Structural properties of Pb₃Mn₇O₁₅ determined from high-resolution synchrotron powder diffraction

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We report on the crystallographic structure of the layered compound Pb₃Mn₇O₁₅. Previous analysis based on laboratory X-ray data at room temperature gave contradictory results in terms of the description of the unit cell. Motivated by recent magnetic bulk measurements of this system, we re-investigated the chemical structure with high-resolution synchrotron powder diffraction at temperatures between 15 K and 295 K. Our results show that the crystal structure of stoichiometric Pb₃Mn₇O₁₅ has a pronounced 2-dimensional character and can be described in the orthorhombic space group Pnma.

I. INTRODUCTION

Since the discovery of the colossal magneto-resistance (CMR) effect in (La,Pb)MnO₃, manganeseites have been comprehensively investigated throughout the last years, e.g. Chatterji. Extensive studies focused especially on members of two groups: the perovskite-type compounds (space groups P3m1, Pbnm) and the layered compounds of the so-called Ruddlesden-Popper series (space group I/mmm) with the general formula Aₙ₊₁MₙO₃ₙ⁺₁, where A is a rare-earth metal and n is the number of corner-shared MnO₆ octahedral sheets forming the layer. Pb₃Mn₇O₁₅ cannot be classified in either of these groups, although, like the n = 1 compounds of the Ruddlesden-Popper series, it grows in a pronounced crystalline anisotropy with alternating monolayers of MnO₆ octahedra and PbO sheets. The first synthesis was reported in literature already thirty years ago, but until recent times little was known about the physical properties. No evidence of CMR is present in the pure compound. Nevertheless, the layered type structure and the presence of a mixed valence state of Mn ions (Mn³⁺/Mn⁴⁺) recently motivated a new thorough investigation: Magnetisation and specific heat measurements on Pb₃Mn₇O₁₅ revealed several magnetic phases including long-range magnetic ordering below Tₙ = 70 K and paramagnetic charge localisation at Tₐ = 250 K. Dielectric properties give rise to formation of polarons, which make Pb₃Mn₇O₁₅ a promising candidate for multiferroic materials. However, the basis for further microscopic investigations of the physical properties is the exact knowledge of the crystal symmetry. The structural properties of the layered compound Pb₃Mn₇O₁₅ have been a matter of debate since the first report on its structure by Darriet et al., using single crystal X-ray diffraction data taken with a laboratory Kα molybdenum source. The crystallographic structure was refined based on the orthorhombic space group Cmcm. Marsh & Herbstein reformulated the structure based on the data of Darriet et al. in the orthorhombic space group Cmcm which involved shifting the origin by about 0.25 in z-direction. Symmetrizing the positions of some pairs of atoms by shifts up to 0.2 Å was thereby necessary. Shortly afterwards, Le Page & Calvert found that a description in P6₃/mcm discloses a new class of systematic absences not accounted for previously. The new hexagonal unit cell of Pb₃Mn₇O₁₅ is related to the orthorhombic description in Cmcm by a₆cratch ortho = (a ortho − b ortho)/2, b₆cratch ortho = b ortho, c₆cratch ortho = c ortho. Nevertheless, Weissenberg and Laue patterns also indicate contradictory results concerning hexagonal and orthorhombic symmetry. In order to settle this discrepancy between the different models and in order to investigate the structural properties as a function of temperature, we performed new measurements on this material employing high-resolution synchrotron radiation.

