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The Synthesis and Characterisation of Ferromagnetic $CaMn_2O_4$ Nanowires

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Abstract

We report the synthesis of 'Marokite' $CaMn_2O_4$ nanowires using a hydrothermal method. Transmission electron microscopy and electron diffraction measurements show that the nanowires are polycrystalline in nature with diameters between 10 nm and 20 nm and lengths ranging from approximately 100 to 500 nm. Most interestingly, in contrast with the bulk material, magnetization measurements show that these nanowires exhibit ferromagnetic ordering with a Curie temperature (T_C) of approximately 40 K.

Key Words: Nanotechnology, Magnetic Properties, Marokite, Nanowires, EXAFS

Introduction

In recent years the scientific community has directed extensive resources into understanding the structure and properties of one-dimensional nanostructures, such as carbon nanotubes, inorganic nanorods and nanowires.[1] These materials provide promising candidates for realising nanoscale electronic, optical and mechanical devices, especially since they exhibit unique physical and chemical properties that are different from their bulk counterparts.

Many studies have focussed on the growth of functional oxide based nanoparticles and nanowires using both templated and template-free chemical solution methods.[2] Nanowires which exhibit Perovskite and Spinel-type structures have been of particular interest for magnetic sensing and recording devices as they exhibit a variety of unique ferroelectric, piezoelectric and colossal magnetoresistive (CMR) properties.[3-11] Investigations have shown that these properties are critically dependent on the dimensions of the material.[12] The interplay among the spin ordering and orbital degrees of freedom in these oxide materials leads to a host of phenomena that are yet poorly understood, such as metal-insulator transitions (MIT), magnetic phase transitions and nanoscale charge and orbital ordering.[13]

$CaMn_2O_4$ was first reported by Gaudefroy *et al*. who determined the structure from naturally occurring marokite mineral forms.[14] Much of the continued research into this material has centred on further structural characterisation and magnetic investigations.[15-20] The structure of $CaMn_2O_4$ has been reported to exhibit a lower symmetry variant of $CaFe_2O_4$ whereby the structure is built up of MnO_6 octahedra which share corners and edges to form channels along the *a* axis providing an 8 co-ordinate site for the Ca cations.[16] It has been widely reported that

$CaMn_2O_4$ is anti-ferromagnetic with a Neél temperature (T_N) of 220 K.[17, 20] More in-depth magnetic studies have been conducted involving the determination of magnetic structures from low temperature neutron diffraction studies and investigations into the effects of Jahn-Teller (JT) distortions on the Mn–O–Mn superexchange pathways.[15, 16] These studies confirmed not only the anti-ferromagnetic spin arrangement but also suggested the presence of recessive ferromagnetic interactions. More recently Spooren *et al.* have reported the synthesis of agglomerates of needle shaped particles of $CaMn_2O_4$ with dimensions of approximately 300 – 600 nm in diameter with lengths of approximately 10 μm.[3] Whilst the authors report that these particles exhibited excellent structural agreement with those previously reported for the bulk material they did not investigate their magnetic properties.

We report here the synthesis of $CaMn_2O_4$ nanowires with dimensions of between 10 nm and 20 nm in diameter and lengths between 100 nm and 500 nm. Magnetic characterisation of these nanowires showed that they exhibit marked differences from the behaviour of the bulk $CaMn_2O_4$. To the best of our knowledge there have been no previous reports of the synthesis of sub-100 nm nanostructures of $CaMn_2O_4$

Results and Discussion

Structure: Phases with varying amounts of Ca were synthesised using the method outlined in the experimental section. With a Ca:Mn ratio of 0.55:1 a phase pure sample of $CaMn_2O_4$ was obtained as verified by x-ray diffraction (XRD) studies. This material will be further discussed in this paper. Alternative Ca:Mn ratios yielded mixed phase materials such as at low calcium contents the materials were composed of $CaMn_2O_4$ and manganese oxides and at higher calcium

