



Preparation of orthorhombic phase YbMnO_3 and $\text{Yb}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$

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The orthorhombic manganite phases o- YbMnO_3 and o- $\text{Yb}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ are obtained through reconstructive transformation at high pressure (3.5 GPa) from material prepared by conventional solid reaction. ^{57}Fe -Mössbauer spectra for o- YbMnO_3 are compared with those recorded earlier for the hexagonal phase h- YbMnO_3 .

1. Introduction

The discovery of colossal magnetic resistance for the generic $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ has led to renewed interest in the magnetic properties of all orthorhombic manganites. With decreasing average ionic radius $\langle r_{R-\text{Ca}} \rangle$ the Curie temperature for $\text{R}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (R = rare earth) decreases and eventually the low temperature ferromagnetic-metallic phase is replaced by an insulating phase. For the undoped manganites RMnO_3 , the Néel temperature undergoes a similar decrease with decreasing $\langle r_R \rangle$ and the low temperature magnetic structures often involve complex multiferroic behaviour.

We plan to use ^{57}Fe -Mössbauer spectroscopy to probe the low temperature magnetic structure in both o- YbMnO_3 and o- $\text{Yb}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$. For this purpose 0.5 at % ^{57}Fe will be introduced into the Mn sub-lattices. However, at ambient pressure, both of these manganites form with the hexagonal $P6_3cm$ structure (rather than orthorhombic $Pnma$) in accordance with our proposed structural phase diagram (Figure 1). This contribution will first describe our efforts to produce o- YbMnO_3 and o- $\text{Yb}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ using three different approaches. Preliminary ^{57}Fe -Mössbauer spectra will then be presented for the orthorhombic phase specimen o- YbMnO_3 and compared with those recorded earlier for hexagonal h- YbMnO_3 .

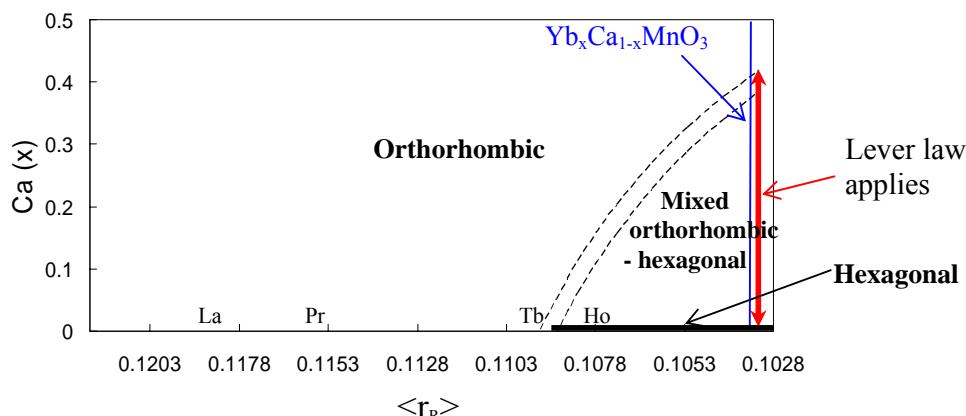


Fig. 1: Structural phase diagram for $\text{R}_{1-x}\text{Ca}_x\text{MnO}_3$. The broken lines indicate the likely orthorhombic phase -mixed phase boundary region based on average radii $\langle r_{R-\text{Ca}} \rangle$.



2. Sample preparation

2.1 Conventional solid state reaction with 6 MPa (60 bar) O₂

The specimen with nominal stoichiometry Yb_{2/3}Ca_{1/3}MnO₃ was prepared in air by conventional solid state reaction and observed to form as a mix of 16.3 wt% h-YbMnO₃ and 83.6 wt% o-Yb_{0.6}Ca_{0.4}MnO₃. This material was then annealed under 6 MPa O₂ at 1000°C for a further 12 hours. However, this treatment did not result in any significant conversion of the phase mixture to o-Yb_{2/3}Ca_{1/3}MnO₃.

2.1 Hydrothermal synthesis at approximately 3.9 MPa (39 bar)

The undoped o-HoMnO₃ and o-DyMnO₃ manganites have been prepared elsewhere by Wang *et al.* using this method [1] so we decided to test this method for the two Yb-based compounds. Our syntheses were performed in 50 mL, Teflon-lined, stainless steel, rotating autoclaves which were filled to 70% of their capacity. First the Yb₂O₃ (together with CaCO₃ when appropriate) was dissolved in 0.1 M HNO₃ at 50°C with constant stirring to form a clear solution. Next KMnO₄ and MnCl₂-4H₂O were mixed in distilled water and sufficient KOH was added to maintain alkalinity. Finally the two solutions were placed in the sealed autoclave and reacted at 250°C under autogenous pressure. Efforts to prepare o-YbMnO₃ (at ADFA over 1 d) and o-Yb_{2/3}Ca_{1/3}MnO₃ (at DelftChemTech over 4 d) failed to produce orthorhombic phase specimens, most likely because the pressure was not high enough. The pressure of water vapour in equilibrium with water at 250 °C is estimated at 3.9 MPa (39 bar). The earlier preparations of o-HoMnO₃ and o-DyMnO₃ were probably accomplished at this lower pressure because they are positioned much closer to the phase boundary of Fig.1. Nevertheless, a positive outcome from this work was that the hydrothermal reaction proved to be an efficient approach for the preparation of h-YbMnO₃ when compared with conventional solid state reaction.

