

Monoclinic $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ ($x = 0.185$) at 160 K

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Single-crystal X-ray diffraction has shown that lanthanum barium manganese trioxide, $\text{La}_{0.815}\text{Ba}_{0.185}\text{MnO}_3$, is monoclinic ($I2/c$) below a first-order phase transition at 187.1 (3) K. This result differs from the $Pbnm$ symmetry usually assigned to colossal magnetoresistance oxides, $A_{1-x}A'_x\text{MnO}_3$ with $x \simeq 0.2$, which adopt a distorted perovskite-type crystal structure. The Mn atom lies on an inversion center, the disordered Li/Ba site is on a twofold axis and one of the two independent O atoms also lies on a twofold axis.

Comment

$\text{La}_{0.815}\text{Ba}_{0.185}\text{MnO}_3$ is one of the manganese oxides in which colossal magnetoresistance (CMR) has been found (Jonker & van Santen, 1950; van Santen & Jonker, 1950). These compounds exhibit various superstructures on the basis of tilting of octahedra (Glazer, 1972). Accordingly, rhombohedral, orthorhombic and monoclinic symmetries have been found in $A_{1-x}A'_x\text{MnO}_3$ systems ($A = \text{La, Nd, Pr and Sm}$, and $A' = \text{Ca, Ba and Sr}$) with $x \simeq 0.2$ (Goodenough, 2004).

Dabrowski *et al.* (1998) have reported the results of X-ray powder diffraction on vacancy-free $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ ceramic compounds with $0.1 < x < 0.24$. At room temperature, these authors found orthorhombic $Pbnm$ symmetry for $x = 0.1$ and rhombohedral $R\bar{3}c$ symmetry for $x = 0.14\text{--}0.24$. For $x = 0.12$, the sample contained both phases. Arkhipov *et al.* (2000) reported the temperature dependence of the lattice parameters of $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$, also employing X-ray powder diffraction. According to their work, orthorhombic $Pbnm$ symmetry is found at temperatures of less than 185 K, whereas a phase with $R\bar{3}c$ symmetry is stable for temperatures higher than 196 K, with a first-order structural phase transition at 190.5 K.

Our investigations confirm the rhombohedral phase at high temperatures as well as the occurrence of a first-order phase transition at 187.1 (3) K, determined on cooling. However, we

have found a structure with monoclinic $I2/c$ symmetry for the low-temperature phase.

Both the rhombohedral and the monoclinic phases of $\text{La}_{0.815}\text{Ba}_{0.185}\text{MnO}_3$ are distorted perovskite-type structures, composed of corner-linked MnO_6 octahedra with La/Ba cations lying in the 12-fold coordinated cavities (Fig. 1). The tilting of the octahedra occurs in the same direction for both phases but with different magnitude, as described by the Mn—O—Mn angle, which takes only one value [$164.7(1)^\circ$] in the rhombohedral phase while there are two in the monoclinic phase (Table 1). The tilting pattern is expressed as $a^-a^-a^-$ and $a^-b^-b^-$ for rhombohedral $R\bar{3}c$ and monoclinic $I2/c$, respectively, which differ significantly from the $a^+a^-a^-$ pattern expected for orthorhombic $Pbnm$ (Glazer, 1972). Distortions of the octahedra in the two structures are also different, as described by the Mn—O distances and the O—Mn—O angles, which are 1.9742 (2) Å and $89.1(1)^\circ$, respectively, in the rhombohedral phase but which take three different values each in the monoclinic phase.

A monoclinic $I2/c$ structure was first reported for the compound $\text{La}_{0.788}\text{Sr}_{0.212}\text{Mn}_{0.958}\text{O}_3$ (Tamazyán *et al.*, 2002). Unlike the La/Sr analogue, which exhibits almost equal Mn—O—Mn angles, $\text{La}_{0.815}\text{Ba}_{0.185}\text{MnO}_3$ has two different Mn—O—Mn angles (Table 1). The Mn—O bonds have almost equal lengths, indicating a very small coherent Jahn–Teller distortion, as was found for the La/Sr compound. The degree of shear distortion of the MnO_6 octahedra is smaller in the La/Ba compound, as shown by the smaller deviations of O—Mn—O bond angles from 90° . The effect of the larger cation radius is evidenced by larger lattice parameters as well as by different A—O ($A = \text{La and Ba or La and Sr}$) distances than in $\text{La}_{0.788}\text{Sr}_{0.212}\text{Mn}_{0.958}\text{O}_3$.

