Studies of the $Ca_4Mn_3O_{10}$ structure obtained using high pressure and high temperature

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Abstract
An ideal $n = 3$ member of the group of Ruddlesden–Popper (RP) phases
$Ca_4Mn_3O_{10}$ was obtained by solid-state reaction under high pressure. This
phase has been studied by transmission electron microscopy, convergent beam
electron microscopy, high-resolution transmission electron microscopy, and
parallel electron energy-loss spectroscopy. The lattice parameters are derived
as $a = b = 0.37$ nm and $c = 2.69$ nm with the space group $I4/mmm$, which
is the space group of the ideal RP phase.

1. Introduction

Doped perovskite manganites show a wide variety of magnetic-field-induced phenomena,
including colossal magnetoresistance (CMR) [1, 2]. This effect is of technological interest as
it can be exploited in the sensitive detection of magnetic fields in magnetic memory devices.

It is well known that perovskite has a three-dimensional structure corresponding to the
case of $n = \infty$ in the Ruddlesden–Popper (RP) series [3]. The RP phases provide an invaluable
experimental model for studying the effect of dimensionality of the magnetic lattice on the
CMR effect. These consist of blocks each of n layers of perovskite alternating with single
(R, A)O rock-salt layers. Though the double-exchange mechanism, which effects the transfer
of an electron through Mn^{3+}–O–Mn^{4+} ions, can be used to explain many aspects, it alone is
not sufficient to give a global explanation of the phenomenon [4–6]. In fact, experiments on
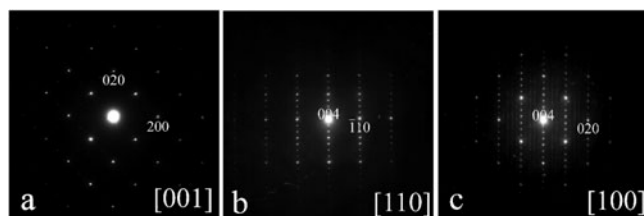the pyrochlore $Tl_2Mn_2O_7(Mn^{4+})$ have demonstrated that CMR can occur even in the absence

Figure 1. ED patterns of $Ca_4Mn_3O_{10}$. (a) [001]; (b) [110]; (c) [100].

of detectable mixed valence [7–9]. So it is also necessary to study compounds which have no mixed manganese valences.

So far, only a few papers have been published on $n = 3$ members of the RP series. Brisi and Lucco-Borlera [10] reported a tetragonal $Ca_4Mn_3O_{10}$ phase from an earlier x-ray powder diffraction analysis, which is considered to have lower symmetry in fact [11]. Henry *et al* [11] studied $Ca_4Mn_3O_{10}$ and $Sr_4Mn_3O_{10}$, and reported that $Ca_4Mn_3O_{10}$ has a space group $Ccc2$. Battle *et al* [12] determined the structure of $Ca_4Mn_3O_{10}$ and reported a space group $Pbca$ according to x-ray and neutron diffraction [12]. A dc magnetization study of $Ca_4Mn_3O_{10}$ was reported by Lago *et al* [7] and attempts have been made to dope the $n = 3$ member with La in order to induce mixed valence, though only low doping levels in bulk samples have been reported to date [11, 13].

Up to now, the popular methods of sample preparation have been the conventional bulk ceramic process, the floating-zone method, the sol–gel solution method, thin-film growth, etc. In this paper, we used solid-state reaction under high pressure in the preparation of our samples. Here we report an ideal RP phase $Ca_4Mn_3O_{10}$ with space group $I4/mmm$ obtained by high-pressure synthesis.

It is well known that the lower Earth's mantle which is at high temperature and under high pressure is mostly composed of perovskite or quasi-perovskite phases. A lot of experiments have demonstrated that perovskite or layered structures are favoured under high pressure. High-pressure techniques have also been successfully adopted in synthesizing superconductor samples [14, 15]. The $Ca_4Mn_3O_{10}$ phases reported in the literature so far were not ideal RP phases, but distorted ones.

