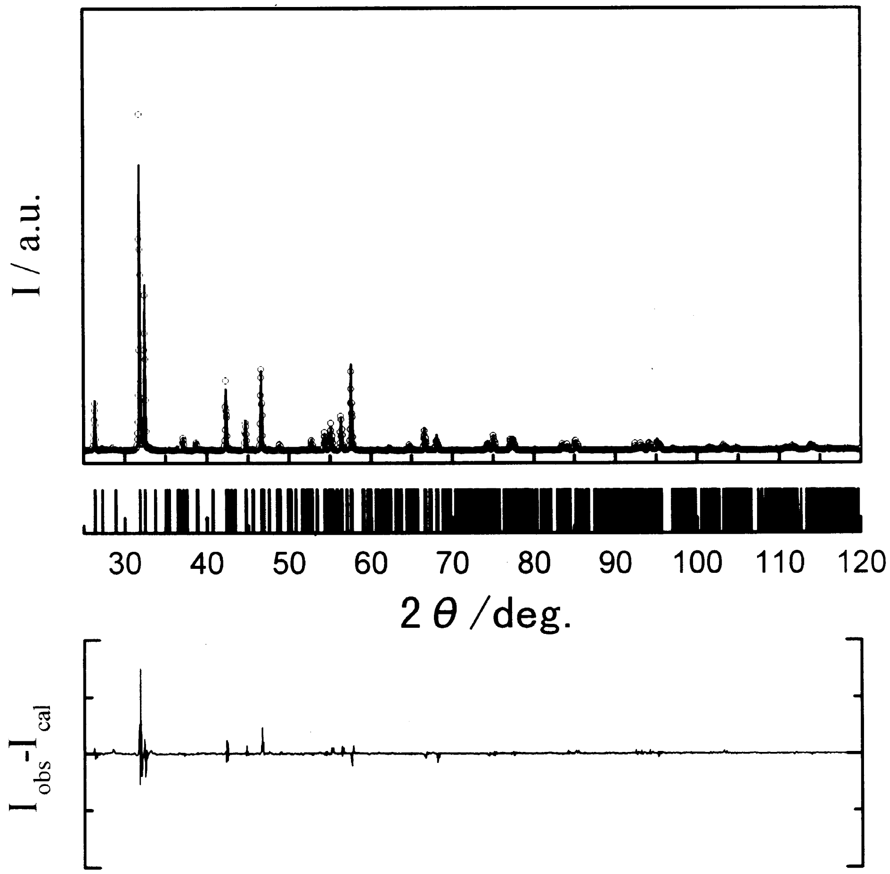

Fig. 1. The observed and calculated profiles of $BaGd_2Mn_2O_7$ at room temperature. Experimental points are shown by circles and the calculated profile by a solid line. The bottom curve is the difference pattern, $y_{obs} - y_{calc}$, and the small bars indicate the angular positions of the allowed Bragg reflections.

