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Twinning and structure of $Eu_{0.6}Sr_{0.4}MnO_3$

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The crystal structure of europium strontium manganese trioxide, $Eu_{0.6}Sr_{0.4}MnO_3$, has been refined using a multiply twinned single crystal containing six twin components. The MnO_6 octahedra show Jahn–Teller distortions with nearly fourfold symmetry, but the octahedral tilting scheme reduces the crystal symmetry to orthorhombic (space group *Pbnm*). The refinement of site occupancies and the analysis of difference Fourier maps show that the Eu^{3+} and Sr^{2+} cations occupy different crystallographic positions with eightfold and twelvefold coordination, respectively.

Comment

The $Ln_{1-x}M_xMnO_3$ manganites, where Ln is a trivalent rare earth element and *M* is a divalent element (Ca, Sr or Ba), are of interest because colossal magnetoresistance (CMR) has been observed for this class of compounds (Jonker & van Santen, 1950). Depending on the value of *x* and the temperature, these compounds display different crystal structures as well as different magnetic and transport properties. The physical properties of these compounds also depend on the rare earth element. The structural data on these compounds available in the literature are mainly obtained from powder diffraction data, and only a limited number of structure determinations and refinements are based on single-crystal diffraction data (Tamazyan *et al.*, 2002). In this paper, we describe the results of a structural investigation based on single-crystal X-ray diffraction on twinned crystals of $Eu_{0.6}Sr_{0.4}MnO_3$.

The structures of the $Ln_{1-x}M_xMnO_3$ compounds are distorted derivatives of the cubic perovskite structure type (a_c = 3.8 Å, space group *Pm*3*m*). Depending on the Ln and *M* elements, the *x* parameter and the temperature, rhombohedral, tetragonal, orthorhombic and monoclinic distortions have been observed (Dabrowski *et al.*, 1999; Jirak *et al.*, 2000; Urushibara *et al.*, 1995; Cox *et al.*, 2001). Symmetry elements of the *m*3*m* cubic point group which are not symmetry elements of the derivative structures become twinning operators. For $Eu_{0.6}Sr_{0.4}MnO_3$, we find that the symmetry is orthorhombic (space group *Pbnm*) with a $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$ supercell of the cubic perovskite cell. Hence, six twin components can be expected. The results of refinements show that all six twin components are present in the sample; the twin

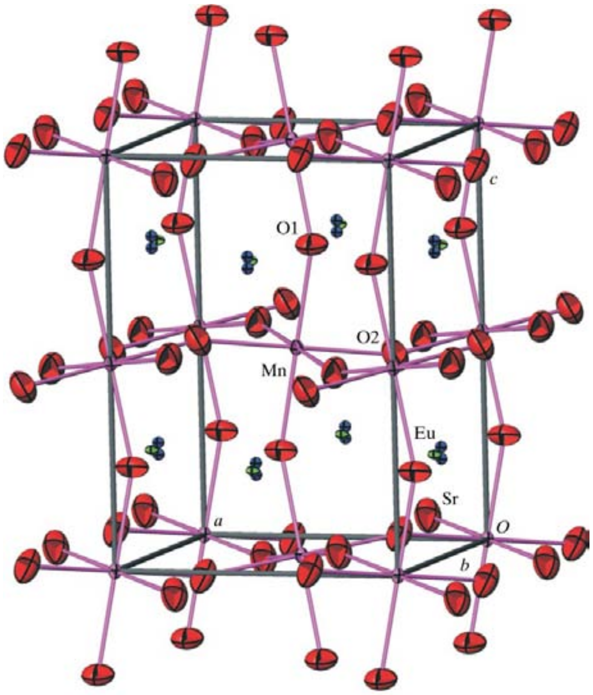

Figure 1
A perspective view of $Eu_{0.6}Sr_{04}MnO_3$. Displacement ellipsoids are shown at the 50% probability level, and the splitting of Eu and Sr positions is also shown.

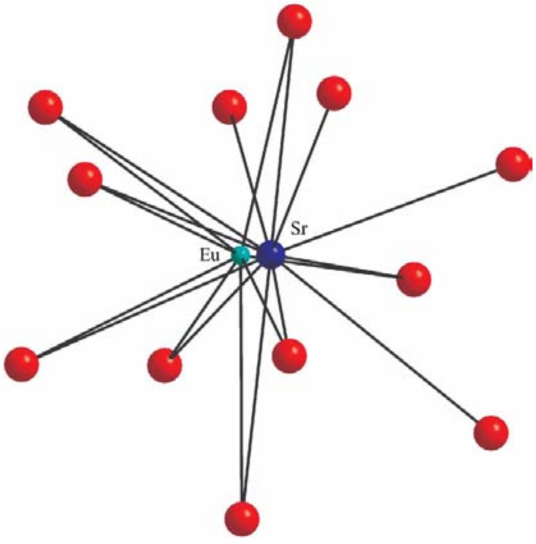

Figure 2
The distorted cuboctahedral coordination of Eu and Sr.