2. Experiments

Well-ground stoichiometric mixtures of $CaCO_3$ and MnO_2 were pelletized and first calcined in air at $1000\,°C$ for 12 h, and then reground, pelletized, and sintered twice at $1250\,°C$ for 24 h in order to get the precursor material Ca_2MnO_4. The powder, of nominal composition $Ca_4Mn_3O_{10}$, for the high-pressure synthesis was obtained by grinding stoichiometric mixtures of Ca_2MnO_4 and MnO_2. The powder was pelletized to a size of 5 mm diameter, 10 mm height, wrapped in a Pt thin film, and then sealed into a BN sample cell (diameter 7 mm, height 12 mm). In the experiment, a pressure of 5.0 GPa was applied at a temperature of $1250\,°C$. The reaction time was maintained for 30 min under these conditions. Then, the heating supply was cut off and the sample was decompressed and cooled to ambient pressure and temperature. Transmission electron microscopy (TEM) experiments were carried out on Philips EM 420, CM 12, and Tecnai electron microscopes.
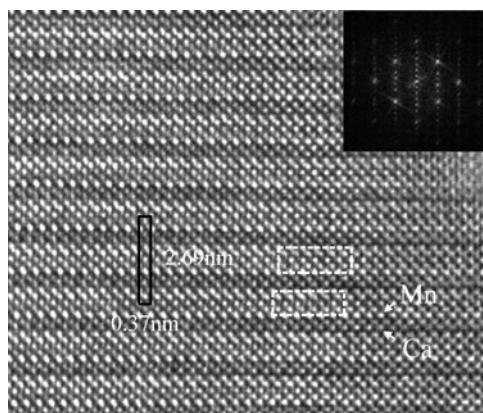
Figure 2. The HRTEM image of Ca$_4$Mn$_3$O$_{10}$ along [100]. One unit cell is outlined using black solid lines, and elements Ca and Mn are marked by small white arrows.

3. Results and discussion

A series of electron diffraction (ED) patterns were obtained from the sample, and the three main zones [001], [110], and [100] are shown in figures 1(a)–(c), respectively. The observed extinction rules in the experimental diffraction patterns are:

hkl: $h + k + l = 2n$

$hk0$: $h + k = 2n$

$0kl$: $k + l = 2n$

$00l$: $l = 2n$

$0k0$: $k = 2n$.

Convergent beam electron diffraction (CBED) experiments were also carried out. From ED and CBED studies, the space group $I4/mmm$ is the definite choice. The cell constants were derived from the ED patterns as: $a = b = 0.37$ nm and $c = 2.69$ nm. The value of the lattice parameter c corresponds to the $n = 3$ member of the RP series.

This phase was also studied by high-resolution electron microscopy (HRTEM). The HRTEM image is shown in figure 2. The layered structure is clearly seen in the image; neighbouring blocks of three layers are separated by a double CaO rock-salt layer and shifted half a unit cell along the a-direction (or b-direction), and followed by a repeat of the three layers plus a rock-salt layer. Consecutive three-layer blocks are marked by white dotted rectangle in the figure in order to show the separation and shifting; the blocks extend infinitely along the ab-plane. This clearly demonstrates that this phase corresponds to the $n = 3$ member of the RP phases. One unit cell is outlined by a black solid line in the image and the lattice constants obtained from the image are consistent with those obtained from ED patterns. The elements Ca and Mn are also indicated, by white arrows, in the image. The fast Fourier transform pattern (diffractogram) of the HRTEM image is also shown in the top right-hand corner of figure 2. Both the diffractogram and the diffraction pattern clearly indicate the details of the layer structure.