contents were composed of $CaMn_2O_4$, manganese oxides and CaO. We saw no evidence for the $CaMnO_3$ Perovskite phase in any of our samples in agreement with earlier results.[3] The $CaMn_2O_4$ material was refined by the Reitveld method using the GSAS suite of programs.[21] The refinement was conducted for 36 variables including zero point and an 18 term shifted Chebyshev background coefficients. The peak shape was refined by employing a pseudovoight function. The refinement profile is given in figure 1 with the refined parameters given in table 1. The refined lattice parameters; a = 3.1479(3) Å, b = 9.95530(11) Å, c = 9.6690(11) Å and cell volume of 302.94(6) $Å^3$ are consistent with those reported previously for bulk materials.[3, 16] Previous structural investigations on Perovskite, $La_{0.67}Ca_{0.33}MnO_3$, nanoparticles have shown a significant lattice contraction as a function of nanoparticle size.[22] However, there is no evidence here of a lattice contraction which is consistent with the observations of Rao *et al*. for $Pr_{0.50}Ca_{0.50}MnO_3$ nanowires.[23] The atom positions were refined using an overall isotropic thermal parameter of U_{iso} = 0.01 x 100. Refinement of the fractional occupancies lead to no real change suggesting that the system is not oxygen or calcium deficient and as such the final refinement is reported with the fractional occupancies set to 1.00. As was observed by Spooren *et al*., it is obvious from the refinement that the peak intensities are affected by preferred orientation consistent with the anisotropic nature of the nanowires.[3] Table 2 gives Mn-O bond lengths derived from the refined data. These bond lengths clearly show that the Manganese site is considerably distorted primarily due to the Jahn-Teller (JT) crystal field splitting of the Mn^{3+} d^4 ion ($t_{2g}^3e_g^1$ electronic configuration) as expected. These results clearly show the typical elongation of the e_g bond lengths (2.45 Å and 2.41 Å respectively) consistent with previous refinements and the shortening of the t_{2g} bonds to give four degenerate bond lengths of approximately 1.9 Å. The validity of all bond lengths and individual bond valences has been

calculated using the bond valence sum program and gives a total valence of +2.8 which is in reasonable agreement with manganese in a +3 oxidation state.[24] The $CaMn_2O_4$ structure is given in figure 2 along with a single MnO_6 octahedral unit showing the distorted nature of the octahedra. It is clear that the structure is not only distorted as a result of Jahn-Teller contributions but that the nanowire geometry also places some strain on the system. However, the polycrystalline nature of these nanowires makes it impossible to fully characterise both the level of strain the nanowire geometry imposes as well as the defect structure.

The Mn environment in the $CaMn_2O_4$ nanowires was further investigated using extended x-ray absorption fine structure (EXAFS) analysis. Mn K-edge EXAFS data was collected using BM26a at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. An excellent correlation between the theoretical model derived from the XRD refinement and the experimental data was observed as shown in figure 3 with a goodness of fit factor, R, of 19.3317. Table 3 gives the observed peak positions and their fitted assignments for the $CaMn_2O_4$ nanowires with the observed EXAFS peak positions being completely consistent with those observed in the Rietveld analysis. Typically the initial nearest neighbour to the Mn is O at a distance of approximately 1.94 Å with next nearest neighbour, attributed to O, observed at 2.39 Å consistent with the 4 short and 2 long bonds of the JT distorted manganese octahedra. The next nearest neighbours can be seen at 2.87 Å, 3.23 Å and 3.82 Å and can be readily attributed to Mn, Ca and O nearest neighbours respectively. It is worth noting that not all shells observed and fitted are easily seen as peaks in the Fourier transform due to the broad nature of the peaks observed, however, the fit to the EXAFS data was significantly improved by the addition of the

shells. These results further confirm the JT distorted nature of the Mn^{3+} octahedral units as has been observed previously in the bulk.[16, 17]

Data collected from the XANES region of the Mn K-edge data for the $CaMn_2O_4$ nanowires was compared with values measured for Mn powder and various Mn oxide standards collected under identical conditions to yield information on the average manganese oxidation state. Figure 4 gives a plot of oxidation state Vs the Mn K-edge potential (E) extracted from the XANES data normalised with respect to the Mn powder. The average manganese oxidation state was calculated from the graph to be 2.92 suggesting that Mn is primarily in the + 3 oxidation state consistent with both the expected oxidation state of $CaMn_2O_4$ and the Rietveld refinement.