2.3 High pressure synthesis at 3.5 GPa (35 kbar)

Undoped o-YbMnO₃ has recently been prepared elsewhere by Huang *et al.* [2, 3] using this approach. In our case, samples of nominal stoichiometry Yb_{2/3}Ca_{1/3}MnO₃ and YbMnO₃ were first prepared by conventional solid state reaction. Up to 250 mg of a powdered specimen was then sealed (by welding) in a platinum capsule and assembled into a hydraulic press. The specimen material was maintained at 3.5 GPa (35 kbar) and 1100°C for 10 h. While still at maximum pressure, the heating current was switched off, with the specimen temperature falling 400°C within 5 seconds. X-ray powder diffraction patterns for the resultant o-YbMnO₃ and o-Yb_{2/3}Ca_{1/3}MnO₃ are shown in Fig. 2. In each case the line positions are compatible with those of a single-phase, orthorhombic perovskite specimen. The mismatch of some of the individual line intensities may be associated with effects resulting from the rapid quench, such as strain, preferred alignment or stacking faulting.

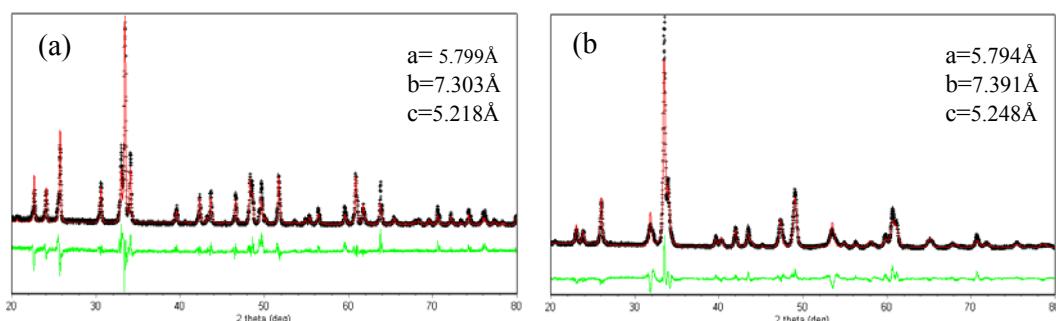


Fig.2: X-ray diffraction patterns for (a) o-YbMnO₃ and (b) o-Yb_{2/3}Ca_{1/3}MnO₃ prepared at 3.5 GPa.



3. ^{57}Fe Mössbauer spectroscopy results

Preliminary ^{57}Fe Mössbauer spectra were recorded for an o-YbMnO₃ specimen in which the Mn sub-lattice had been doped with 0.5% ^{57}Fe . These spectra are presented in Fig. 3 together with those recorded earlier for h-YbMnO₃. Compared with h-YbMnO₃, the isomer shift for o-YbMnO₃ is more positive, implying a slightly smaller electron density at the ^{57}Fe probe nucleus. The quadrupole interaction is of similar magnitude but opposite sign. The saturation magnetic hyperfine field, B_{hf} , is about 6% smaller. Most significantly, B_{hf} is inclined at an angle of $\approx 42^\circ$ (rather than 90°) with respect to the principal z-axis of the electric field gradient (Table 1).

Table 1: Parameters fitted to the ^{57}Fe Mössbauer spectra recorded for h-YbMnO₃ and o-YbMnO₃

T [K]	Phase	$\delta_{\alpha\text{-Fe}}$ [mm/s]	Γ [mm/s]	$eQV_{zz}/2$ [mm/s]	B_{hf} [T]	θ [°]
300	h	0.292	0.339	-1.68		
	o	0.357	0.341	+1.56		
4.2	h	0.420	0.389	-1.60	47.1	90
	o	0.487	0.445	+1.79	44.3	41.8

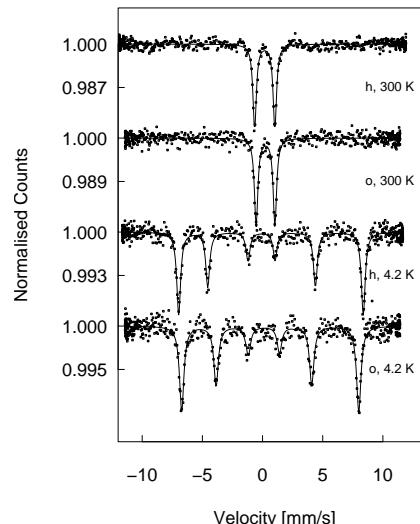


Fig.3: ^{57}Fe Mössbauer spectra recorded for h-YbMnO₃ and o-YbMnO₃

Conclusion

Following the example of Huang *et al* [2], the orthorhombic specimens have been successfully prepared at the high pressure of 3.5 GPa. The solid state reaction under 6 MPa O₂ and the hydrothermal syntheses were not successful, presumably because the pressures achieved were too small. However, the hydrothermal reaction proved much more efficient for the preparation of ambient pressure phases (compared with the tedious conventional solid state reaction). In future work, the ^{57}Fe Mössbauer investigation of o-YbMnO₃ will be continued as a function of temperature and then extended to o-Yb_{2/3}Ca_{1/3}MnO₃.

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