II. EXPERIMENTAL DETAILS

A. Sample Preparation and Characterisation

Single crystals were grown by the flux method, as described in. The flux agent PbO was chosen since it is known as an effective solvent for many oxide compounds and allows to avoid incorporation of foreign ions into the lattice. The synthesis of Pb₃Mn₇O₁₅ single crystals started with heating a mixture of 93 % by weight of high purity PbO and 7 % by weight of Mn₂O₃ in a platinum crucible at 1000 °C for 4 h. Afterwards, the crucible was cooled to 900 °C at a cooling rate of 2.5 °C/h, followed

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by non-constrained cooling to room temperature. Single crystals with a plate-like hexagonal form and a shiny black surface were found on the solidified liquid surface. The plates measured up to 40 mm in diameter and were extracted mechanically from the flux. Afterwards, the crystals were carefully ground for synchrotron powder diffraction investigations. Thermogravimetric analysis was employed to verify the oxygen content in our sample. The powder sample was heated from room temperature up to 800 °C in a 5% H2/95% He flux at a heating rate of 2 °C/minute. A mass spectrometer analysed the evolution of H2O. Finally, from the weight loss of the sample the initial oxygen content was calculated. The oxygen content of our sample has been determined to Pb3Mn7Ox with x = 14.93±0.05.

B. High-resolution synchrotron measurements

High-resolution synchrotron radiation powder diffraction patterns were collected at the powder diffraction station of the Swiss Light Source Materials Science (SLS-MS) beamline using a multi crystal analyzer detector [5, 10]. The instrumental contribution to the peak profile was reduced to negligible levels by carefully optimizing the beamline optics and the detector while observing the crystal analyzer rocking curve with the attenuated direct beam [11]. The photon energy (λ = 0.617793(1) Å) was determined using the silicon standard from NIST Si640c, whereas the instrumental resolution function was evaluated using Na2Ca3Al2F14, a standard powder known for being characterized by Bragg peaks with a negligible intrinsic contribution to the instrumental line shape. During the acquisitions, the detector arm was continuously rotated at a constant speed, recording the data at high reading frequency, which are rebinned to the appropriate step size after the measurements. Temperature dependent measurements between 15 K and 295 K in steps of 50 K were performed using the Janis Cryostat. The Pb3Mn7O15 powder was mounted in the cryostat in 0.2 mm Lindemann capillaries and the capillary spun at approximately 10 Hz during the 2θ scan.

III. RESULTS

The powder diffraction pattern at T=15 K is shown in Fig. 1. Refinements, based on different space groups reported earlier [5, 7, 8], gave unsatisfactory agreement with the observed pattern, due to a systematic splitting of peaks indicating a lowering of the space group symmetry. The inset of Fig. 1 shows a small angular section around the expected (110) reflection in a hexagonal setting as reported by Darriet et al. [5]. The splitting was observed at all temperatures, excluding a structural phase transition as shown by the continuous change of the orthogonal distortion, not reaching the hexagonal symmetry up to 295 K (Fig. 1B). The value of splitting shows a temperature dependence and amount to 2θ = 0.03° and T = 295 K to 2θ = 0.1° at T = 15 K. From an investigation of the subgroup relationships starting from the high symmetry hexagonal P63/mcm structure, the orthorhombic space group Pnma is obtained. The different structures reported earlier are related in the following way: Orthorhombic Cmcm used by Marsh & Herbst-Stein [7] is a translationsgleiche (a symmetry element is removed, but translation symmetry is maintained) subgroup of P63/mcm of index 3. Cmca2 used by Darriet et al. [5] is also translationsgleich of index 2 of space group Cmcm. Space group Pnma is reached by a klassengleiche (in our case, the C-centering has been removed) subgroup of Cmcm of index 2. The crystallographic a-axis is now perpendicular to the layers, in contrast to previous descriptions with perpendicular c-axis.

All preceding interpretations were based on the same data set taken by Darriet et al. [5] on a laboratory X-ray single crystal diffractometer. Although the angular resolution at the synchrotron is considerably improved compared to a laboratory instrument, the peak splitting of about 2θ = 0.03° at room temperature is resolvable on a standard X-ray laboratory instrument. A possible explanation for the discrepancy in the structural description might be a different oxygen content of our sample compared to the previous studies. Investigations on the layered manganites BaTb2Mn2O7 and BaSm2Mn2O7 [12, 13] have shown that phase transitions from tetragonal to orthorhombic symmetry occur as a function of oxygen or nitrogen annealing, suggesting some tolerance for oxygen non-stoichiometry.
FIG. 2: Layered structure of Pb$_3$Mn$_7$O$_{15}$. The Pb atoms are interconnecting the Mn-O-layers (on-line version: Mn (red); O (blue); Pb (green)).

