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2004 J. Phys.: Condens. Matter 16 3879

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Structural phase transitions in the ordered double perovskite $\text{Sr}_2\text{MnTeO}_6$

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Received 24 March 2004


Published 28 May 2004

Online at stacks.iop.org/JPhysCM/16/3879

DOI: 10.1088/0953-8984/16/23/008

Abstract

The crystal structure of the ordered double perovskite $\text{Sr}_2\text{MnTeO}_6$ has been refined at ambient temperature from high resolution neutron and x-ray powder diffraction data in the monoclinic space group $P12_1/n1$ with $a = 5.7009(1) \text{ \AA}$, $b = 5.6770(1) \text{ \AA}$, $c = 8.0334(1) \text{ \AA}$ and $\beta = 90.085(1)^\circ$. This represents a combination of in-phase (+) and out-of-phase (–) rotations of virtually undistorted MnO_6 and TeO_6 octahedra in the (– – +) sense about the axes of the ideal cubic perovskite. High temperature x-ray powder diffraction shows three structural phase transitions at approximately 250, 550 and 675 °C, each corresponding to the disappearance of rotations about one of these axes. The first transition was analysed by differential scanning calorimetry and showed a thermal hysteresis with an enthalpy of 0.55 J g^{-1} . We propose the ($P12_1/n1 \rightarrow I12/m1 \rightarrow I4/m \rightarrow Fm\bar{3}m$) sequence of structural transitions which has not been previously reported for a double perovskite oxide.

 Supplementary data files are available from stacks.iop.org/JPhysCM/16/3879

1. Introduction

The study of transition metal oxides with double perovskite type structure, $\text{A}_2\text{BB}'\text{O}_6$, began in the early 1950s, and many of the double perovskites were discovered and studied from the late 1950s to the mid-1970s [1]. In the late 1990s these ordered perovskites gained attention due to their magnetoresistance properties at room temperature, $\text{Sr}_2\text{FeMoO}_6$ [2], and their ability to support superconductivity, $\text{Sr}_2\text{YRu}_{0.85}\text{Cu}_{0.15}\text{O}_6$ [3].

These studies, however, have been mainly focused on the effect of the systematic change of size and oxidation state of the A, B and B' cations on the magnetic and electrical properties of the resulting oxides. Such attention has not been paid to the structural aspects of these materials and, consequently, the crystal structures of several technologically important compounds have been misassigned, a clear example being $\text{Sr}_2\text{FeMoO}_6$, the crystal structure of which has been explained considering at least four different space groups, from distorted tetragonal $P4_2/n$ to 'ideal' cubic $Fm\bar{3}m$ [4].

In an ABO_3 simple cubic perovskite, described by the $Pm\bar{3}m$ space group with a primitive cell parameter, a_p , distortions arise from three mechanisms: cation displacements within the BO_6 octahedra and distortions and tiltings of these octahedra. Glazer [5] classified the resulting structures considering that the most important factors determining the crystal structure of a perovskite oxide were the tilts of the rigid octahedra, although many of the resulting space groups also allow them to be distorted. Glazer's classification scheme did not, however, consider perovskites in which two different B cations order in the lattice. It was Woodward [6] who extended that scheme to the $\text{A}_2\text{BB}'\text{O}_6$ ordered double perovskites (described by the $Fm\bar{3}m$ space group and a $2a_p$ cell parameter when ideal cubic). Since Woodward, many authors have published similar, and sometimes more complicated, schemes in which a combination of distortions and different types of B-cation ordering are responsible for the reduction of symmetry [4, 7, 8].

The high degree of pseudosymmetry inherent to these materials makes them excellent candidates for the observation of structural phase transitions which can then be related to their physical properties. It is widely known that the topology (the arrangement of atoms) of the perovskite structure is thermodynamically extremely stable, whereas its actual crystal structure (the position of the atoms) appears to be very unstable [9]. Literature concerning detailed determination of the structural transitions of ordered double perovskite type oxides is very scarce, and only recently have there appeared systematic crystallographic studies [10–13].

