Structural study of $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ ($0.08 \leq x \leq 0.12$) system by neutron powder diffraction

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Abstract

Neutron powder diffraction experiments and magnetic measurements in polycrystalline $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ ($x = 0.08, 0.10, 0.12$) point towards a possible charge and orbital order in this system. The analysis of structural and magnetic data show that the samples present structural phase transformation from $Pnma$ to $P2_1/m$ space group and the system has a C-type antiferromagnetic configuration at low temperature. A detailed analysis of the bond distances signals a small Jahn-Teller distortion of only one ($x=0.08$) or of the two Mn ions ($x=0.10, 0.12$). We identify the partially occupied e_g orbitals and this explains the C-type magnetic structure.

Keywords: Structural properties, Magnetic properties, Neutron scattering.

1. Introduction

Manganites with perovskite like structure have been extensively studied from the mid 90's due the colossal magnetoresistance (CMR) and great variety of other physical properties that they exhibit [1-3] like charge order, orbital order, phase segregation, etc. Within them, CaMnO_3 crystallizes in an orthorhombic structure and possess antiferromagnetic (AFM) behavior with a G-type structure [4, 5]. Doped manganites, based on CaMnO_3 system, as $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ [6,7], $\text{CaMn}_{1-x}\text{B}_x\text{O}_3$ [8-10] (with Ln =lanthanide and B a cation having a valence larger than 4+), or deficient oxygen manganites have shown CMR. Some of these systems present an insulator-metal (I-M) transition, ferromagnetic (FM) order that increases when increasing their Curie temperature (T_C), and the coexistence of this FM order with a metallic phase (FMM). The models to explain the enhance of FMM and the apparition of the I-M transitions in systems with doping of Ca sites is the double exchange (DE) interaction that appears due to the introduction of Mn^{3+} in the parent (Mn^{4+}) compound. The e_g electrons introduced promote the appearance of CMR for which phase separation could play an important role as shown for other CMR manganites [1].

Besides the apparition of DE, the introduction of Mn^{3+} increases the Jahn-Teller distortion. The accommodation of this distortion, for particular values of the doping level, can induce interesting phenomena like orbital order (OO), or even charge order (CO) that can modify the crystallographic structure, the magnetic interactions and the magnetic structure.

In particular the $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ ($0 < x < 0.12$) system has been produced as single crystal by floating zone technique [8] and in polycrystalline form by solid state conventional methods [11]. For this system were identified several regions from the structural point of view [9]. At low temperature (1.5K), these region correspond to $Pnma$ structure ($x < 0.06$), $P2_1/m$ structure ($0.06 < x < 0.12$), and $P2_1/m$ with OO and CO ($x > 0.12$). This last region characterized by the apparition of superstructure reflection in the electron diffraction patterns (thus having a cell larger than the average $P2_1/m$ description). In the last two regions, when heating above a temperature that strongly depends on x , a structural transition appears in which the $Pnma$ structure is recovered. In the whole range, a paramagnetic to antiferromagnetic (PM-AFM) transition is observed about 160 K, while the AFM is accompanied by a weak FM phase in the $x < 0.06$ region.

2. Experimental details

Polycrystalline $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ ($x=0.08, 0.10$ and 0.12) samples were prepared by the usual solid state reaction method from a stoichiometric mixture of high purity CaCO_3 (99.999%), MnO_2 (99.99%) and MoO_2 (99%) in air at sintering temperature of 1250°C by 12 hours at $2.5^\circ\text{C}/\text{min}$ of heating and cooling rate. Neutron powder diffraction (NPD) data were collected on D1B ($\lambda=1.28\text{ \AA}$) diffractometer of ILL (Grenoble). The diffraction patterns were taken in the temperature range between 5 K and 330 K. A pattern was taken every 5 K in an angular range of $10^\circ < \theta < 130^\circ$. The NPD patterns were analyzed by Rietveld method employing the FullProf software for study the structural and magnetic phase. Magnetization measurements were performed in vibrating magnetometer Versalab of Quantum-Design in the temperature range between 50 K and 300 K.