FIG. 3: (a) Temperature dependence of the lattice parameters $a$ and $c$ in Pb$_3$Mn$_7$O$_{15}$. The orthogonal $a$-axis is vertical to the layer structure and corresponds to the hexagonal $c$-axis in the description of 8. (b) The in-plane lattice parameter ratio corresponding to the hexagonal lattice (black square) is not reached up to 295 K, therefore only an orthorhombic description (open triangles) is possible in our case.

FIG. 4: Projection of the low temperature structure ($T = 15$ K) on the $b$-$c$ plane. Only manganese (white open circles) and lead (gray closed circles) are shown. Arrows indicate the direction of displacements of the lead atoms from $T = 295$ K to $T = 15$ K.

Based on the $Pnma$ space group we obtained satisfactory agreement between the measured data sets and calculations ($R = 8.9\%$ for $T = 15$ K and $R = 13.8\%$ for $T = 295$ K) as shown in Table II. The unit cell comprises 8 formula units leading to 30 independent atoms per unit cell (see Fig. 2). Manganese ions are distributed among the general 8$d$ position and the special positions 4$a$, 4$b$ and 4$c$. The MnO$_6$ octahedra can be grouped into undistorted (4$a$, 4$b$), weakly distorted (4$c$, 8$d$) and strongly distorted octahedra (8$d$) with respect to the angles of the main axis of the octahedra (see Table II). The weakly and undistorted octahedra form layers around $x = 0$ and $x = 0.5$ bridged by pairs of strongly distorted octahedra. The layers show a small modulation within the unit cell along the $b$ direction, where the mean displacement along the $a$ direction of all manganese atoms within a layer decreases with temperature from $\Delta \bar{x} = 0.005$ relative length units at $T = 295$ K to $\Delta \bar{x} = 0.003$ at $T = 15$ K. The decrease of the modulations with temperature goes with a reduction of the lattice constant $b$ with simultaneous increase along the $c$ direction, so that the pseudo-hexagonal arrangement of Mn atoms gets stretched along $c$ at low temperatures. The variation of lattice parameters as function of temperature is shown in Fig. 3.

As reported earlier 8, the Pb atoms, equally located on two different symmetry sites 8$d$ and 4$c$, are closely confined around layers at $x = 0.25$ and $x = 0.75$, halfway in-between the MnO$_6$ layers. The Pb layers follow a similar modulation along $b$ with displacement along $a$ as the MnO$_6$ layers. Projected on the (100) planes the lead atoms lie on lines along the $<011>$ and $<001>$ directions. At $T = 15$ K the lead atoms get displaced as indicated in Fig. 4 where the atoms of the $x = 0.25$ layers are systematically shifted towards the positive $c$ directions, while atoms on the $x = 0.75$ layer are shifted in the opposite direction.

IV. DISCUSSION

As discussed by Volkov et al. 1 there are two factors which can cause polyhedral distortions of the MnO$_6$ octahedra in Pb$_3$Mn$_7$O$_{15}$. The first factor is the Jahn-Teller
effect which originates from degenerate orbital states of the Mn$^{3+}$ ions in a regular octahedral crystal field. The valence state of the Mn ions is discussed explicitly below. Secondly the stereo-active lone pairs of the 6s$^2$ electrons in Pb$^{2+}$ can lead to significant shifts of some oxygen positions due to repulsion of the lone pair with Pb-O bonds. This assumption can be supported by the fact, that strongly distorted MnO$_6$ octahedra consist of oxygen ions which are in close proximity to Pb ions.