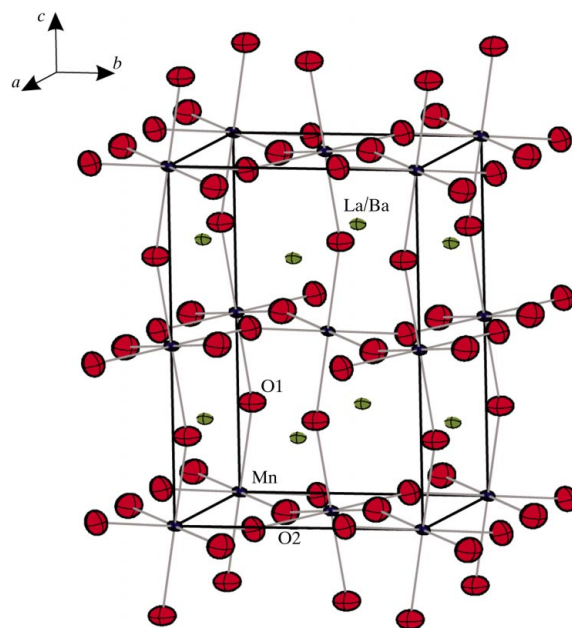


Figure 1

A perspective view of the monoclinic crystal structure of $\text{La}_{0.815}\text{Ba}_{0.185}\text{MnO}_3$.

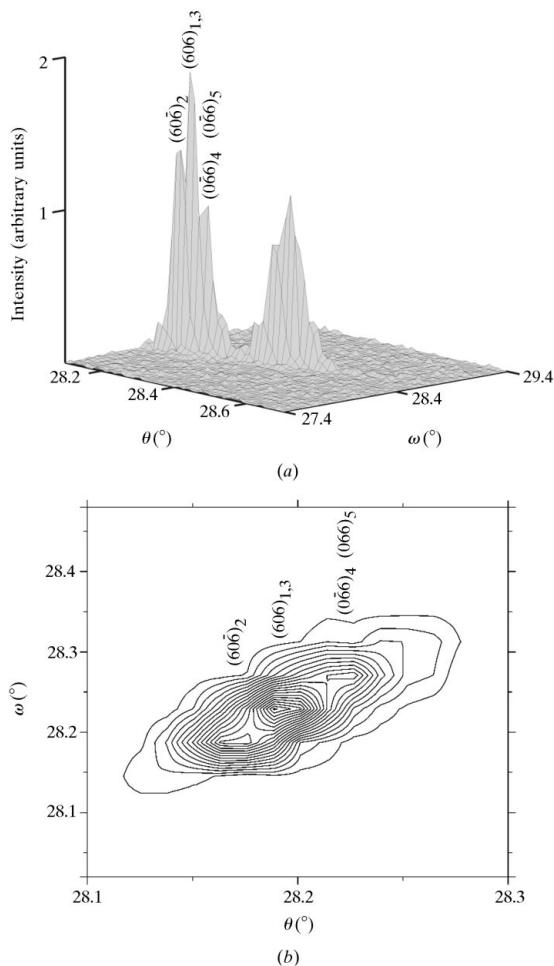


Figure 2
The ω - θ profile of the $(333)_c$ reflection. (a) A three-dimensional plot showing both the $K\alpha_1$ and the $K\alpha_2$ peaks. Miller indices with subscripts referring to the five twin domains given in Table 2 are indicated. (b) A contour plot of the $K\alpha_1$ peak.

We report here the discovery of a second monoclinic structure for the class of perovskite-type compounds $A_{1-x}A'_xMnO_3$ with $x \simeq 0.2$. In light of this result, the (x, T) phase diagrams of these systems would need to be revised (Zhou & Goodenough, 2001).

Experimental

Single crystals of nominal composition $La_{0.8}Ba_{0.2}MnO_3$ were grown by the non-crucible floating zone technique (Mukovskii *et al.*, 2001). Electron microprobe analysis revealed an La:Ba:Mn ratio of 0.815 (10):0.185 (6):0.996 (8). The nominal and real Ba contents differ as a result of evaporation of barium during melting.