3. Results and Discussion

3.1 Structural characterization

The NPD patterns as a function of the temperature for $x=0.08$, plotted in Fig. 1, evidence a structural transition at $T_E \approx 260\text{ K}$ (splitting and shift of peaks marked with Δ), this transition is also observed in other two samples at 283 K ($x=0.10$) and 304 K ($x=0.12$). Fig. 1 also reveals the apparition of an antiferromagnetic order at low temperature (with $T_N = 162\text{ K}$, apparition of peaks marked with $\blacklozenge$) this transition is observed at 165 K and 161 K for $x=0.10$ and 0.12 samples respectively. Tables 1 to 3 summarize the parameters obtained from Rietveld analysis at different temperatures: high temperature, intermediate temperature, low temperature, T_E and T_N temperature. Figure 2 presents the refined patterns for $x=0.08$ at 320 K and 5 K (at this temperature top bars correspond to structural reflections and bottom bars correspond to magnetic reflections, details concerning magnetic structure are given in subsection 3.2). The splitting of some peaks in the monoclinic structure (below T_E) is evidenced by the insets in Fig 2. The quality of the refinement allows us to confirm that a structural transition from orthorhombic ($Pnma$) to monoclinic ($P2_1/m$) space group takes place. Both transitions have been observed and reported by Maignan et. al. [6], thereby our results obtained are in concordance with those obtained by them.

The evolution of the lattice parameters as a function of the temperature is shown in Fig 3 for $x=0.08$, 0.10 and 0.12. In all cases, entering (on cooling) into the monoclinic phase is accompanied by an anisotropic evolution of cell parameters. This consists on a decrease of b parameter and an increase of a and c (except in the case of $x=0.12$ where these two parameters are nearly unaltered during the transition). Structural transition is quite wide and the evolution of cell parameters extends in temperature down to T_N or even below. This evolution indicates a redistribution of the electronic density around Mn ions towards the a - c plane, which is at the origin of the structural transition. Effectively, such a redistribution drives to shortening of the b lattice parameter (due to the loss of electron density) and an enlargement of a and c (due to the gain of electron density).

In Fig. 4a we present the evolution of Mn-O bond distances between Mn ion and equatorial oxygens (Oeq) for $x=0.08$. The picture is divided in two regions: at left the $P2_1/m$ and right the $Pnma$ region. For the first one there are two crystallographic positions for Mn, Mn1 and Mn2, while in the $Pnma$ region there is only one crystallographic position for Mn. Between 5 K and 234 K ($T < T_E$) the values are continuous and within the experimental dispersion, two equatorial Mn-O bond distances can be clearly distinguished for Mn1 but hardly for Mn2. Besides, mean equatorial distance is larger for Mn1. Apical bond distances are very similar for both crystallographic positions below the transition (Fig 4b). On another hand, the octahedron volumes (depicted in Fig 4c) show similar values for Mn1 and Mn2 (although Mn1 is slightly larger). Mn-O bond distances evidence that Mn1 octahedron is distorted but Mn2 is nearly regular. The distortion parameter is usually defined as:

$$\Delta = 10^4 \times \sqrt{\frac{1}{6} \sum_{i=1}^6 (d_i - \langle d \rangle)^2}$$

Where d_i are the individual Mn-O bond distances of the octahedra and $\langle d \rangle$ their average. In order to minimize the effect of data dispersion, we have made the average of Δ for all data points with $T < 50K$ ($\langle \Delta \rangle$). For the case $x=0.08$ we have obtained $\langle \Delta \rangle = 25$ for Mn1 and 9 for Mn2. This signals that electrons introduced by Mo substitution are mainly placed at Mn1. Moreover, the orbital occupied by e_g electrons would be a $d_{3z^2-r^2}$ pointing towards the longest equatorial bond of Mn1 (Mn1-O2eq in Fig. 4d and in Table I).