Here we report the synthesis, room temperature crystal structure determination and the structural phase transitions that occur at elevated temperatures of the ordered double perovskite $\text{Sr}_2\text{MnTeO}_6$, which was previously wrongly described as an ordered double-perovskite with a tetragonal cell of $a = 8.03 \text{ \AA}$ and $c = 8.13 \text{ \AA}$, in an article in which no crystallographic data were presented [14].

2. Experimental details

Polycrystalline $\text{Sr}_2\text{MnTeO}_6$ was synthesized by the freeze-drying method. Stoichiometric quantities of SrCO_3 , $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ and TeO_2 were dissolved in dilute aqueous nitric acid. The solution was drop-by-drop frozen under liquid nitrogen. The frozen solution was subsequently freeze-dried and the powder obtained was ground and calcined at $900 \text{ }^\circ\text{C}$ for 6 h. The sample was ground, pelleted and calcined four times for 8 h at $975 \text{ }^\circ\text{C}$. Phase purity was confirmed by x-ray powder diffraction and the expected content of Sr, Mn and Te by inductively coupled plasma atomic emission spectroscopy (ICP-AES) performed with an ARL Fisons 3410 spectrometer (content: observed Sr, 36(1), Mn, 11.4(1) and Te, 28(1); calculated Sr 38.6, Mn 12.1, Te 28.1).

High resolution neutron powder diffraction data were collected at room temperature on Instrument D2B (Institut Laue Langevin (ILL), Grenoble, France). Thermal neutrons of wavelength 1.594 \AA were incident on 10 g of polycrystalline $\text{Sr}_2\text{MnTeO}_6$, packed in an 8 mm diameter vanadium can. Data were collected in the angular range $5^\circ \leq 2\theta \leq 162^\circ$ in steps of 0.05° with an integration time of 50 000 monitor counts per step and with each point in the diffraction pattern being recorded by six independent detectors for subsequent normalization and summation, giving an overall collection time of approximately 3 h for the entire data set.

Room temperature x-ray powder diffraction data were collected in the range $17^\circ \leq 2\theta \leq 105^\circ$ with an integration time of 17 s per 0.02° step using a Philips X'Pert-MPD x-ray diffractometer with secondary beam graphite monochromated Cu K α radiation.

Temperature resolved x-ray diffraction data were collected using an Anton Paar HTK16 temperature chamber with a platinum stage mounted in the same diffractometer. The sample for high temperature measurement was mixed with acetone and a high temperature resin and applied to the Pt stage. In order to monitor the evolution of several characteristic peaks, data were collected in the following angular ranges every 10°C from 50 to 600°C : $43^\circ \leq 2\theta \leq 53^\circ$ and $81.5 \leq 2\theta \leq 84.5^\circ$. Higher quality, temperature dependent x-ray diffraction data for subsequent Rietveld refinement were collected in the range $17^\circ \leq 2\theta \leq 87^\circ$ in steps of 0.05° with an integration time of 12 s per step between 50 and 750°C every 50°C .

Differential scanning calorimetry (DSC) measurements between room temperature and 580°C (the upper temperature limit of the instrument) were performed using a Perkin-Elmer DSC7, with heating and cooling rates of $10^\circ\text{C min}^{-1}$, under an inert N₂ atmosphere.