Crystal data

$Ba_{0.185}La_{0.815}MnO_3$
 $M_r = 241.6$
 Monoclinic, $I2/c$
 $a = 5.564$ (2) Å
 $b = 5.510$ (2) Å
 $c = 7.802$ (3) Å
 $\beta = 90.18$ (3)°
 $V = 239.19$ (14) Å³
 $Z = 4$
 $D_x = 6.706$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 18.4$ – 29.8 °
 $\mu = 22.37$ mm⁻¹
 $T = 160$ K
 Rectangular prism, translucent dark brown
 0.13 × 0.06 × 0.05 mm

Data collection

Nonius MACH3 diffractometer
 ω scans
 Absorption correction: ψ scan (HABITUS; Herrendorf & Bärnighausen, 1997)
 $T_{min} = 0.193$, $T_{max} = 0.327$
 1567 measured reflections
 1567 independent reflections

1184 reflections with $I > 3\sigma(I)$
 $\theta_{max} = 39.9$ °
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -9 \rightarrow 14$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F
 $R[F^2 > 3\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.033$
 $S = 1.68$
 1567 reflections
 31 parameters
 Weighting scheme based on measured s.u.'s
 $w = 1/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 3.02$ e Å⁻³
 $\Delta\rho_{min} = -2.99$ e Å⁻³
 Extinction correction: B–C type 1
 Gaussian isotropic (Becker & Coppens, 1974)
 Extinction coefficient: 0.0028 (1)

Table 1
Selected geometric parameters (Å, °).

Mn–O1	1.9755 (7)	La–O1 ^{iv}	2.457 (4)
Mn–O2	1.975 (3)	La–O2 ^v	2.599 (3)
Mn–O2 ⁱ	1.968 (3)	La–O2 ⁱⁱ	2.932 (3)
La–O1 ⁱⁱ	2.8014 (5)	La–O2 ^{iv}	2.947 (3)
La–O1 ⁱⁱⁱ	3.053 (4)	La–O2 ^{vi}	2.594 (3)
O1–Mn–O2 ^{vii}	89.54 (12)	Mn–O1–Mn ^{ix}	161.7 (2)
O1–Mn–O2 ⁱ	89.81 (12)	Mn–O2–Mn ^x	166.44 (17)
O2–Mn–O2 ^{viii}	89.75 (14)		

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z$; (ii) $x - \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x, -y, -z + 1$; (iv) $-x, -y + 1, -z + 1$; (v) $x, y, z + 1$; (vi) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x, -y, -z$; (viii) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (ix) $-x, y, -z + \frac{1}{2}$; (x) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$.

Table 2

Twin volume fractions as refined in monoclinic $I2/c$ for $La_{0.815}Ba_{0.185}MnO_3$ at 160 K.

Twin Domain	V1	V2	V3	V4	V5
Volume Fraction	0.61 (2)	0.29 (1)	0.05 (1)	0.04 (1)	0.02 (1)

A piece cut from the crystalline material was used for single-crystal X-ray diffraction. We found a crystal structure with space group $R\bar{3}c$ at room temperature (296 K), in accordance with previous studies (Arkhipov *et al.*, 2000). At 160 K, the diffraction peaks appeared to be split in ω scans. The centering of 25 reflections showed an eightfold pseudo-cubic supercell, $2a_c \times 2a_c \times 2a_c$ (the subscript c refers to the primitive cubic perovskite unit cell), with $a = 7.830$ (3) Å, $b = 7.802$ (3) Å, $c = 7.832$ (2) Å, $\alpha = 90.12$ (2)°, $\beta = 90.56$ (3)° and $\gamma = 90.13$ (3)°. The distortions from cubic lattice symmetry indicate that the true lattice is $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$, with either orthorhombic $Pbnm$ or $Imcm$, or monoclinic $I2/c$ symmetry [see Fig. 1 of Tamazyan *et al.* (2002)]. The splitting of reflections can be explained by twinning. Because the transition is first-order, every symmetry operator of the $m\bar{3}m$ point group that is not part of the crystal class (mmm or $2/m$) may become a twinning operator (Tamazyan *et al.*, 2002) and any orientation of the low-temperature structure within the hypothetical cubic perovskite lattice may occur. This is confirmed by the orientations of the five twin domains (out of a total of 12) with significant volume fractions (Table 2). Among them, two pairs of domains are related by a fourfold axis. The characteristic n -fold splitting of the pseudo-cubic $(hh0)_c$ and $(hhh)_c$ reflections is identified