It is also worth mentioning that near (but below) T_E basal distances are similar (between Mn1 and Mn2) but apical ones are very different. On cooling basal distances separate while apical ones become equal. This coincides with the region when lattice parameters evolve more rapidly (on cooling b decreases while a and c increase). This would signal an intermediate temperature region, just below T_E , where the orbitals occupied by e_g electrons, localized at Mn1, site would point to the apical oxygen, instead of to the basal one.

The results obtained for $x=0.10$ (top panel of Fig. 5) are similar in the sense that the volume of Mn1 is slightly larger than that of Mn2. However, octahedra distortions become very similar for the two Mn sites. According to distances in Table 2, both Mn positions present a basal bond longer than the other (and longer than the apical bond). We find the same behavior for $x=0.12$. In fact, the distortion parameter (averaged for all data between the lowest temperature and 50K) render, for $x=0.10$, $\langle\Delta\rangle=24$ and 19 for Mn1 and Mn2; and 24 and 21 for $x=0.12$. Moreover, the two longer basal bonds found in these two compositions are those pointing to the same basal oxygen (O2a).

Fig 6 shows the evolution of Mn1-Oeq-Mn2 bond angle for the sample with $x=0.08$ (Fig 6a), $x=0.10$ (Fig 6b) and $x=0.12$ (Fig 6c). The graphs indicate that the Mn-O-Mn angle is more closed at low temperature ($T < 95K$, $x=0.08$) for O2eq than for O1eq, while this characteristic is more marked for $x=0.10$ in the whole $P2_1/m$ region (except around 200 K and, its behavior is similar in $x=0.12$ doping. In tree cases the angle ranges from 153° to 160° , inclusive in the $Pnma$ region.

3.2 Magnetic characterization

The magnetic measurements performed on the three members of $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ ($x=0.08$, 0.10 and 0.12) are closely similar. Fig. 7 shows the DC magnetization of $x=0.08$ as a function of the temperature in a zero field cool (ZFC)-field cool (FC) cycle. When cooling below $\sim 104K$, a sudden enhancement of the magnetic moment takes place. However, the magnetization reached at 50 K is only $0.027 \mu_B/\text{f.u.}$, so a FM phase can be discarded. The inset of Fig. 7 shows two features. One corresponds to the PM-AFM transition at T_N according to NPD results, the second one, which takes place at T_E , corresponds to the temperature where the structural transition from $P2_1/m$ to $Pnma$ takes place. In manganites, structural transitions of this type are usually due to a change in

orbital occupancies that govern (according to Goodenough-Kanamory-Anderson rules) the magnetic interactions between Mn ions, thus giving rise to a maximum in the magnetization. In this case, as we discuss above, Mn1-O2eq and Mn1-O1eq bond distances enlarge and shrink respectively (on cooling) indicating the orientation of occupied e_g orbitals on the former bond.

As shown in Fig. 1, neutron powder diffraction patterns show the appearance of a series of magnetic peaks below T_N . These peaks show a periodicity different from that of the structural ones and can be indexed with propagation vector $\vec{k} = (\frac{1}{2} \ 0 \ \frac{1}{2})$ (the same for $x=0.08, 0.10$ and 0.12). In order to obtain possible candidates for the magnetic ordering, we performed a symmetry analysis using BasiReps program (included in FullProf_suite). In the formalism used by FullProf the magnetic moment of atom j in cell l is calculated according to:

$$\vec{m}_{l,j} = \sum_{\vec{k}} \vec{S}_{\vec{k},j} \exp(-2\pi i \vec{k} \cdot \vec{R}_l)$$

Where $\vec{R}_l$ is the position of cell l expressed in units of cell parameters, the sum extends over all propagation vectors, and $\vec{S}_{\vec{k},j}$ are the Fourier components of the magnetic moment. These may be written as linear combinations of the basis vectors of the irreducible representations of the vector group G_k :

$$\vec{S}_{\vec{k},j} = \sum_{a,m} C_{a,m}^{\vec{k}\nu} \psi_{a,m;j}^{\vec{k}\nu}$$