Figure 5 shows typical transmission electron microscopy (TEM) images of the $CaMn_2O_4$ material. The images show high nanowire purity with no evidence for the presence of bulk powder. These nanowires are predominantly 10 nm in diameter, although some are as large as 20 nm with a length ranging roughly from 100 to 500 nm as illustrated in figure 5. These dimensions are significantly smaller than those recently reported in the literature.[3] Selected area electron diffraction (SAED) patterns were recorded using a diffraction lens of 120 cm and a typical example is shown in the inset of figure 5. These nanowires are clearly highly crystalline, further confirming the PXRD data. SAED measurements performed on an isolated 20 nm nanowire (figure 6) exhibits a clear pattern which corresponds to the polycrystalline structure of the nanowire. The dark field image from the selected diffraction area shows the crystalline region (bright areas of the image) associated with the diffraction spots in the circle in figure 6, which again confirms the polycrystalline nature of the nanowires. Figure 7 illustrates SAED

measurements performed on three intake nanowires plus manifestly what appears to be a broken nanowire due to the sonification of the sample. The electron diffraction pattern and dark field imaging of a single diffraction spot confirm the polycrystallinity but also suggests that these nanowires exhibit large single crystalline domains of up to 45 nm for this particular nanowire as shown for the top nanowire in figure 7. Porous manganese oxides are prone to defects such as intergrowths making the growth of large single crystals difficult. These defects often lead to the formation of grain boundaries between small single crystals.[25] Energy dispersive x-ray (EDX) analysis performed on this material showed no significant changes in stoichiometry either between different nanowires or along the length of individual nanowires thus confirming the uniform nature of these nanowires. A typical EDX spectrum is shown in figure 8 whereby the Ca and Mn contributions can be clearly seen. Since sample preparation of the nanowires for TEM-EDX analysis constitutes mounting the sample on copper TEM grids a large contribution from Cu is also observed.

Magnetic properties: The results of magnetization measurements are shown in figure 9. In contrast to bulk $CaMn_2O_4$, these nanowires clearly demonstrate ferromagnetic (FM) ordering below the Curie temperature, $T_C \approx 40$ K (figure. 9a), which is further confirmed by the hysteresis curves shown in figure 10. At $T \leq T_C$ the M *vs.* H dependence exhibits strong hysteretic properties in the low field range which suggests FM ordering. However, an observed absence of saturation in higher magnetic fields signifies an additional presence of a paramagnetic component, which is also responsible for a slight increase of the moment at low temperatures, figure 9a. Above ~ 250 K the material exhibits Curie-Weiss behaviour as indicated by the linear fit for the temperature dependence of the inverse magnetization (1/M), see figure 9b, and gives

an extrapolated Curie-Weiss temperature (θ) of -599(5) K which suggests the presence of anti-ferromagnetic (AFM) ordering and a Curie constant of 2.76(2) ergKOe^{-2}mol^{-1}. Below 250 K but above T_C the material does not obey the Curie-Weiss law and there is evidence of a weak AFM transition at a Néel temperature (T_N) of approximately 215 K (Figure 9c) which is typical of the AFM ordering in bulk $CaMn_2O_4$ reported previously.[16] In 3d-oxides the orbital moment of the 3d ions is essentially quenched by the oxygen crystal field (J = S).[16] The spin angular momentum was calculated from the Curie constant using equations 1 and 2.

$$C = \frac{N\mu_{eff}^2 \mu_B^2}{3k_B} \quad (1)$$

$$\mu_{eff} = g\sqrt{S(S+1)} \quad (2)$$

where N is Avogadro's number, k_B is the Boltzmann constant, μ_B is the Bohr magneton, μ_{eff} is the effective magnetic moment of the Mn^{3+} ion and g is the Landé factor (g = 2.00 for spin only moment). The resulting values of μ_{eff} (4.70 μ_B) and S (1.9) are slightly lower than the expected μ_{eff} of 4.89 μ_B and S of 2 for Mn^{3+} (d_4) in a high spin state. These results suggest that, whilst predominantly manganese has a valence of Mn^{3+} consistent with the results extracted from the XRD refinement and EXAFS analysis, a small amount of Mn^{4+} may be present in the system. The hysteresis curve at 2 K shows a well pronounced exchange bias effect (see the inset in figure 10) such that the loop is shifted towards negative field suggesting either the presence of small amounts of an anti-ferromagnetic (AFM) phase and a coupling at the interface between FM and AFM phases or canting of the magnetic moments at the nanowire interface. The magnetic behaviour in bulk $CaMn_2O_4$ has been reported extensively as antiferromagnetic.[16, 17, 20] The magnetic structure has also been reported from neutron diffraction studies and can be described as containing both ferromagnetic and dominating AFM interactions.[16] Nanowires investigated

in this paper also appear to show both FM and AFM ordering, however, in this case the nanowires exhibit robust ferromagnetic properties at low temperatures and are only weakly antiferromagnetic in the intermediate temperature regime.