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volume ratios are given in Table 2. Structural distortions corresponding to the lowering of symmetry from cubic to orthorhombic are Jahn–Teller (JT) distortions of the MnO_6 octahedra and tiltings of these octahedra (Fig. 1). In contrast to other orthorhombic distorted perovskite structures, where the JT distortions of MnO_6 correspond to three different lengths for Mn—O bonds, the JT distortions in this structure are almost tetragonal, with nearly equal Mn—O bond lengths [1.9489 (12) Å for Mn—O1 and 1.949 (6) Å for Mn—O2^{i}; symmetry code: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, z$]. However, the MnO_6 octahedra tilting scheme reduces the symmetry to orthorhombic instead of tetragonal. A perspective view of the structure is shown in Fig. 1. In the ideal cubic perovskite structure, the Ln atoms are surrounded by 12 O atoms in a cuboctahedral coordination. A mismatch of Ln—O and Mn—O bond lengths causes tilting of the octahedra and deforms the cuboctahedron, making it suitable to accommodate smaller Ln cations. Their coordination numbers might be reduced from 12 to 7 depending on the Ln ionic radii. In $Eu_{0.6}Sr_{0.4}MnO_3$, the ionic radii of the Eu^{3+} and Sr^{2+} ions differ by a large amount. The smaller Eu^{3+} ions prefer sixfold or sevenfold coordination, while the larger Sr^{2+} ions prefer tenfold or twelvefold coordination. This is probably the reason why the Eu and Sr atoms do not occupy the same crystallographic position. The Eu^{3+} ions are shifted from the center of the distorted cuboctahedron, resulting in a reduced coordination number of 8 (Fig. 2 and Table 1). The Sr^{2+} ions have a small shift in a direction perpendicular to the mirror plane, but remain close to the center of the twelvefold-coordinated polyhedron. Their coordination numbers can be considered as 12, with two relatively long Sr—O distances (Fig. 2 and Table 1). The distance between the Eu and Sr positions is 0.307 (6) Å. It is assumed that replacement of Eu^{3+} by Sr^{2+} transforms the same amount of Mn^{3+} into Mn^{4+}. Bond-valance-sum (BVS) calculations (Brown & Altermatt, 1985) yield a value of 3.58 for the Mn site. This value differs from that expected for an $Mn^{3+}_{0.6}/Mn^{4+}_{0.4}$ mixture, *viz*. 3.4, by ~5%. The BVS values for Eu^{3+} and Sr^{2+} are 2.46 and 2.98, respectively. Such a large deviation of the BVS values from the expected values shows that the coordination polyhedron around the Eu/Sr position is too large for Eu^{3+} and too small for Sr^{2+}. Accordingly, an Eu/Sr ordering could be expected but was not detected. We believe that the observed splitting of the Eu and Sr positions partially reduces local deformations caused by the difference in ionic radii. On the other hand, these local deformations may cause local stresses on the MnO_6 octahedra, which may play an essential role in determining the physical properties of this material.

