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Epitaxial stabilization of hexagonal $RMnO_3$ (R = Eu–Dy) manganites

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Epitaxial thin films of $RMnO_3$ (R = Sm, Eu, Gd, Dy) have been prepared using liquid injection MOCVD. The formation of a high-temperature hexagonal modification for $DyMnO_3$ and bulk hexagonal $EuMnO_3$ and $GdMnO_3$, which does not exist for the bulk compounds, has been observed on $ZrO_2(Y_2O_3)$ (111) substrates at 900 °C due to epitaxial stabilization.

Stable hexagonal $LuMnO_3$-type structures (space group $P6_3cm$) have been found for $RMnO_3$ compounds where R is a trivalent rare-earth cation with a small ionic radius. This structure can be described as dense oxygen-ion packing (ABCACB) with Mn^{3+} ions having a coordination number CN = 5 (five-fold trigonal bipyramidal coordination) and R^{3+} with CN = 7 (seven-fold monocapped octahedral coordination).[1] $YMnO_3$, which belongs to this structural type, is considered to be a prospective ferroelectric material for electronic applications.[2]

A metastable perovskite *Pnma* phase can be obtained instead of the hexagonal $RMnO_3$ by high pressure synthesis,[3] by 'soft chemistry' synthesis[4] or by epitaxy on perovskite substrates.[5] The high pressure effect can be easily understood taking into account the significant decrease of the unit cell volume (8–9%) in going from the hexagonal to the perovskite structure.[1]

For $DyMnO_3$, whose stable modification structure is that of a perovskite, the hexagonal phase was obtained by quenching from high temperature ($\geqslant$1600 °C).[4] However, for $GdMnO_3$, direct extrapolation gives too high a phase transition temperature (*ca.* 2800 °C, which is well above the melting point of manganites). We supposed[5] that the most suitable way for the synthesis of metastable hexagonal manganites would be epitaxial stabilisation, as in the case of $BaCu_3O_4$,[6] $RNiO_3$ (R = Pr–Gd),[7] $NdMn_7O_{12}$,[8] and $LuCoO_3$.[9]

The calculations made using available data for stable hexagonal phases show that the $ZrO_2(Y_2O_3)$ (111) substrate has in-plane lattice parameters closest to the parameters of the hypothetical phases ($r > r_{Dy}$) and excellent coincidence of oxygen crystallographic positions at the interface. Deposition runs were performed using a liquid injection MOCVD device;[10,11] the deposition temperature was 900 °C, the oxygen partial pressure was 0.33 kPa, and the total pressure was 0.67 kPa (the deposition rate was *ca.* 50 Å min^{-1}). $Mn(thd)_3$ and $R(thd)_3$, where thd = 2,2,6,6-tetramethylheptane-3,5-dionate, were used as volatile precursors (0.02 M solution in diglyme, molar ratio of R : Mn producing stoichiometric films was *ca.* 1.4). Deposition of films with approximate thickness of 1000 Å was performed simultaneously on $ZrO_2(Y_2O_3)$ (111), $ZrO_2(Y_2O_3)$ (001), $LaAlO_3$ (001) (pseudocubic notations), and MgO (001) substrates. Thin films were characterised by X-ray diffraction using a four-circles Siemens D5000 diffractometer equipped with secondary graphite monochromator.

All the films on MgO and $ZrO_2(Y_2O_3)$ (001) were polycrystalline but were strongly textured and exhibited a perovskite structure. Films on $LaAlO_3$ were epitaxial and consisted of perovskite only. XRD patterns of $DyMnO_3$, $GdMnO_3$ and $EuMnO_3$ deposited on $ZrO_2(Y_2O_3)$ (111) are essentially different (Fig. 1). Observed reflections [both symmetric (00*l*) and asymmetric (111), (112)] are typical for a hexagonal $LuMnO_3$-type structure. A new hexagonal phase appears as a *c*-oriented one which was confirmed by ϕ-scans (Fig. 2) and pole figures. Epitaxial relations were established as follows:

$$(001)_{hex.}\ RMnO_3 \mathbin{//} (111)\ ZrO_2(Y_2O_3);$$
$$<1\bar{1}0>_{hex.}\ RMnO_3 \mathbin{//} <1\bar{1}0>\ ZrO_2(Y_2O_3)$$

A sketch of the epitaxy is given in Fig. 3. The intensity of the (00*l*) reflections decreased from Dy to Eu and vanished for Sm, together with an increase of the perovskite reflection intensity. The hexagonal $DyMnO_3$ appeared as a nearly pure phase. The