Where a runs from 1 to the dimension of the representation Γ_ν , m runs from 1 to the number of times the irreducible representation is contained in the global reducible representation, $C_{a,m}^{\vec{k}\nu}$ are refinable parameters and $\psi_{a,m;j}^{\vec{k}\nu}$ the basis vectors. According to BasiReps program, the combination of $P 2_1/m$ space group and $(\frac{1}{2} \ 0 \ \frac{1}{2})$ propagation vector gives rise to two representations ($\nu=1,2$) of dimension three ($a=1,2,3$), contained once each in the global reducible representation ($m=1$). Basis vectors for the two possible values of j are listed in Table 4, which also shows the two ordering, corresponding to each representation, allowed by symmetry: A-type along x and z directions combined with C-type along y -direction ($A_x C_y A_z$); and C-type along x and z directions combined with A-type along y -direction ($C_x A_y C_z$).

Refinement using $A_x C_y A_z$ -type magnetic structure does not reproduce the observed intensities correctly. Besides, very good refinement is obtained with $C_x A_y C_z$ -type (e.g.

for $x=0.08$ magnetic R-factor is $R_M=2.6\%$). After many different tests, the best results were obtained when magnetic moments of both Mn ions are constrained to be equal and aligned in (101) direction (this meaning with A_y component equal to zero). This implies that magnetic refinements have a unique degree of freedom (instead of 6), and that the magnetic structure is purely C-type.

Symmetry analysis and Rietveld refinement corroborates an antiferromagnetic order and that there is no evidence of long range ferromagnetic order. Thus, it is worth to remark that the small FM signal appearing in the $M(T)$ curve cannot be ascribed to the apparition of long range FM ordering. The antiferromagnetic structure is represented in the inset of Fig. 8 showing the spin directions of Mn cations at 5 K for $x=0.08$ doping (it is the same for the three compositions studied). In this C-type AFM structure, magnetic moments form ferromagnetic chains along (101) direction. This is the same direction when the longest basal bond is found (in one of the two Mn sites for $x=0.08$; and in the two Mn sites for $x=0.10$ and 0.12). C-type magnetic structure must thus be due to a partial orbital occupancy along the bond(s) Mn1-O2eq. These bonds form parallel lines and induce a FM alignment along these lines that are coupled AFM as predicted by Goodenough-Kanamory-Anderson rules. Fig 8 shows the refined magnetic moment as a function of the temperature in $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ ($x=0.08, 0.10, 0.12$) samples. Curves suggest that the doping with Mo cation does not affect considerably the value of magnetic moment and the value around of $2.4 \mu_B$ suggest that not all Mn cation contribute to the magnetic ordering. This fact cannot be related to the small FM appearing in the $M(H)$ curve. In the case that the missing magnetic moment ($\sim 0.6 \mu_B$) would be FM ordered, they would be detected by NPD and it is not the case.

4. Conclusions

The polycrystalline $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ ($x=0.08, 0.10$ and 0.12) system has been characterized by NPD and magnetic measurements, it permits to determine T_N at 162, 165 and 161 K and T_E at 260, 283 and 304 for $x=0.08, 0.10$ and 0.12 respectively. For $x=0.08$ we have found that the structural transition from $Pnma$ to $P2_1/m$ is accompanied by a significantly different distortion of the two crystallographic positions occupied by Mn. Differences reside in the equatorial bond distances: one Mn (Mn1) clearly presents two different distances in the equatorial plane [the largest is aligned along (101) direction]. This is accompanied by a slightly different volume for the two sites, being

the largest that of the more distorted Mn. For $x=0.10$ and 0.12 the distortion of both MnO_6 octahedra is quite similar, but in both cases the largest bonds are aligned along the (101) direction. Our results demonstrate that the structural transition is due to an ordering of the occupied e_g orbitals within equatorial planes. This explains the anisotropic variation of cell parameters that would be driven to the concomitant anisotropic redistribution of the electron density: occupied e_g orbitals are isotropically distributed above T_E and concentrate in the basal planes below this temperature. Moreover, within the basal planes occupied e_g orbitals locate in (101) direction enlarging Mn-Mn distance in this direction and shrinking it in the perpendicular (-101) direction. Two different Mn-Mn distances within the basal plane are not allowed in $Pnma$ symmetry, and thus the cell becomes monoclinic.