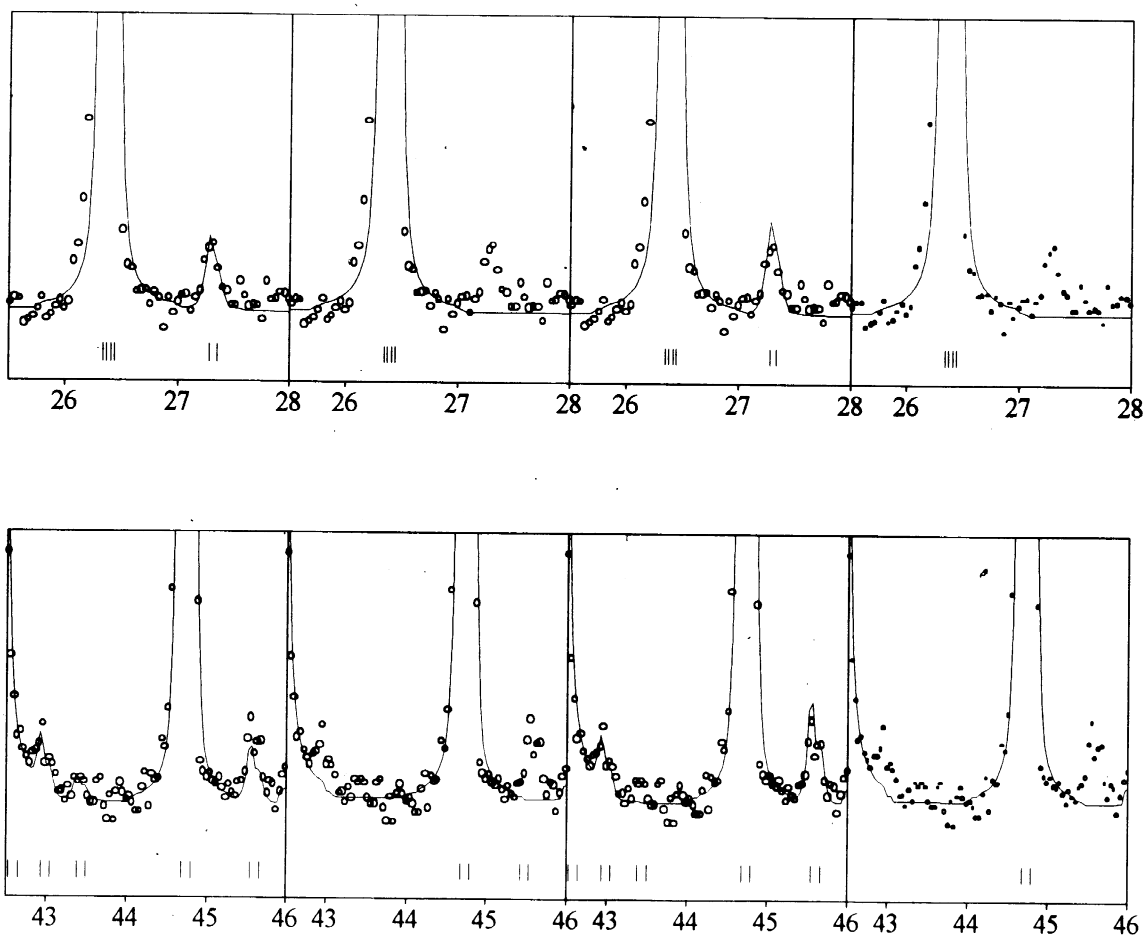

Fig. 2. X-ray diffraction patterns of $BaGd_2Mn_2O_7$ near some superlattice lines for the space group (a) *P4₂nm*, (b) *P-4n2*, (c) *P4₂/mnm* and (d) *I4/mmm*. The calculated and observed patterns are shown on the top solid lines and circles, respectively. The vertical marks under diffraction patterns show positions calculated for Bragg reflections.

two O2, O3 and O4 ions, coordinate to the central Mn ion with a rather shorter distance (mean distance = 0.196 nm), although these four oxygen ions are not on the identical plane. A tilting of the MnO_6 octahedron is emphasized by arrows in Fig. 3. On the other hands the distances between Mn and O1 or O5 are a little longer. Since the average distance between the trivalent Mn and the oxygen ions is 0.205 nm from the ionic radii of Shannon [15], only O5 is largely separated. The O5 ions are located on the outer end of perovskite blocks in the $BaGd_2Mn_2O_7$ structure and approaches to (Ba/Gd)2 ions. It is seen from these results that the Mn ion centered on the octahedron is not on the

Table 1
Crystallographic data for $BaGd_2Mn_2O_7$ from Rietveld refinement at room temperature

Space group	*P4₂/mnm* (No. 136)
a (nm)[a]	0.55024(1)
c (nm)[a]	2.02457(5)
Volume (nm^3)	0.61297
Z	4
Calculated density ($g\ cm^{-3}$)	7.300440
No. of reflections	556
No. of profile parameters refined	14
No. of structure parameters refined	17
No. atom (asymmetric unit)	8
Reliability factor (%)	
R_{wp}	14.32
R_P	10.97
R_E	7.41
R_I	5.92
R_F	6.34

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

Table 2
Fractional atomic coordinates of $BaGd_2Mn_2O_7$ at room temperature

Coordinates atom	Site	*x*[a]	*y*[a]	*z*[a]
(Ba,Gd)1	4f	0.254(1)	0.254(1)	0
(Ba,Gd)2	8j	0.2626(8)	0.2626(8)	0.1849(2)
Mn	8j	0.252(2)	0.252(2)	0.3973(6)
O1	4g	0.79(1)	−0.79(1)	0
O2	8h	0	0.5	0.118(3)
O3	4e	0	0	0.097(6)
O4	4e	0	0	0.394(6)
O5	8j	0.184(6)	0.184(6)	0.289(3)