According to the stoichiometry of the formula unit, the Mn ions in Pb$_3$Mn$_7$O$_{15}$ are in a mixed valence state Mn$^{3+}$/Mn$^{4+}$ with a ratio 4/3. Assuming the Jahn-Teller effect to be responsible for the distortion, one can distribute Mn$^{3+}$ ions onto interlayer Mn sites (Mn4, Mn5) and Mn$^{4+}$ ions onto the undistorted positions (Mn6, Mn7) in a straightforward way. Assuming further that the remaining Mn atoms have equal probability to be in either of the oxidation state, one obtains the total ratio of Mn$^{3+}$/Mn$^{4+}$ = 4/3 corresponding to the stoichiometry of the formula unit. The distribution of tri- and tetravalent Mn ions can be estimated from Mn-O bond lengths via bond-valence sums (BVS). The BVS is proportional to the sum over the deviation (r$_0$ - r), where r is the measured bond length and r$_0$ an empirical parameter for the mean cation-anion distance. Since the r$_0$ values for Mn$^{3+}$ and Mn$^{4+}$ are very similar, one single r$_0$ value (1.76 Å) can be used as an estimate for the calculations [14]. The results (Table II) are less satisfactory than reported by Volkov et al. [1], but we assume it more accurate since the lower symmetric space group we used allows an investigation of non-averaged bond-lengths. After this analysis it is less evident to connect unambiguously the strongly distorted octahedra (Mn4, Mn5) with the Jahn-Teller effect (see Table III). At this point no final conclusion can be drawn about the mixed valence state in Pb$_3$Mn$_7$O$_{15}$ since Mn ions on all crystallographic sites seem to be in average in a state between tri- and tetravalency which cannot be connected to the degree of octahedral distortion.

V. CONCLUSIONS

We re-investigated the mixed valence Mn$^{3+}$/Mn$^{4+}$ manganite Pb$_3$Mn$_7$O$_{14.93}$ using X-ray synchrotron powder diffraction. The oxygen content was verified by thermogravimetry. Rietveld refinement showed that our data can be well described within the orthorhombic space group $Pnma$ and that there is no structural phase transition in the observed temperature range 15 $\leq$ T $\leq$ 295 K. The refined space group is different to several previous descriptions reported in literature, which were all analyzed from the data set taken by Darriet et al. [5]. The crystal symmetry stays unchanged in the investigated temperature regime, the pseudo-hexagonal arrangement of the Mn atoms gets stretched along the c axis at low temperatures and the Pb atoms experience a systematic displacement. Earlier investigations [1] based on a higher symmetry phase and magnetization data suggest three different types of MnO$_6$ octahedra distinguished by the degree of distortion and the valence state of the Mn ions. Our synchrotron measurements on the same crystals as in [1] show that this classification is less significant in the lower symmetric description and that BVS calculations could not clarify unambiguously the Mn valence states.

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| Reference | This paper | This paper |
|-----------|------------|------------|
| Temperature [K] | 295 | 295 | 295 | 295 | 15 |
| space group | $Cmc2_1$ (No. 36) | $Cmcm$ (No. 63) | $P6_3/mcm$ (No. 193) | $Pnma$ (No. 62) | $Pnma$ (No. 62) |
| cell parameters | orthorhombic | orthorhombic | hexagonal | orthorhombic | orthorhombic |
| a [Å] | 17.28 (1) | 17.28 (1) | 9.98 (1) | 13.595100 (21) | 13.551275(15) |
| b [Å] | 9.98 (1) | 9.98 (1) | 9.98 (1) | 17.295435 (25) | 17.148983(18) |
| c [Å] | 13.55 (1) | 13.55 (1) | 13.55 (1) | 10.038134 (14) | 10.09088(10) |
| volume [Å$^3$] | 2336.76 | 2336.76 | 1168.78 | 2360.30 | 2345.03 |
| data | SLS-MS | SLS-MS |
| wavelength [Å] | Mo K$_\alpha$ | Mo K$_\alpha$ | |
| number of reflections | 904 | n.a. | n.a. | |
| sin($\Theta/\lambda$) [Å$^{-1}$] | 0.67 | 0.65 | 0.65 |
| $\chi^2$ | 1.70 | 2.26 |
| $R$ [%] | 13.8 | 8.9 |
| $R_{Bragg}$ [%] | 6.9 | 4.4 |
TABLE II: O-Mn-O angles $\alpha$ and atomic distances $d(O-Mn)$, $d(Mn-O)$ of the MnO$_6$ octahedra in Pb$_3$Mn$_7$O$_{15}$ at $T = 15$ K.