3. Room temperature crystal structure

In the following discussion, all Miller indices are, unless otherwise stated, given with respect to a cell of approximate dimensions $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$, where a_p is the primitive cubic perovskite parameter. The room temperature crystal structure was refined simultaneously from x-ray and high resolution neutron diffraction data by the Rietveld method [15] using the GSAS software package [16]. The large number of weak reflections observed in both diffraction patterns indicates a significant distortion of the cubic perovskite structure. The resolution of the 'characteristic' (404) (the unique (444) in the $2a_p \times 2a_p \times 2a_p$ cubic $Fm\bar{3}m$ lattice) into (404), ($\bar{4}04$) and (044) peaks and the observed weak diffraction maxima at d values (and with Miller indices) of 3.57 ($\bar{1}11$, 111), 2.65 (021), 2.55 (210, 120), 2.22 ($\bar{1}13$, 113), 2.14 (212, $\bar{2}12$, $\bar{1}22$, 122) and 1.94 Å ($\bar{2}21$, 221, 023) that violate the I -centring condition on hkl , $h + k + l = 2n$ preclude all of the possible distortions given by Woodward [4, 6] of higher than monoclinic symmetry. The remaining space groups to be considered are, therefore, the monoclinic $P12_1/n1$ (no. 14:b2) and the triclinic $P\bar{1}$ (no. 2). Another space group, $P2_1/m$ (no. 11), has been proposed by López *et al* [17] for the ALaMgTeO₆ (A = Na, K) double perovskites, in which the authors observe that the La and A cations order in alternate planes, but this model did not produce a satisfactory fit to our data.

The simultaneous refinement from x-ray and neutron diffraction data was carried out in $P12_1/n1$ as no evidence was found for further lowering of symmetry. Peak profiles were fitted using a modified pseudo-Voigt function [18] with an axial divergence asymmetry correction to the neutron diffraction data [19]. In both cases, backgrounds were fitted with a linear interpolation function using 15 coefficients. The contrast provided between Mn and Te when refining x-ray and neutron diffraction data simultaneously (the ratio of scattering factors for x-rays and neutrons, Te/Mn, being 4.32 and 2.01 [20], respectively) allowed the free refinement of Mn and Te fractions over the B and B' sites. No evidence for mis-site disorder or vacancy formation was observed. Three independent oxygen fractions were also allowed to refine but all remained close to unity. In the final model, Mn, Te and all oxygen fractions were fixed at unity. The isotropic thermal parameters of all atoms were allowed to refine freely. Final refined parameters and statistics are given in table 1 and selected bond distances and angles in table 2. Rietveld fits to the x-ray and neutron diffraction data are shown in figures 1 and 2, respectively.

The resulting crystal structure is primarily characterized by the tilting of the different MnO₆ and TeO₆ octahedra along the three axes of the primitive perovskite (figure 3). Rotations

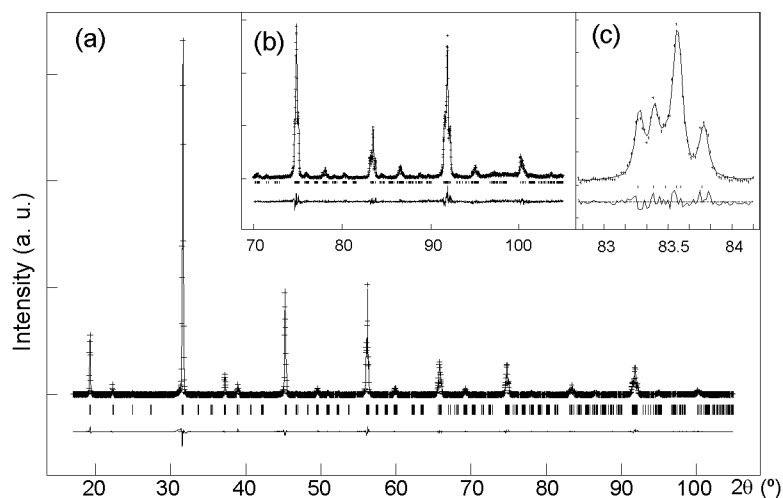


Figure 1. (a) Rietveld fit of $\text{Sr}_2\text{MnTeO}_6$ to the room temperature x-ray diffraction data in space group $P12_1/n1$ showing observed, calculated and difference curves. Inset are (b) the fit to the high angle data and (c) further detail of the fit to the ‘split-(404)’ peak (see text).