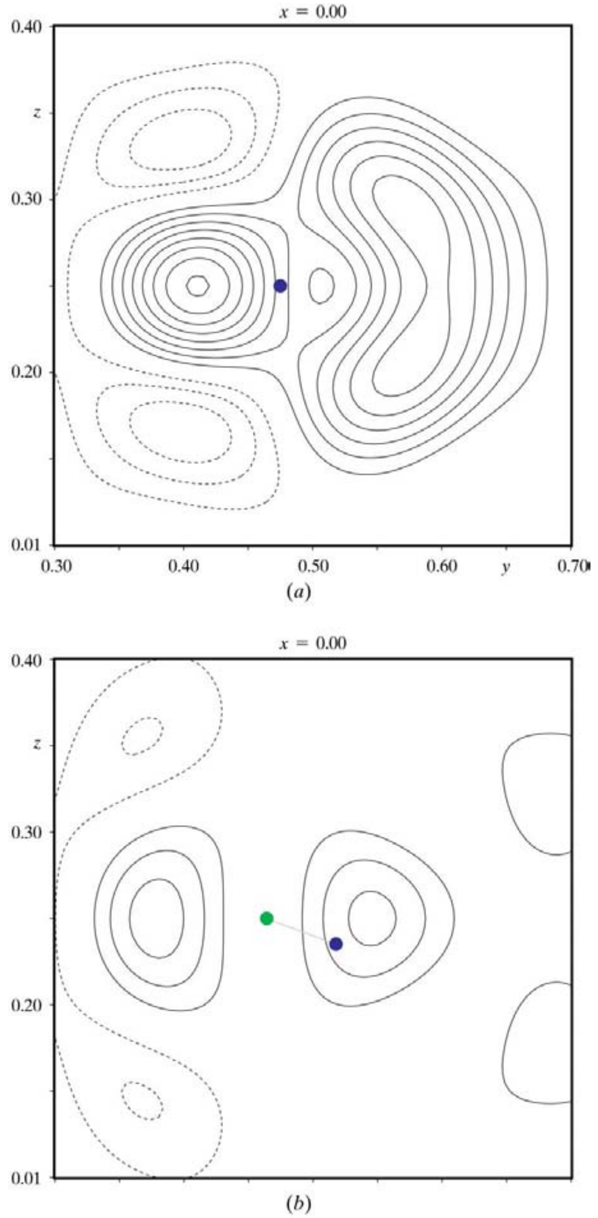

Figure 3
yz sections of difference Fourier maps. Contour lines are at intervals of 0.5 e Å^{-3}. (*a*) Structure model with one Eu/Sr position (filled circle) and (*b*) structure model with split Eu (filled circle, left) and Sr (filled circle, right) positions.

Experimental

A cylindrical rod of single-crystalline $Eu_{0.6}Sr_{0.4}MnO_3$ was grown by the floating zone technique with radiation heating (Mukovskii *et al.*, 2001). Feed rods were prepared from Mn_3O_4, $SrCO_3$ and Eu_2O_3 powders, which were mixed in accordance with the desired metal composition $Eu_{0.6}Sr_{0.4}Mn$. The metal composition of the single-crystalline sample from the same batch was determined by electron microprobe analysis. $SrSO_4$, $MnTiO_3$ and a glass containing Eu_2O_3 (12 wt%; P&H Developments Ltd, England) were used as standards for Sr, Mn and Eu, respectively. The analytical result is in good agreement with the nominal metal composition Eu:Sr:Mn = 0.590 (7):0.406 (8):1.004 (8).

Crystal data

$Eu_{0.59}Sr_{0.41}MnO_4$
M_r = 228.50
Orthorhombic, *Pbnm*
a = 5.429 (1) Å
b = 5.443 (1) Å
c = 7.660 (2) Å
V = 226.35 (8) Å^3
Z = 4
D_x = 6.700 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 18.7–23.1°
μ = 31.12 mm^{-1}
T = 293 (2) K
Prism, black
0.08 × 0.05 × 0.02 mm

Data collection

Nonius MACH3 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*HABITUS*; Herrendorf & Bärnighausen, 1997)
$T_{\min} = 0.150$, $T_{\max} = 0.603$
2578 measured reflections
2578 independent reflections
1539 reflections with $I > 3\sigma(I)$

$R_{\rm int} = 0.000$
$\theta_{\max} = 30.1°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.044$
$S = 1.28$
2574 reflections
38 parameters
$w = 1/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.05$ e Å^{-3}
$\Delta\rho_{\min} = -2.85$ e Å^{-3}
Extinction correction: B-C type 1 Gaussian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.0011 (2)

Table 1
Selected geometric parameters (Å, °).

Mn—O1	1.9489 (12)	Sr—O1$^{\rm ii}$	2.367 (10)
Mn—O2	1.954 (6)	Sr—O1$^{\rm vii}$	3.067 (10)
Mn—O2$^{\rm i}$	1.949 (6)	Sr—O1$^{\rm iii}$	2.784 (7)
Eu—Sr	0.307 (6)	Sr—O1$^{\rm viii}$	2.713 (7)
Eu—O1$^{\rm ii}$	2.409 (7)	Sr—O2	2.819 (8)
Eu—O1$^{\rm iii}$	2.504 (5)	Sr—O2$^{\rm ii}$	3.093 (8)
Eu—O2	2.578 (5)	Sr—O2$^{\rm i}$	2.405 (8)
Eu—O2$^{\rm i}$	2.460 (5)	Sr—O2$^{\rm iii}$	2.892 (8)
Eu—O2$^{\rm iii}$	2.701 (5)	Sr—O2$^{\rm iv}$	2.722 (8)
Eu—O2$^{\rm iv}$	2.701 (5)	Sr—O2$^{\rm v}$	2.250 (8)
Eu—O2$^{\rm v}$	2.460 (5)	Sr—O2$^{\rm ix}$	2.935 (8)
Eu—O2$^{\rm vi}$	2.578 (5)	Sr—O2$^{\rm vi}$	2.688 (8)
O1—Mn—O2$^{\rm vii}$	90.2 (2)	Mn$^{\rm xi}$—O1—Mn	158.6 (4)
O1—Mn—O2$^{\rm i}$	90.3 (2)	Mn$^{\rm xii}$—O2—Mn	159.9 (3)
O2—Mn—O2$^{\rm x}$	90.9 (2)		

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (ii) $-x, -y+1, -z+1$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x, y, -z+\frac{1}{2}$; (vii) $-x+1, -y+1, -z+1$; (viii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ix) $-x, -y+1, z-\frac{1}{2}$; (x) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (xi) $-x+1, -y+1, z+\frac{1}{2}$; (xii) $-x+\frac{1}{2}, y-\frac{1}{2}, z$.