On another hand, the proposed occupation of e_g orbitals implies FM interactions between neighboring Mn connected by these orbitals and antiferromagnetic in all other cases. Accordingly, the C-type AFM structure found by NPD has the ferromagnetic lines along (101) direction, in accordance with the orientation of the longest bonds.

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Fig. 1. NPD patterns of the $\text{CaMn}_{0.92}\text{Mo}_{0.08}\text{O}_3$ sample in function of the temperature between 12.07 K and 48.07 K.

Fig. 2. Rietveld analysis from NPD data of the $\text{CaMn}_{0.92}\text{Mo}_{0.08}\text{O}_3$ sample recorded at 4 K (top) and 320 K (down). Insets emphasize the shift and splitting of reflections due to structural transition.

Fig. 3. Temperature dependence of the lattice parameters of the $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ system. Top panel corresponds to $x=0.08$; middle panel to $x=0.10$; and down panel to $x=0.12$.

Fig. 4. Evolution of Mn-O bond distance for x=0.08. 4a is presenting the Mn-O_{eq} bond distances; 4b is presenting the Mn-O_{ap} bond distances; 4c is presented the volume of MnO₆ octahedra. 4d is the representation of MnO₆ octahedra in the ac plane.

Fig. 5. MnO₆ volume of x=0.10 (top) and x=0.12 (down) sample.

Fig. 6. Evolution of the Mn-Oeq-Mn angle in function of the temperature for $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ with: (a) $x = 0.08$, (b) 0.10 and (c) 0.12 .

Fig. 7. Magnetization as a function of temperature for $x=0.08$ performed at 1 kOe applied field. On inset is appreciated the inflection corresponding to T_N and T_{CO} .

Fig. 8. Evolution of the antiferromagnetic moment for the $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ ($x=0.08, 0.10$ and 0.12) system. On inset representation of antiferromagnetic C-type phase in $\text{CaMn}_{1-x}\text{Mo}_x\text{O}_3$ ($x=0.08, 0.10$ and 0.12) system.

Table 1

Structural details of $\text{CaMn}_{0.92}\text{Mo}_{0.08}\text{O}_3$ (lattice parameters, atomic positions and bond distances) obtained by Rietveld refinement of NPD data at different temperatures. In $Pnma$ SG, Ca and O1 occupy $4c$ Wyckoff position ($x \frac{1}{4} z$), Mn/Mo occupy $4b$ ($0 \ 0 \ \frac{1}{2}$) and O2 occupy $8d$ ($x \ y \ z$). In $P2_1/m$ all orbits split into two positions, Ca1, Ca2, O1 and O2 occupy Wyckoff position $2e$ ($x \ \frac{1}{4} z$), Mn/Mo occupy positions $2b$ ($\frac{1}{2} \ 0 \ 0$) and $2c$ ($0 \ 0 \ \frac{1}{2}$), O3 and O4 occupy $4f$ ($x \ y \ z$). Agreement parameters are also included.