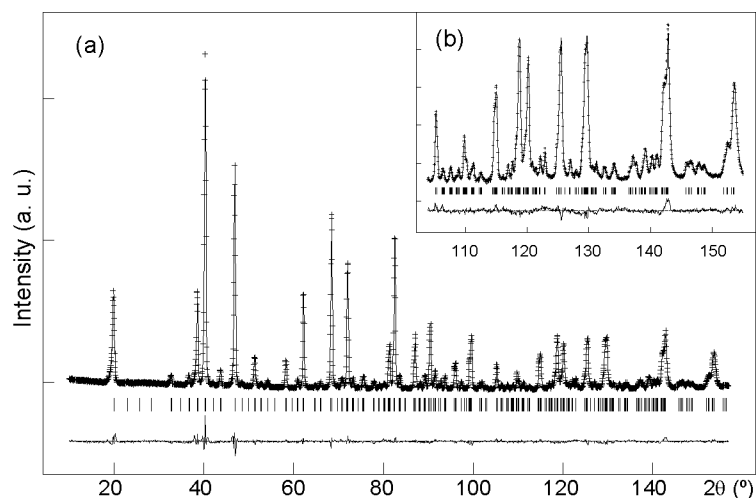


Figure 2. (a) Rietveld fit of $\text{Sr}_2\text{MnTeO}_6$ to the room temperature D2B neutron diffraction data in space group $P12_1/n1$ showing observed, calculated and difference curves with (b) the fit to the high angle data, inset.

around the c axis are in phase (+) and rotations normal to the c axis are anti-phase (–). It is also worth mentioning the negligible distortion of both octahedra with little variance in the M–O distances and internal angles very close to 90° , as shown in table 2.

4. Temperature dependent x-ray diffraction

Temperature dependent x-ray diffraction data, from 50 to 750°C measured in the range $17^\circ \leq 2\theta \leq 87^\circ$, were fitted by the Rietveld method using the GSAS program. Atomic positions for all atoms not fixed by symmetry and all isotropic thermal factors were allowed

Table 1. Refined parameters and *R* factors for Sr₂MnTeO₆ in space group *P*12₁/*n*1 at room temperature from x-ray and D2B neutron data (*a* = 5.7009(1) Å, *b* = 5.6770(1) Å, *c* = 8.0334(1) Å, β = 90.085(1). Volume = 259.994(10) Å³, *Z* = 2. *R* factors (x-rays/neutrons): *R*_{wp} = 14.7/5.1%, *R*_p = 8.0/3.4%, χ² = 2.10).

Atom	Wyckoff symbol	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (× 100 Å ²)
Sr	4e	0.5015(3)	0.015 32(18)	0.2492(3)	0.78(2)
Mn	2a	0	0	0	0.55(5)
Te	2b	0	0	0.5	0.38(3)
O1	4e	0.9453(4)	0.0065(4)	0.7350(3)	0.83(5)
O2	4e	0.2906(4)	0.2379(5)	0.9713(4)	0.91(6)
O3	4e	0.7591(4)	0.2874(5)	0.0283(4)	1.14(6)

Table 2. Selected bond distances and angles of Sr₂MnTeO₆.

Bond distances (Å)			
Mn–O1	2.1513(27) × 2	Te–O1	1.9145(27) × 2
Mn–O2	2.1501(22) × 2	Te–O2	1.9213(24) × 2
Mn–O3	2.1448(24) × 2	Te–O3	1.9209(24) × 2
Mean	2.149	Mean	1.919
Calculated ^a	2.17	Calculated ^a	1.91
Internal angles (deg)			
O1–Mn–O2	90.36(27)	O1–Te–O2	90.07(13)
O1–Mn–O3	90.01(22)	O1–Te–O3	90.14(6)
O2–Mn–O3	91.55(24)	O2–Te–O3	90.30(6)
External angles (deg)			
Mn–O1–Te	162.15(8)	Mn–O3–Te	163.29(4)
Mn–O2–Te	162.23(7)		

^a Value calculated considering the following ionic radii (in Å) and coordination numbers, CN: Mn_{CN=6}²⁺ = 0.83, Te_{CN=6}⁶⁺ = 0.56 and O_{CN=2}²⁻ = 1.34 [21].

to refine but with all oxygens constrained to have equal thermal factors. A surface roughness absorption correction [22] was refined to compensate for a slightly uneven surface arising from application of the sample to the Pt stage. The peak profile was again modelled by a pseudo-Voigt function and the background by a linear interpolation function with 15 coefficients. As all sites have been shown to be fully occupied by refinement from ambient temperature x-ray and neutron diffraction data, no attempt was made to refine any atomic fractions.