Table 2
Refined twin volume fractions in orthorhombic (*Pbnm*) $\rm Eu_{0.6}Sr_{0.4}MnO_3$.

Twin domain	*V*1	*V*2	*V*3	*V*4	*V*5	V6
Volume fraction	0.417 (3)	0.212 (2)	0.098 (1)	0.140 (1)	0.079 (1)	0.054 (1)

All reflections found using the SEARCH procedure of *CAD-4 Software* (Enraf–Nonius, 1988) were indexed in the pseudo-cubic eightfold $2a_{\rm c} \times 2a_{\rm c} \times 2a_{\rm c}$ perovskite unit cell. The crystal quality was tested by rotation photographs along the three crystallographic directions of the related perovskite lattice and by performing ω scans on selected Bragg reflections. They showed splitting, hinting at possible twinning. The diffraction pattern indexed on the basis of the $2a_{\rm c} \times 2a_{\rm c} \times 2a_{\rm c}$ unit cell may be interpreted as being a result of overlapping of diffraction patterns from three orthorhombic structures with $2^{1/2}a_{\rm c} \times 2^{1/2}a_{\rm c} \times 2a_{\rm c}$ unit cells related to each other by the threefold symmetry axis of the pseudo-cubic unit cell. The axial mirror planes of the pseudo-cubic lattice may become twinning operators too, increasing the number of possible twin components to 6. The $2^{1/2}a_{\rm c} \times 2^{1/2}a_{\rm c} \times 2a_{\rm c}$ orthorhombic unit cell has been observed for many $\mathrm{Ln}_{1-x}M_x\mathrm{MnO}_3$ compounds. The space group *Pbnm* was used to describe the structures of these compounds. For the structure determination, the integrated intensity of Bragg reflections were collected in half a sphere of reciprocal space. The common symmetry of overlapped orthorhombic diffraction patterns determining the Laue symmetry is $\bar{1}$. Refinement confirms the six-component twin model described above. The following twin matrices have been applied to the Miller indices (*hkl* are multiplied from the left): $M1 = (100/010/001)$, $M2 = (0\bar{1}0/100/001)$, $M3 = (\frac{1}{2}\frac{1}{2}\frac{1}{2}/\frac{1}{2}\frac{1}{2}\frac{\bar{1}}{2}/\bar{1}10)$, $M4 = (\frac{1}{2}\frac{1}{2}\frac{\bar{1}}{2}/\frac{1}{2}\frac{1}{2}\frac{1}{2}/1\bar{1}0)$, $M5 = (\frac{1}{2}\frac{\bar{1}}{2}\frac{1}{2}/\frac{1}{2}\frac{\bar{1}}{2}\frac{\bar{1}}{2}/110)$, $M6 = (\frac{1}{2}\frac{\bar{1}}{2}\frac{\bar{1}}{2}/\frac{1}{2}\frac{1}{2}\frac{1}{2}/\bar{1}\bar{1}0)$. Initially, the same positional and displacement parameters were refined for both Eu and Sr, but difference Fourier maps showed that they do not occupy the same position (Fig. 3*a*). The refinement of separate positions reduced the *R* value from 0.048 to 0.040, and features in the difference Fourier map were also considerably reduced (Fig. 3*b*). Because of large correlations, it was not possible to refine anisotropic displacement parameters for Sr. The relatively large isotropic displacement parameter of Sr is believed to reflect disorder (the shift of Sr from the mirror plane), giving rise to correlation between the *y* coordinate and the displacement parameter. The Eu/Sr ratio was refined by restraining the sum of occupancies of the Eu and Sr positions to 1. The refined values [0.589 (7) Eu + 0.411 (7) Sr] are in excellent agreement with the results of the microprobe analysis. The maximum and minimum values in the final electron-density difference map were observed near the Eu/Sr positions at (0.04; 0.35)/4 and (0.06; 0.47)/4, respectively.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1988); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *JANA2000* (Petricek & Dusek, 2000); program(s) used to refine structure: *JANA2000*; molecular graphics: *DIAMOND* (Brandenburg, 1999); 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: BC1078). Services for accessing these data are described at the back of the journal.

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