Temperature (K)	320		260 (T _E)	200	162 (T _N)	5
Space group	$Pnma$		$P2_1/m$			
a (Å)	5.2948(1)	a (Å)	5.2954(8)	5.3011(7)	5.3077(4)	5.3076(4)
b (Å)	7.4550(1)	b (Å)	7.4456(8)	7.4282(1)	7.4178(4)	7.4011(4)
c (Å)	5.2716(4)	c (Å)	5.2685(7)	5.2741(5)	5.2771(3)	5.2776(2)
		β (Deg)	89.88(9)	89.38(1)	89.09(1)	88.83(2)
V (Å ³)	208.08(5)	V (Å ³)	207.73(1)	207.67(5)	207.74(5)	207.27(6)
R _F (%)	1.67	R _F (%)	1.38	1.35	1.66	1.70
χ^2	1.58	χ^2	1.49	1.62	1.99	1.97
Ca x	0.0326(9)	Ca1 x	-0.0304(3)	-0.0344(3)	-0.0318(8)	-0.0259(3)
z	-0.0069(5)	z	-0.0021(4)	0.0093(7)	0.0094(8)	0.0144(9)
		Ca2 x	0.4621(3)	0.4657(1)	0.4628(3)	0.4592(8)
		z	0.4873(1)	0.4971(7)	0.4952(3)	0.4910(4)
O1 x	0.4880(2)	O1 x	0.5039(9)	0.5159(5)	0.5169(1)	0.5063(7)
z	0.0680(4)	z	-0.0680(7)	-0.0669(6)	-0.0687(5)	-0.0628(6)
		O2 x	0.0200(2)	0.0126(6)	0.0101(8)	0.0165(2)
		z	0.5691(2)	0.5745(8)	0.5719(4)	0.5684(6)
O2 x	0.2135(7)	O3 x	0.2117(2)	0.2148(5)	0.2148(8)	0.2155(2)
y	-0.0335(3)	y	0.0303(9)	0.0337(1)	0.0329(5)	0.0421(1)
z	0.2119(5)	z	0.2105(6)	0.2131(1)	0.2127(5)	0.2125(5)
		O4 x	0.2842(6)	0.2862(7)	0.2858(1)	0.2846(1)
		y	-0.0374(5)	-0.0348(2)	-0.0349(1)	-0.0319(2)
		z	0.7144(8)	0.7125(5)	0.7116(1)	0.7105(4)
Mn-Oap X 2 (Å)	1.898(7)	Mn1-Oap X 2 (Å)	1.895(7)	1.892(1)	1.892(6)	1.880(1)
		Mn2-Oap X 2 (Å)	1.899(6)	1.899(6)	1.892(8)	1.887(6)
Mn-O1eq X 2 (Å)	1.909(5)	Mn1-O1eq X 2 (Å)	1.899(1)	1.890(8)	1.885(5)	1.888(4)
		Mn2-O1eq X 2 (Å)	1.903(5)	1.900(5)	1.898(2)	1.907(1)
Mn-O2eq X 2 (Å)	1.900(9)	Mn1-O2eq X 2 (Å)	1.913(9)	1.920(1)	1.937(3)	1.941(2)
		Mn2-O2eq X 2 (Å)	1.901(9)	1.914(4)	1.908(3)	1.907(9)

Table 2

Structural details of $\text{CaMn}_{0.9}\text{Mo}_{0.1}\text{O}_3$ (lattice parameters, atomic positions and bond distances) obtained by Rietveld refinement of NPD data at different temperatures. In $Pnma$ SG, Ca and O1 occupy 4c Wyckoff position ($x \frac{1}{4} z$), Mn/Mo occupy 4b ($0 \ 0 \ \frac{1}{2}$) and O2 occupy 8d ($x \ y \ z$). In $P2_1/m$ all orbits split into two positions, Ca1, Ca2, O1 and O2 occupy Wyckoff position 2e ($x \ \frac{1}{4} z$), Mn/Mo occupy positions 2b ($\frac{1}{2} \ 0 \ 0$) and 2c ($0 \ 0 \ \frac{1}{2}$), O3 and O4 occupy 4f ($x \ y \ z$). Agreement parameters are also included