On the basis of the cell parameters obtained and the bond lengths reported by Battle *et al* [12], an approximate structural model is proposed; this is shown in figure 3. The three layers of Mn–O octahedra interspersed with single CaO layers are followed by a CaO double layer. This is repeated, with the same layer structure shifted by half a unit cell in both a- and
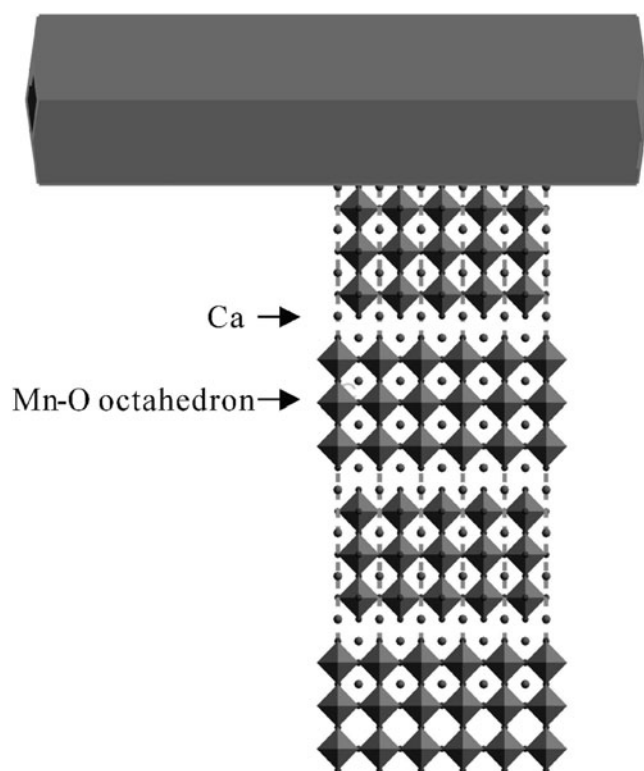
Figure 3. The proposed model of $Ca_4Mn_3O_{10}$.

b-directions. The ED patterns and HRTEM images were simulated from the model using the simulation program Cerius2.0 installed at the University of Mainz [16]. The simulated HRTEM images are shown in figures 4(c) and (d). It can be seen that the agreement in figure 4 is very convincing.

In order to confirm the composition of the phase, parallel electron energy-loss spectroscopy (EELS) studies were carried out *in situ* in the electron microscope. The parallel EELS measurements indicated that this phase is composed of Ca, Mn, and O elements. The result of the quantitative analysis of the elemental contents is in very close agreement with the nominal composition of the sample. This demonstrates again that the phase discussed above is undoubtedly the $n = 3$ member of the RP series.

4. Conclusions

An ideal $n = 3$ member of the RP phase series $Ca_4Mn_3O_{10}$ with the space group $I4/mmm$ was obtained by solid-state reaction under high pressure. Since the reaction rate is much faster at high pressure than at ambient pressure, the procedure is much faster. Ideal perovskite and also the layered structures are stable at high pressure; therefore the RP phases with layered structures or other layered structures which are distorted RP structures with large periodicity are favoured and easily obtained at high pressure. Some phases which are difficult or even impossible to obtain under normal pressure can be obtained at high pressure. So this method will play an important role in the research on CMR materials.
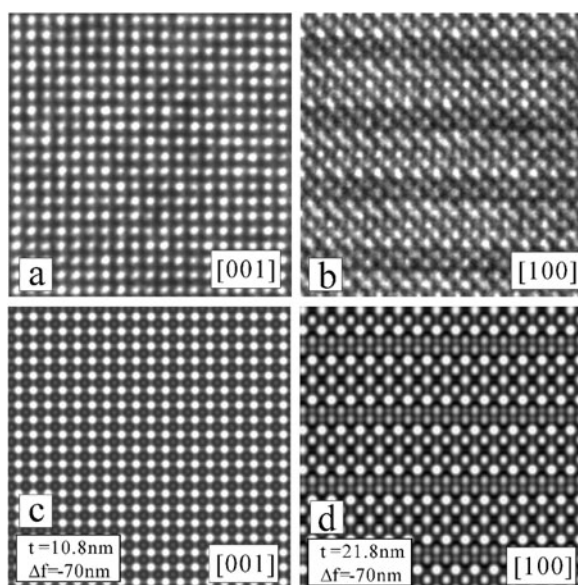
Figure 4. HRTEM images. (a) The experimental image along [001]; (b) the experimental image along [100]; (c) the simulated image along [001]; (d) the simulated image along [100].

Acknowledgments

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