Size has been shown to have a large effect on the observed magnetic properties. Decreasing particle size into the nano regime of ferromagnetic Perovskite materials has been shown to increase T_C. [22, 26] Néel proposed that fine particles of antiferromagnetic materials should exhibit ferromagnetism and/or superparamagnetism.[27] In comparison with bulk NiO, which is anti-ferromagnetic, NiO nanoparticles have been reported to exhibit superparamagnetism.[28, 29] More recently $Pr_{0.5}Ca_{0.5}MnO_3$ nanowires with diameters of approximately 50 nm have been shown to be ferromagnetic in comparison with their antiferromagnetic bulk counterpart as a result of the nanowire size and geometry.[23] It has been shown previously by many authors that doping of the La site in antiferromagnetic bulk $LaMnO_3$ with Ca leads to ferromagnetic ordering by introducing Mn^{4+} into the system.[30, 31] The effects of small amounts of Mn^{4+} arising as a result of Ca deficiencies in the $CaMn_2O_4$ nanowires should also be considered. However, it is worth noting that in $La_{1-x}Ca_xMnO_3$ when x is smaller than 0.18 there is insufficient Mn^{4+} present to promote ferromagnetic ordering.[32] It has also been shown previously that mixed manganese valence states induced by cation deficiencies in similar bulk porous manganese oxide systems typically result in ferrimagnetic/canted antiferromagnetic ordering or spin glass states.[33] Zouari *et al*. achieved a mixed spin state in bulk $CaMn_2O_4$ through the addition of Fe^{3+} (d_5) on to the Mn^{3+} (d_4) site. Whilst both $CaMn_2O_4$ and $CaFe_2O_4$ exhibit antiferromagnetic ordering, the mixed Fe/Mn systems resulted in ferrimagnetic order due to the different magnetic moments associated with the Mn^{3+} and Fe^{3+} ions.[34] Since there is no evidence in the structural analysis to

suggest that significant amounts of $Mn^{4+}$are present in the system, it is therefore unlikely that the FM ordering observed for these nanowires arises as a result of small amounts of Mn^{4+}. In addition, as these nanowires are built up of $CaMn_2O_4$ single crystals, it can be suggested that Mn^{4+} is possibly present at the grain boundaries between single crystals, thus, resulting in the exchange bias observed. Since these nanowires are similar to those reported by Rao *et al.,* a similar mechanism for the observed FM ordering can be suggested. The ferromagnetic ordering probably arises as a result of the higher surface to volume ratio afforded by the nanowire geometry such that surface effects dominate those of the bulk nanowire possibly resulting in uncompensated spins and a loss of the long range AFM ordering observed in the bulk. It has also been shown previously for Perovskite thin films that strain effects arising from the substrate also play an important role in the observed magnetic properties.[35] Thus, whilst there is no direct evidence of a large lattice distortion in these nanowires with comparison to the bulk, shape anisotropy could also play a key role such that the one-dimensional nature of the nanowires could be expected to radically alter the magnetic behaviour of nanowires with respect to the bulk material.

Conclusions

We report here the synthesis of uniform Marokite-type $CaMn_2O_4$ nanowires with dimensions below 20 nm. We demonstrate that the nanowire geometry critically changes the behaviour of the nanowires with respect to bulk $CaMn_2O_4$. These results suggests that nanowire geometry coupled with strain and quantum confinement effects leads to the FM ordering in this material probably as a result of uncompensated spins. Since many ferromagnetic manganites exhibit a metal insulator transition around T_C along with colossal magnetoresistance, further investigation

of this material is required. This work clearly demonstrates the potential for the synthesis of a new class of materials based on the marokite structure which exhibit unique novel properties different to those observed for their bulk counterparts.