The structural model in space group *P*12₁/*n*1, deduced for this phase at room temperature, was fitted up to 450 °C. Figure 4 shows the disappearance of two ‘characteristic’ diffraction maxima in the 43° ≤ 2θ ≤ 53° range which do not satisfy the *hkl* with *h* + *k* + *l* = 2*n* reflection condition. Refined values of two particular structural parameters, the fractional *y* coordinates of Sr and O1 in space group *P*12₁/*n*1, up to 450 °C, are shown in figure 5. These coordinates show a significant displacement from *y* = 0 at low temperature and tend to zero at approximately 250 °C, coincident with the disappearance of observed intensity in the ‘characteristic’ diffraction maxima of figure 4. This corresponds to a transition from monoclinic *P*12₁/*n*1 to monoclinic *I*12/*m*1 symmetry (M–M transition), the difference between the two symmetries being the absence or presence of a mirror plane, *m*, located at *y* = 0. Small non-zero values of the two *y* coordinates (of Sr and O1) above 250 °C arise from

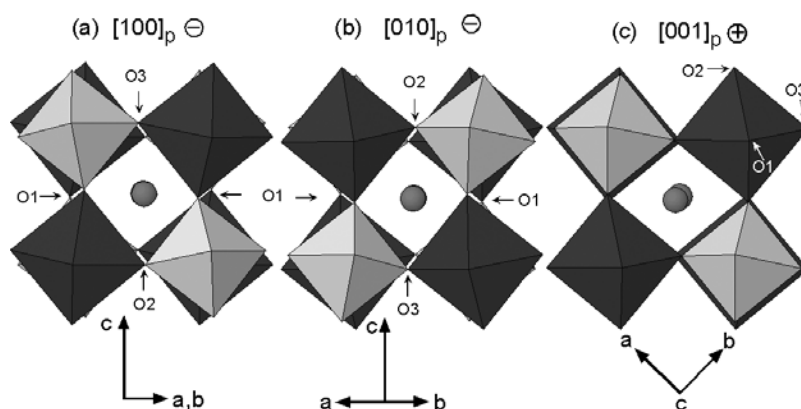


Figure 3. Projections of the room temperature structure of $\text{Sr}_2\text{MnTeO}_6$ along the three primitive axes of the cubic perovskite showing in-phase (+) and out-of-phase (−) rotations. Each structural transition at higher temperatures corresponds to the disappearance of rotations about one of these primitive axes. Dark octahedra represent MnO_6 and light octahedra TeO_6 . Spheres are Sr atoms.

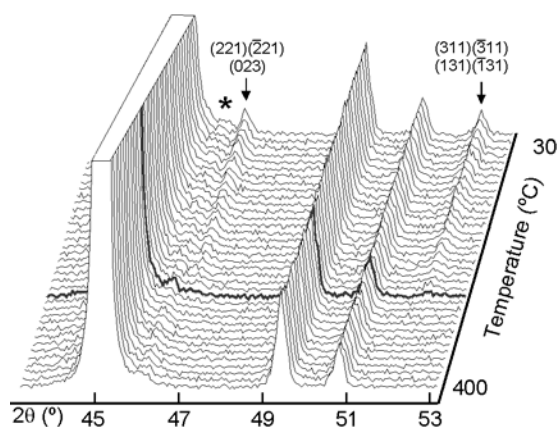


Figure 4. Evolution of selected 'characteristic peaks' (see text) of $\text{Sr}_2\text{MnTeO}_6$ with temperature showing the presence of the (221)/ $\bar{2}21$ /023 and (311)/ $\bar{3}11$ /131/131 peaks below 250 °C (bold curve). A weak diffraction maximum from the Pt sample stage is marked (*).

correlations between them and have no physical significance. The final structural model above 250 °C was therefore refined in space group $I12/m1$. DSC measurements (figure 6) also show a thermal hysteresis with an enthalpy of 0.55 J g^{-1} between 250 and 300 °C, a temperature range which is consistent with the temperature for the M–M phase transition obtained from x-ray diffraction measurements.