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

Table 3
Interatomic distances of $BaGd_2Mn_2O_7$

	Interatomic distance (nm)[a]
(Ba,Gd) 1–O1×4	0.297(6)
(Ba,Gd) 1–O2×4	0.308(4)
(Ba,Gd) 1–O3×2	0.278(8)
(Ba,Gd) 1–O4×2	0.288(9)
(Ba,Gd) 2–O2×2	0.237(3)
(Ba,Gd) 2–O3×1	0.271(8)
(Ba,Gd) 2–O4×1	0.244(8)
(Ba,Gd) 2–O5×2	0.324(4)
(Ba,Gd) 2–O5×2	0.240(3)
(Ba,Gd) 2–O5×1	0.220(5)
Mn–O1×1	0.210(2)
Mn–O2×2	0.1970(9)
Mn–O3×1	0.193(2)
Mn–O4×1	0.196(2)
Mn–O5×1	0.225(6)

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

Table 4
Bond angles of $BaGd_2Mn_2O_7$

Bond angle (°)	
∠O1–Mn–O5	175(3)
∠O2–Mn–O2	162(3)
∠O3–Mn–O4	178(4)
∠Mn–O1–Mn	163(4)
∠Mn–O2–Mn	162(3)
∠Mn–O3–Mn	173(7)
∠Mn–O4–Mn	176.2(8)

center point of the octahedron. The environment of oxygen coordination around (Ba/Gd) ion is shown in Fig. 4. (Ba/Gd)1–oxygen (O1,O2,O3,O4) distances are almost the same, while the distances around (Ba/Gd)2 are widely dispersed. The overview of $BaGd_2Mn_2O_7$ is shown in Fig. 5. The way of rotation of oxygen octahedra surrounding the Mn ions are schematically drawn. The MnO_6 octahedra tilt each other around an axis along the [110] direction,

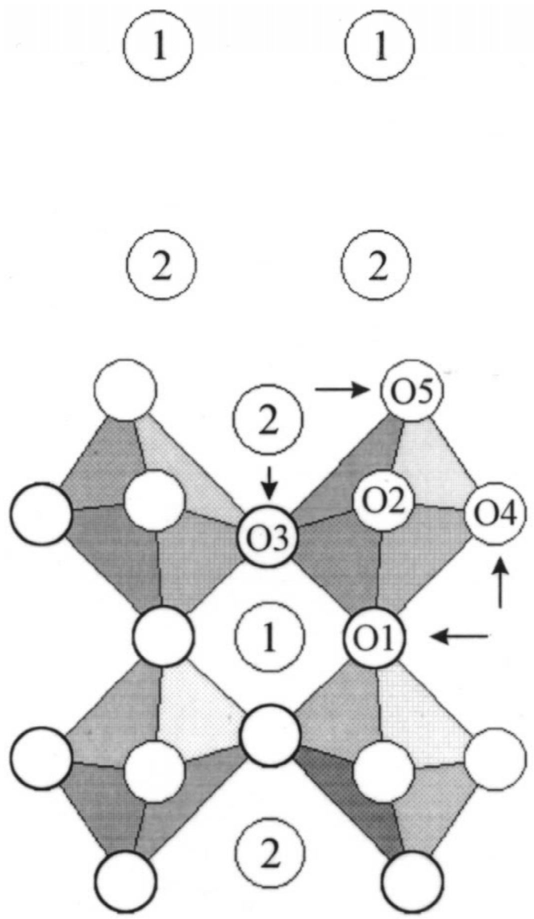

Fig. 3. MnO_6 octahedra of $BaGd_2Mn_2O_7$. The numbers 1 and 2 correspond to (Ba/Gd)1 and (Ba/Gd)2, respectively.