Temperature (K)	320		283 (T _E)	200	165 (T _N)	10
Space group	$Pnma$				$P2_1/m$	
a (Å)	5.3178(3)	a (Å)	5.3216(4)	5.3278(9)	5.3295(1)	5.3306(4)
b (Å)	7.4651(1)	b (Å)	7.4522(2)	7.4268(3)	7.4173(2)	7.4041(9)
c (Å)	5.2896(1)	c (Å)	5.2903(4)	5.2938(8)	5.2944(3)	5.2953(6)
β (Deg)		β (Deg)	89.52(7)	88.93(7)	88.79(1)	88.53(4)
V (Å ³)	209.98(7)	V (Å ³)	209.79(4)	209.43(8)	209.24(5)	208.93(5)
R _F (%)	1.99	R _F (%)	1.84	1.75	1.77	1.86
χ^2	1.48	χ^2	1.47	1.60	1.64	2.05
Ca x	0.0325(6)	Ca1 x	-0.0312(2)	-0.0283(4)	-0.0333(4)	-0.0282(3)
z	-0.0067(4)	z	0.0063(1)	0.0103(0)	0.0103(5)	0.0140(0)
		Ca2 x	0.4663(2)	0.4608(9)	0.4642(1)	0.4588(3)
		z	0.4918(9)	0.4929(0)	0.4928(7)	0.4931(7)
O1 x	0.4876(9)	O1 x	0.5140(9)	0.5190(5)	0.5181(4)	0.5087(4)
z	0.0679(0)	z	-0.0653(1)	-0.0682(8)	-0.0671(6)	-0.0634(6)
		O2 x	0.0117(5)	0.0092(7)	0.0108(1)	0.0147(6)
		z	0.5726(2)	0.5726(0)	0.5709(5)	0.5675(4)
O2 x	0.2133(2)	O3 x	0.2142(4)	0.2128(3)	0.2119(5)	0.2145(5)
y	-0.0340(4)	y	0.0337(2)	0.0346(8)	0.0360(5)	0.0412(8)
z	0.2123(2)	z	0.2118(3)	0.2143(6)	0.2141(4)	0.2150(1)
		O4 x	0.2874(4)	0.2862(5)	0.2878(5)	0.2869(3)
		y	-0.0345(2)	-0.0344(1)	-0.0332(4)	-0.0332(2)
		z	0.7127(7)	0.7125(5)	0.7126(2)	0.7128(2)
Mn-Oap X 2 (Å)	1.901(5)	Mn1-Oap X 2 (Å)	1.896(3)	1.893(8)	1.890(2)	1.881(7)
		Mn2-Oap X 2 (Å)	1.903(3)	1.896(9)	1.893(2)	1.887(3)
Mn-O1eq X 2 (Å)	1.914(9)	Mn1-O1eq X 2 (Å)	1.899(2)	1.905(7)	1.907(9)	1.901(9)
		Mn2-O1eq X 2 (Å)	1.912(1)	1.890(6)	1.888(2)	1.894(8)
Mn-O2eq X 2 (Å)	1.910(4)	Mn1-O2eq X 2 (Å)	1.918(6)	1.934(5)	1.930(5)	1.937(5)
		Mn2-O2eq X 2 (Å)	1.924(8)	1.929(1)	1.937(8)	1.938(4)

Table 3

Structural details of $\text{CaMn}_{0.88}\text{Mo}_{0.12}\text{O}_3$ (lattice parameters, atomic positions and bond distances) obtained by Rietveld refinement of NPD data at different temperatures. In $Pnma$ SG, Ca and O1 occupy 4c Wyckoff position ($x \frac{1}{4} z$), Mn/Mo occupy 4b ($0 \ 0 \ \frac{1}{2}$) and O2 occupy 8d ($x \ y \ z$). In $P2_1/m$ all orbits split into two positions, Ca1, Ca2, O1 and O2 occupy Wyckoff position 2e ($x \ \frac{1}{4} \ z$), Mn/Mo occupy positions 2b ($\frac{1}{2} \ 0 \ 0$) and 2c ($0 \ 0 \ \frac{1}{2}$), O3 and O4 occupy 4f ($x \ y \ z$). Agreement parameters are also included.