Experimental

X-ray diffraction data was collected using the Phillips Xpert PW3719 diffractometer using Cu Kα radiation (40 kV and 40 mA) over the range $25 \leq 2\theta \leq 60$ and fitted using the GSAS suite of programs.[21] EXAFS and XANES data were collected on BM26a at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Data was collected in transmission mode at room temperature using a Si (111) double-crystal monochromator at the Mn K-edge (6539 eV). Signal processing was performed by the XPROSS system developed at the Daresbury Laboratories. Multiple experimental data scans were summed using the Athena program. The background was subtracted and normalised using the EXSPLINE program. The data was simulated using k^3-weighted EXAFS employing theoretical phase shifts calculated with Hedin-Lundqvist exchange potentials and von Barth ground states using the program EXCURV98. Theoretical fits were obtained by adding shells of backscattering atoms around the central Mn absorber atom and refining the Fermi energy, E_f, the absorber-scattered distances, r, and the Debye-Waller factor, $2\sigma^2$, in order to maximise the goodness of fit, R. R is not only dependent on the validity of the constructed shell model but is also reliant on the signal to noise ratio and the experimental data range. XANES data was analysed using the EXBROOK software. A JEOL 2000FX transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV was used for TEM bright and dark field imaging as well as selected area electron diffraction (SAED). Samples were dispersed in ethanol, sonicated and a drop of the mixture was placed on a 400

mesh carbon-coated copper grid for investigation. Energy dispersive x-ray (EDX) analysis was performed using an Oxford Instruments INCA energy system fitted to the TEM. Magnetic measurements were performed using a Quantum Design MPMS XL SQUID magnetometer at temperatures between 1.8 and 300 K in fields up to 30 kOe.

$CaMn_2O_4$ nanowires were synthesised in a similar method to the one described by Zhu *et al*.[5] Stoichiometric ratios of $Ca(NO_3)_2$ (ANALR, 98.5%) and manganese sources $KMnO_4$ (ANALR, 99.5%) and $MnCl_2$ (Aldrich 98%) with the ratio 0.3:0.7 respectively, were dissolved with stirring in distilled deionised water (40 mL). Potassium hydroxide pellets (~78 mmol, Aldrich, 85%) were added to this solution with stirring. The resulting precipitate was transferred to a teflon lined autoclave and placed in an oven at 210 ^oC for 72 hours. The nanowires were than filtered under vacuum and washed using dd-H_2O before being allowed to dry overnight at 60 ^oC in an oven.

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Figure Legends

Figure 1: Refinement profile for $CaMn_2O_4$ showing the experimentally observed trace (circles), the calculated trace from the proposed Marokite model (full line) and the difference between the two. Space group Pbcm; *a* = 3.1479(3) Å, *b* = 9.9530(11) Å, *c* = 9.6690(11) Å, V = 302.94(6) $Å^3$; χ^2 = 7.623, wRp = 1.29%, Rp = 0.96%.

Figure 2: Schematic representation of (a) the $CaMn_2O_4$ structure where the dark grey spheres represent the Ca ions and the light grey squares represent the MnO_6 octahedral units, corner and edge shared to form the manganese oxide framework. The black spheres represent the oxygen atoms at the corners of the octahedra. (b) Octahedal unit showing the Jahn-Teller (JT) distortion where the light grey spheres represent the Mn^{3+} ion and the black spheres represent the O ions.

Figure 3: (a) Typical EXAFS experimental $k^3x(k)$ (black line) and the corresponding theoretical fit (grey line) for the Mn K-edge of the $CaMn_2O_4$ nanowires obtained by adding successive back scattering shells around a central Mn atom and (b) Absolute values of the Fourier transform of $k^3x(k)$ into reciprocal (r) space for the $CaMn_2O_4$ nanowires.

Figure 4: Measured XANES edge shift normalised with respect to Mn powder. Where the black squares represent the Mn standards and the grey circle represents the $CaMn_2O_4$ nanowires.

Figure 5: Typical transmission electron microscopy (TEM) bright field images of $CaMn_2O_4$ nanowires showing a size distribution ranging between 10 nm and 20 nm in diameter. The scale bar represents 100 nm and 200 nm in image (a) and image (b) respectively. Inset in image (a)

gives a typical selected area electron diffraction pattern showing the polycrystalline nature of these nanowires.