| Atom | Site   | $\alpha$ | $d(O-Mn)$ | $d(Mn-O)$ | BVS     |
|------|--------|----------|-----------|-----------|---------|
| Mn1  | 8d     | O1-Mn1-O12 | 172 (2)  | 1.97 (2)  | 1.86 (2) | +3.458 (89) |
|      |        | O2-Mn1-O12 | 173 (2)  | 1.87 (2)  | 2.06 (2) |
|      |        | O16-Mn1-O17 | 174.3 (1.8) | 2.16 (2)  | 1.94 (2) |
| Mn2  | 8d     | O4-Mn2-O12 | 172.9 (1.9) | 1.92 (2)  | 1.91 (2) | +3.700 (88) |
|      |        | O6-Mn2-O10  | 174.3 (2.0) | 2.00 (2)  | 1.89 (2)  |
|      |        | O9-Mn2-O16  | 173.7 (1.9) | 1.98 (2)  | 1.95 (2)  |
| Mn3  | 8d     | O5-Mn3-O13 | 173.8 (1.6) | 2.14 (2)  | 2.28 (2) | +3.331 (79) |
|      |        | O7-Mn3-O11  | 171.5 (1.9) | 1.89 (2)  | 2.04 (2) |
|      |        | O8-Mn3-O17  | 171.9 (2.0) | 1.82 (2)  | 1.89 (2) |
| Mn4  | 8d     | O2-Mn4-O14 | 160.3 (1.6) | 2.13 (2)  | 2.17 (2) | +3.121 (75) |
|      |        | O3-Mn4-O5   | 164.0 (1.8) | 1.96 (2)  | 1.84 (2) |
|      |        | O10-Mn4-O15 | 161.6 (1.8) | 1.97 (2)  | 2.05 (2) |
| Mn5  | 8d     | O1-Mn5-O14 | 166.9 (2.0) | 1.83 (2)  | 2.00 (2) | +3.417 (89) |
|      |        | O3-Mn5-O4   | 161.8 (1.6) | 2.24 (2)  | 2.13 (2) |
|      |        | O11-Mn5-O15 | 164.5 (1.9) | 1.81 (2)  | 1.98 (2) |
| Mn6  | 4a     | O2-Mn6-O2  | 180.0 (1.9) | 1.95 (2)  | 1.95 (2) | +3.385 (81) |
|      |        | O11-Mn6-O11 | 180 (2)  | 1.94 (2)  | 1.94 (2) |
|      |        | O17-Mn6-O17 | 180.0 (1.9) | 2.03 (2)  | 2.03 (2) |
| Mn7  | 4b     | O1-Mn7-O1  | 180 (2)  | 2.08 (3)  | 2.08 (3) | +3.812 (101) |
|      |        | O10-Mn7-O10 | 180 (2)  | 2.00 (2)  | 2.00 (2) |
|      |        | O16-Mn7-O16 | 180 (2)  | 1.77 (2)  | 1.77 (2) |
| Mn8  | 4c     | O6-Mn8-O7  | 176 (3)  | 1.85 (3)  | 2.09 (3) | +3.917 (113) |
|      |        | O12-Mn8-O13 | 175 (2)  | 1.92 (2)  | 1.88 (2) |
|      |        | O6-Mn8-O7  | 175 (2)  | 1.92 (2)  | 1.88 (2) |
| Mn9  | 4c     | O4-Mn9-O5  | 178.3 (1.9) | 1.88 (2)  | 1.93 (2) | +4.034 (112) |
|      |        | O4-Mn9-O5  | 178.3 (1.9) | 1.88 (2)  | 1.93 (2)  |
|      |        | O8-Mn9-O9  | 175 (3)  | 2.04 (3)  | 1.82 (3) |