Figure 7 shows the temperature resolved x-ray data of the 'characteristic' (404) reflection in the angular range $81.5^\circ \leq 2\theta \leq 84.5^\circ$ from 50 to 600 °C. At low temperatures, this reflection is composed of a triplet (of $\text{Cu K}\alpha_1/\text{K}\alpha_2$ doublets), corresponding to the (404), $\bar{4}04$ and (044) reflections, which is maintained through the M–M transition. This triplet merges to a single reflection above 550 °C, indicating the disappearance of the monoclinic distortion.

Rietveld fits to the higher quality temperature dependent data show that only at temperatures above 700 °C are the diffraction data well fitted by an 'ideal' cubic, $Fm\bar{3}m$ double perovskite. Between 550 and 675 °C the data show a significant splitting of several

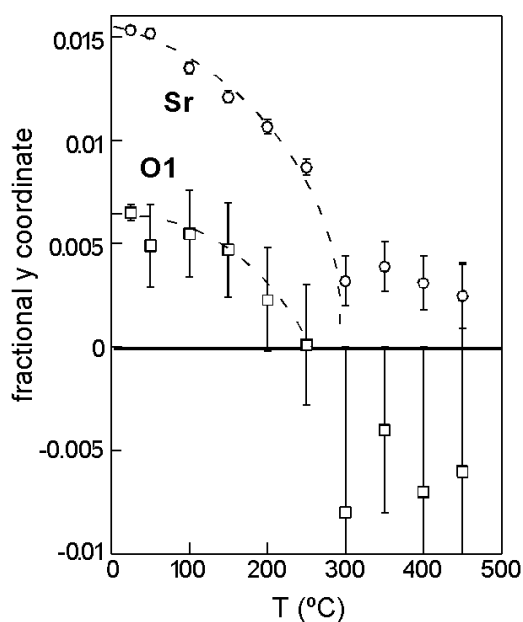


Figure 5. Refined y coordinates of Sr and O1 from x-ray diffraction data in space group $P12_1/n1$. Note that both coordinates being equal to zero generates the plane, m , characteristic of $I12/m1$ symmetry.

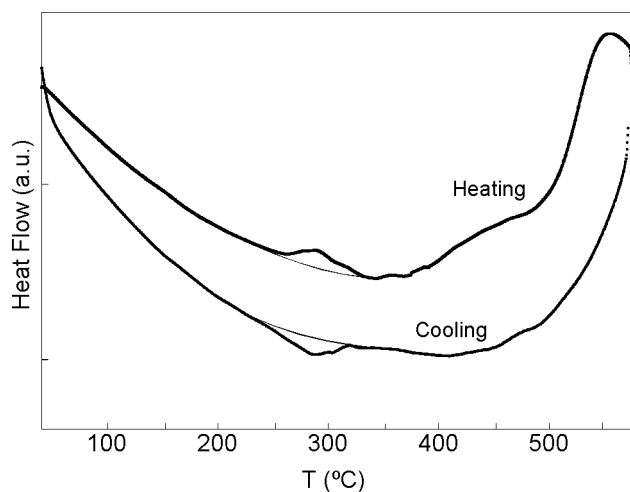


Figure 6. Differential scanning calorimetry of Sr₂MnTeO₆. A thermal hysteresis is observed between 250 and 300 °C.

reflections consistent with space group symmetry $I4/m$. It was possible to distinguish between our proposed sequence of transitions, via $I4/m$ symmetry as opposed to via the previously observed $R\bar{3}$ intermediary [13], due to the (404) reflection (figure 7) not being split as would be expected in space group $R\bar{3}$. Rietveld fits to data within this temperature interval were also compared for both models with the tetragonal model giving a significantly better fit than the rhombohedral one, with typical values of χ^2 being 4.8 and 5.7, respectively.