Figure 6: Bright field and dark field imaging of an isolated 20 nm nanowire and its associated selected area electron diffraction pattern. The dark field image corresponds to the diffraction spots in the circle showing a polycrystalline nanowire. The scale bar in both the bright field and dark field images represents 200 nm.

Figure 7: Bright field and dark field imaging of three isolated 10 nm nanowires and their associated selected area electron diffraction pattern. The dark field image corresponds to the diffraction spots in the circle showing the polycrystalline nature of these nanowires. The scale bar in both the bright field and dark field images represents 100 nm.

Figure 8: Typical Energy dispersive x-ray (EDX) spectrum confirming the presence of both Ca and Mn within these nanowires. Note: the sample is prepared on a Cu grid for TEM analysis hence the strong Cu contribution to the spectra.

Figure 9: Magnetization measurements for $CaMn_2O_4$ nanowires. (a) Zero Field Cooled (ZFC) (open circles) and Field Cooled (FC) (filled circles) magnetization measurements showing ferromagnetic behaviour below T_C = 40 K. (b) 1/M *vs.* temperature dependence showing Curie-Weiss behaviour between 250 and 300 K where the dashed line indicates a liner fit and (c) FC measurements showing an anomaly at ~ 215 K.

Figure 10: Hysteresis curves for $CaMn_2O_4$ nanowires at 2 K, 10 K, 25 K, 40 K, 100 K and 300K. Inset shows the shift of the hysteresis curve at 2 K due to exchange bias coupling.

Tables Legends

Table 1: Structural parameters observed for $CaMn_2O_4$ refined from powder x-ray diffraction data (errors given in brackets).

Atom	Position	x	y	**z**
Ca	4d	0.7387(21)	0.1469(4)	0.7500
Mn	8e	0.1812(11)	0.1111(3)	0.0669(3)
O1	4c	0.5742(34)	0.2500	0.0000
O2	4d	0.2426(61)	0.1876(14)	0.2500
O3	8e	0.7785(40)	0.9660(11)	0.1114(9)

[Space group Pbcm; a = 3.1479(3) Å, b = 9.9530(11) Å, c = 9.6690(11) Å, V = 302.94(6) $Å^3$; χ^2 = 7.623, wRp = 1.29%, Rp = 0.96%.]

Table 2: Bond lengths, calculated bond valences and bond angles observed for $CaMn_2O_4$ refined from powder x-ray diffraction data (errors given in brackets).

Mn-O bond lengths (Å)		Mn – O bond calculated valences	Selected Mn – O – Mn bond angles (°)	
Mn – O1	2.45(1)	0.157	Mn – O1 – Mn	102.0(6)
Mn – O1	1.965(6)	0.575	Mn – O2 – Mn	132.1(7)
Mn – O2	1.937(5)	0.620	Mn – O3 – Mn	93.1(5)
Mn – O3	1.97(1)	0.568		
Mn – O3	2.41(1)	0.173		
Mn – O3	1.891(7)	0.702		
Total valence		2.795		

[Note the number next to the O denotes the atomic site of the oxygen.]

Table 3: Observed shells with the corresponding neighbour assignments for the first five shells of the $CaMn_2O_4$ nanowires at the Mn K-edge (errors given in brackets). The goodness of fit parameter, R, is given as 19.3317.

Observed shell distance (Å)	Calculated shell distance* (Å)	Classification
1.937(4)	1.941(7)	Mn – O
2.39(2)	2.43(1)	Mn – O
2.872(6)	2.783(7)	Mn – Mn
3.23(2)	3.367(5)	Mn – Ca
3.82(3)	3.904(3)	Mn – O

[* Calculated shell distances have been taken from the average distances observed in the Rietveld refinement of the x-ray diffraction data and the structural model calculated from the refinement data.]

Table of Contents text: Ferromagnetism is observed in ‘Marokite’ type $CaMn_2O_4$ nanowires with diameters between 10 nm and 20 nm. The structure can be described as MnO_6 octahedral units linked to form a manganese oxide framework with the Ca ions occupying tunnels formed within this framework (see picture where the pink squares are MnO_6 octahedra and the yellow spheres are Ca ions).