by means of measured ω - θ sections and compared with the number of maxima expected for different symmetries (Tamazyán *et al.*, 2002). Fig. 2 shows that the $(333)_c$ reflection is split into three peaks in accordance with monoclinic symmetry and at variance with orthorhombic symmetry. Twin matrices applied to the Miller indices (hkl are multiplied from the left) are the following: $M1 = (100|010|001)$, $M2 = (\frac{1}{2}\frac{1}{2}|\frac{1}{2}\frac{1}{2}|\bar{1}\bar{1}0)$, $M3 = (\frac{1}{2}\frac{1}{2}|\frac{1}{2}\frac{1}{2}|\bar{1}\bar{1}0)$, $M4 = (\frac{1}{2}\frac{1}{2}|\frac{1}{2}\frac{1}{2}|\bar{1}\bar{1}0)$, $M5 = (010|100|001)$. Structure refinements against all reflections led to $R(\text{obs}) = 2.70, 3.23$ and 3.46% for $I2/c$, $Pbnm$ and $Imcm$, respectively. Additional tests were made by computing partial R values with the contributions of superlattice reflections only, which led to $R(\text{obs})/R(\text{all}) = 8.50/17.7, 11.93/74.1$ and $18.27/31.1$ for $I2/c$, $Pbnm$ and $Imcm$, respectively. Measured intensity data show 45 observed reflections violating the I -centering. However, they are weak and belong mainly to $\{110\}$ in the eightfold pseudo-cubic superlattice. Such reflections can be explained as produced by $\lambda/2$ radiation, since $\{220\}$ reflections are very strong. The particularly high partial $R(\text{all})$ value for $Pbnm$ demonstrates that the observed reflections violating the I -centering are not a result of structural effects. Because many studies of orthorhombic and monoclinic manganites report lattice parameters with $a > b$, we performed additional refinements in this setting and checked the possibility of $\beta < 90^\circ$. However, the splitting of the reflections prevented the unambiguous assignment of correct values to a and b ($a > b$ or $a < b$). The best fit to the diffraction data was obtained in the monoclinic setting with $a > b$. This choice is confirmed by the observed maxima positions in the ω - θ section in Fig. 2, since the middle position of the strongest peak is only possible by assuming $a > b$ (by assuming $a < b$, the strongest peak would have occurred on the right side at higher θ). In the difference Fourier map the largest residuals are located 0.36 and 0.60 \AA , respectively, from the La/Ba atom.

Data collection: *DATCOL* in *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *SETANG* and *LS* in *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997) and *HABITUS* (Herrendorf & Bärnighausen, 1997); program(s) used to solve structure: *JANA2000*

(Petricek *et al.*, 2000); program(s) used to refine structure: *JANA2000*; molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *JANA2000*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1071). Services for accessing these data are described at the back of the journal.

References

- Arkhipov, V. E., Bebenin, N. G., Dyakina, V. P., Gaviko, V. S., Korolev, A. V., Mashkautsan, V. V., Neifeld, E. A., Zainullina, R. I., Mukovskii, Ya. M. & Shulyatev, D. A. (2000). *Phys. Rev. B: Condens. Matter*, **61**, 11229–11231.
- Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–153.
- Brandenburg, K. (2005). *DIAMOND*. Version. 3.0c. Crystal Impact GbR, Bonn, Germany.
- Dabrowski, B., Rogacki, K., Xiong, X., Klamut, P. W., Dybzinski, R., Shaffer, J. & Jorgensen, J. D. (1998). *Phys. Rev. B: Condens. Matter*, **58**, 2716–2723.
- Enraf-Nonius (1989). *CAD-4 Software*. Enraf-Nonius, Delft, The Netherlands.
- Glazer, A. M. (1972). *Acta Cryst.* **B28**, 3384–3392.
- Goodenough, J. B. (2004). *Rep. Prog. Phys.* **67**, 1915–1993.
- Herrendorf, W. & Bärnighausen, H. (1997). *HABITUS*. University of Karlsruhe, Gießen, Germany.
- Jonker, G. H. & van Santen, J. H. (1950). *Physica (Amsterdam)*, **16**, 337–349.
- Mukovskii, Ya., Arkhipov, V., Arsenov, A., Bebenin, N., Dyakina, V., Gaviko, V., Korolev, A., Karabashev, S., Mashkautsan, V., Neifeld, E., Shulyatev, D. & Zainullina, R. I. (2001). *J. Alloys Compd.* **326**, 108–111.
- Petricek, V., Dusek, M. & Palatinus, L. (2000). *JANA2000*. Institute of Physics, Prague, Czech Republic.
- Santen, J. H. van & Jonker, G. H. (1950). *Physica (Amsterdam)*, **16**, 599–600.
- Spek, A. L. (1997). *HELENA*. University of Utrecht, The Netherlands.
- Tamazyán, R., van Smaalen, S., Arsenov, A. & Mukovskii, Ya. (2002). *Phys. Rev. B: Condens. Matter*, **66**, 224111–1–224111-7.
- Zhou, J.-S. & Goodenough, J. B. (2001). *Phys. Rev. B: Condens. Matter*, **64**, 024421–1–024421-4.