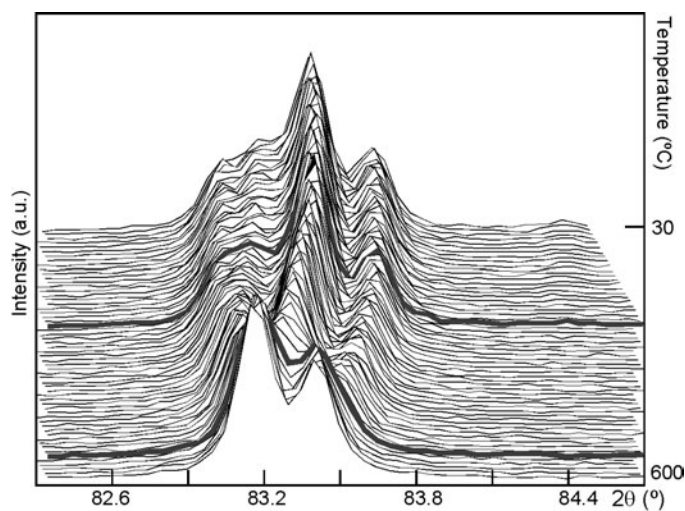


Figure 7. Temperature dependent x-ray diffraction data of the (404) reflection. Temperatures of 250 and 550 °C, corresponding to monoclinic–monoclinic and monoclinic–tetragonal phase transitions, are marked by bold lines.

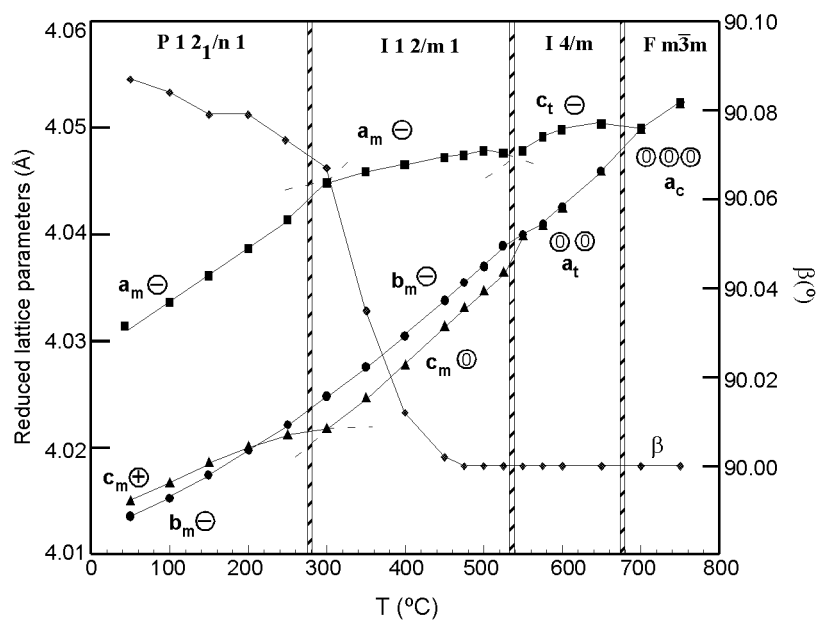


Figure 8. Evolution of reduced refined lattice parameters and monoclinic angle, β , of $\text{Sr}_2\text{MnTeO}_6$ from temperature dependent x-ray diffraction data. Assigned space group symmetries, the transitions between these symmetries and the associated rotation senses (0, + or –) around the three primitive axes are also shown. Reduced lattice parameters were calculated as follows for the various space group symmetries: monoclinic ($P12_1/n1$ and $I12/m1$): $a_m = a/\sqrt{2}$, $b_m = b/\sqrt{2}$; $c_m = c/2$; tetragonal ($I4/m$): $a_t = a/\sqrt{2}$, $c_t = c/2$; cubic ($Fm\bar{3}m$): $a_c = a/2$.