Temperature	320		304 (T _E)	200	161 (T _N)	10
Space group	<i>Pnma</i>			<i>P2₁/m</i>		<i>P2₁/m</i>
<i>a</i> (Å)	5.3227(1)	<i>a</i> (Å)	5.3238(5)	5.3280(1)	5.3312(9)	5.3355(5)
<i>b</i> (Å)	7.4635(9)	<i>b</i> (Å)	7.4573(6)	7.4207(7)	7.4170(7)	7.4040(7)
<i>c</i> (Å)	5.2914(9)	<i>c</i> (Å)	5.2882(3)	5.2938(5)	5.2934(1)	5.2973(5)
		β (Deg)	89.69(6)	88.96(4)	88.76(3)	88.51(6)
V (Å ³)	210.20(6)	V (Å ³)	209.94(8)	209.43(8)	209.25(7)	209.19(9)
R _F (%)	4.47	R _F (%)	3.95	4.17	4.12	3.70
χ ²	1.20	χ ²	1.15	1.17	1.15	1.21
Ca x	0.0303(9)	Ca1 x	-0.0311(9)	-0.0352(8)	-0.0298(8)	-0.0363(8)
z	-0.0135(7)	z	-0.0100(1)	0.0192(4)	0.0035(1)	0.0114(7)
		Ca2 x	0.4629(2)	0.4643(6)	0.4571(3)	0.4637(7)
		z	0.4896(8)	0.4894(1)	0.4915(8)	0.4860(5)
O1 x	0.4830(8)	O1 x	0.5261(6)	0.5143(7)	0.5273(4)	0.5185(1)
z	0.0707(4)	z	-0.0770(2)	-0.0758(8)	-0.0680(8)	-0.0653(4)
		O2 x	-0.0005(8)	0.0124(3)	0.0128(5)	0.0078(6)
		z	0.5638(9)	0.5703(1)	0.5781(5)	0.5680(2)
O2 x	0.2145(7)	O3 x	0.2193(9)	0.2183(9)	0.2109(5)	0.2129(9)
y	-0.0332(4)	y	0.0292(2)	0.0369(8)	0.0333(2)	0.0419(3)
z	0.2120(8)	z	0.2126(7)	0.2137(5)	0.2161(3)	0.2128(3)
		O4 x	0.2929(1)	0.2862(5)	0.2832(3)	0.2883(3)
		y	-0.0362(9)	-0.0271(9)	-0.0343(2)	-0.0309(3)
		z	0.7166(8)	0.7084(2)	0.7142(3)	0.7131(8)
Mn-Oap X 2 (Å)	1.905(5)	Mn1-Oap X 2 (Å)	1.913(2)	1.899(5)	1.893(8)	1.885(1)
		Mn2-Oap X 2 (Å)	1.894(8)	1.893(2)	1.901(3)	1.886(4)
Mn-O1eq X 2 (Å)	1.920(1)	Mn1-O1eq X 2 (Å)	1.880(4)	1.885(4)	1.914(4)	1.903(9)
		Mn2-O1eq X 2 (Å)	1.921(2)	1.911(3)	1.874(1)	1.900(2)
Mn-O2eq X 2 (Å)	1.904(9)	Mn1-O2eq X 2 (Å)	1.882(4)	1.947(8)	1.941(5)	1.931(9)
		Mn2-O2eq X 2 (Å)	1.959(8)	1.906(8)	1.922(7)	1.943(4)

Table 4

Basis vectors of the two irreducible representations of $P2_1/m$ space group with propagation vector $(\frac{1}{2} \ 0 \ \frac{1}{2})$ for each of the two generators of the space group for Wyckoff positions $2b$ and $2c$.

Oder type	SG-generator	Basis vector		
$C_x A_y C_z$	$x \ y \ z$	(100)	(010)	(001)
	$-x \ y+\frac{1}{2} \ -z$	(100)	(0-10)	(001)
$A_x C_y A_z$	$x \ y \ z$	(100)	(010)	(001)
	$-x \ y+\frac{1}{2} \ -z$	(-100)	(010)	(00-1)