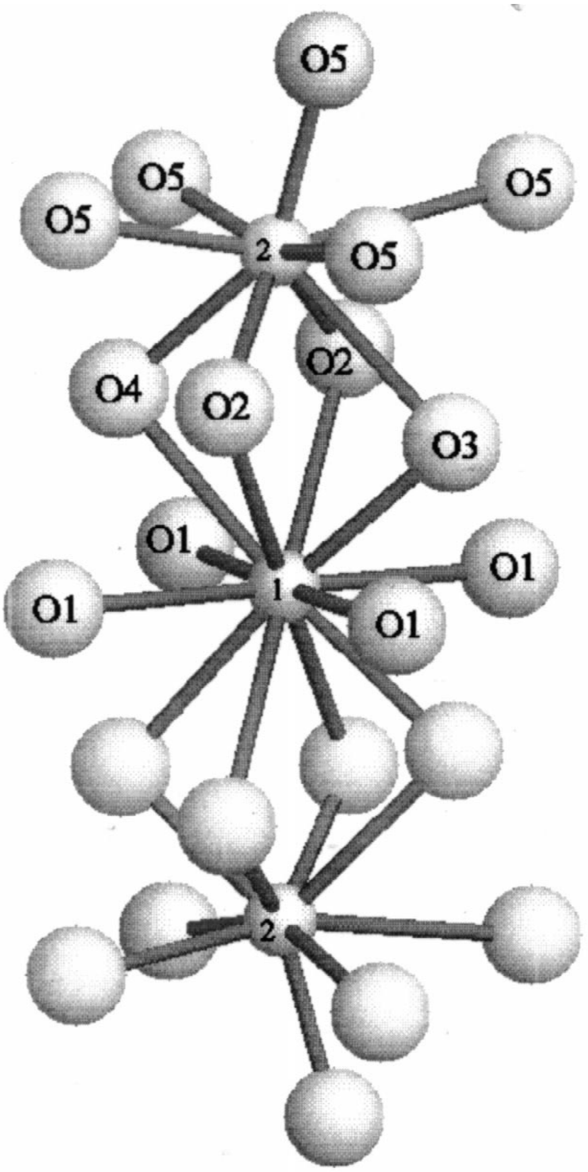

Fig. 4. Environment around the Ba/Gd site. The numbers 1 and 2 correspond to (Ba/Gd)1 and (Ba/Gd)2, respectively.

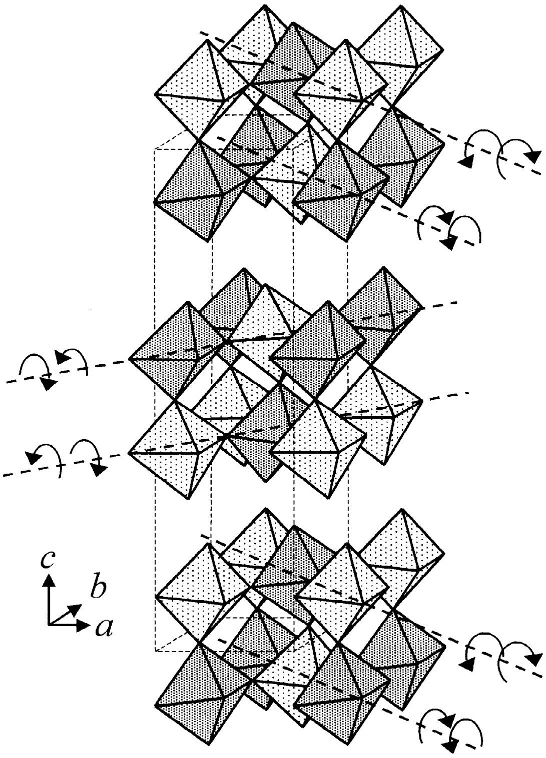

Fig. 5. The layer structure of MnO_6 octahedra tetragonal $BaGd_2Mn_2O_7$ with superstructure.

where a neighboring MnO_6 octahedron on an identical rotation axis tilts mutually towards the reverse direction. Therefore all the MnO_6 octahedra tilt towards a mutually reverted direction against the neighboring MnO_6 octahedra on the plane perpendicular to the *c*-axis and also against the neighboring MnO_6 along the *c*-axis. Also the direction of the rotation axis near $c=0$ is different by 90° from the rotation axis near $c=1/2$. The tilting angle of the MnO_6 octahedra is approximately 6°.

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