Evolution of the refined lattice parameters, reduced to be comparable to the primitive cubic perovskite parameter, a_p , and space group symmetries, are shown in figure 8. In order to ensure

that it was possible to distinguish the non-equivalent axes, axis lengths were interchanged then refined and, in all cases, converged to the same solution. It was therefore possible to unambiguously determine the rotational sense (+ or -) about the axes of the primitive perovskite, at all temperatures except 200 °C, where $b/\sqrt{2}$ and $c/2$ are equal. These rotational senses are also shown in figure 8, adjacent to the corresponding axes. It can be seen that, below the T-C transition at approximately 675 °C, there is one axis significantly longer than the other two. Out-of-phase rotations (-) about this 'long axis' are maintained from ambient temperature up to the T-C transition but, despite maintaining the same rotation sense, this 'long axis' shows two marked discontinuities around 250 and 550 °C. Of the two shorter axes, one, which is the unique axis b in both monoclinic space groups, varies smoothly across the entire temperature interval measured. It is this axis which has out-of-phase rotations (-) in both monoclinic symmetries that disappear, without any apparent discontinuity in the lattice parameter, during the monoclinic $I12/m1$ to tetragonal $I4/m$ transition. Conversely, the other 'short axis' shows a discontinuity at the monoclinic $P12_1/n1$ to monoclinic $I12/m1$ transition, coincident with the disappearance of in-phase (+) rotations.

In summary, only above 700 °C is the 'ideal' cubic, $Fm\bar{3}m$ ordered double perovskite structure observed. At lower temperatures, three transitions are observed, each corresponding to the removal of rotations of the MnO₆ and TeO₆ octahedra around one of the three crystallographic axes of the primitive cubic perovskite from the three rotation (- - +) monoclinic $P12_1/n1$ symmetry observed at room temperature. This sequence of structural phase transitions ($P12_1/n1 \rightarrow I12/m1 \rightarrow I4/m \rightarrow Fm\bar{3}m$) was previously reported for the fluoride Cs₂RbDyF₆ [23], but this represents, to the authors' knowledge, the first time that this sequence has been observed in a double perovskite oxide.

5. Conclusions

The ordered double perovskite Sr₂MnTeO₆ has been synthesized by the freeze-drying method. The room temperature crystal structure, determined from high resolution neutron and x-ray powder diffraction data, is monoclinic with space group symmetry $P12_1/n1$. This represents a combination of in-phase (+) and out-of-phase (-) rotations of virtually undistorted MnO₆ and TeO₆ octahedra in the (- - +) sense about the axes of the ideal cubic perovskite. Sr₂MnTeO₆ undergoes three structural phase transitions at approximately 250, 550 and 675 °C, each corresponding to the disappearance of rotations about one of these axes. The first transition was analysed by differential scanning calorimetry and showed a thermal hysteresis with an enthalpy of 0.55 J g⁻¹. The sequence $P12_1/n1 \rightarrow I12/m1 \rightarrow I4/m \rightarrow Fm\bar{3}m$ of structural transitions has been observed for the first time in a double perovskite oxide.

Acknowledgments

This work has been funded by the 'Ministerio de Ciencia y Tecnología' (MCyT). L Ortega-San Martin acknowledges MCyT for a Doctoral Fellowship (DGICYT-PB97-0062). Dr J P Chapman thanks MCyT for funding (MAT 2001-0064). The authors gratefully acknowledge Dr G Cuello for assistance with data collection and the ILL, Grenoble, France for provision of beam-time on Instrument D2B. We also thank Professor José Luis Pizarro of the 'Departamento de Mineralogía y Petrología, Universidad del País Vasco' for fruitful crystallographic discussions.

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