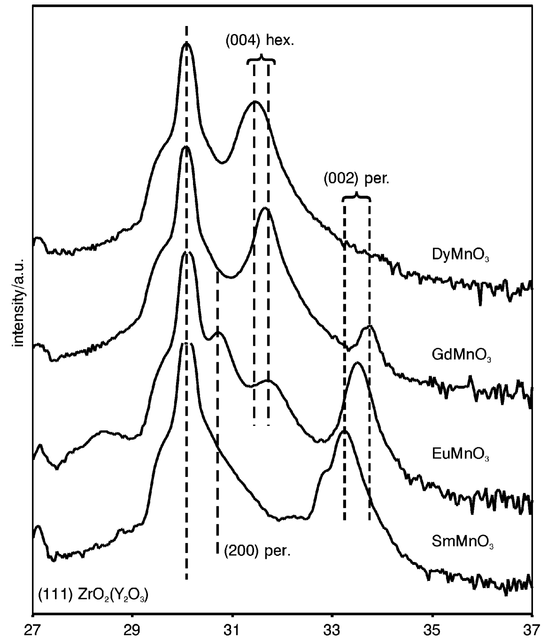

Fig. 1 θ–2θ XRD patterns for 100 nm thick films of $RMnO_3$ (R = Sm, Eu, Gd, Dy) on ZrO_2 (Y_2O_3) (111) (note the significant shift of the hexagonal *c* parameter).

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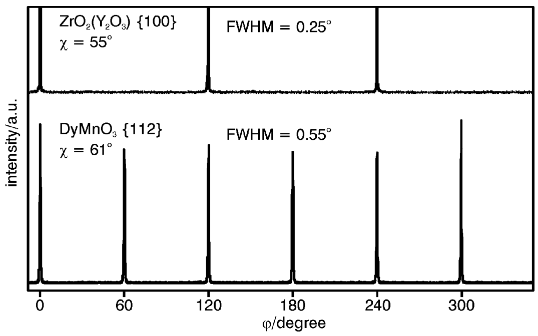

Fig. 2 ϕ-Scans for the $ZrO_2(Y_2O_3)$ (111) substrate and the hexagonal $DyMnO_3$ thin film.

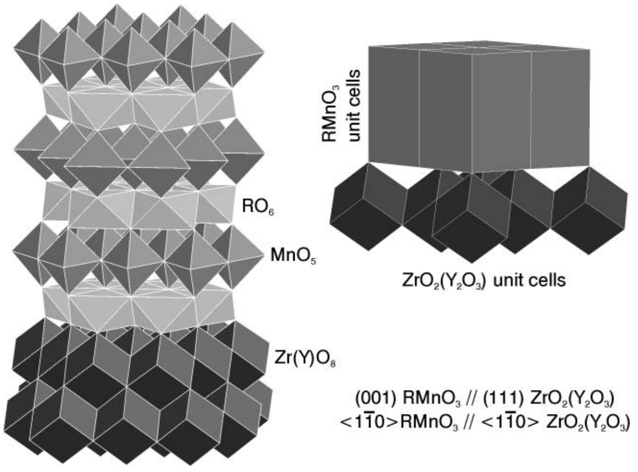

Fig. 3 Epitaxy relationship between hexagonal manganite and $ZrO_2(Y_2O_3)$ (111): polyhedra and unit cell representations.

coexistence of oriented hexagonal and perovskite phases for R = Eu, Gd was proven by pole figures for corresponding zones of the both phases. Noteworthy is the increase of $GdMnO_3$ film thickness to 3000 Å, which resulted in an increased intensity of the perovskite reflections but with no further increase of the intensity of the hexagonal phase reflections. Thus, the hexagonal phase grew in the vicinity of the interface and the perovskite component formed in the upper part of the film; 100 nm seems to be nearly the critical thickness for $GdMnO_3$.

The apparent decrease of the hexagonal *c* parameter with the increase of rare-earth ionic radius (Fig. 1) was explained by significant strain. All films are stretched in-plane as is seen by comparison with lattice parameters of bulk materials (Fig. 4a), but the unit cell volume remains close to that extrapolated from data for heavier rare-earths (Fig. 4b).

Following thermodynamic estimation,[6] when the energy gap between the equilibrium and non-equilibrium states does not exceed 10–15 kJ mol^{-1}, the latter can be stabilized by the free energy gained from diminishing the surface energy term due to coherent interface formation. We believe that this effect results in the appearance of high-temperature or even non-existing phases at much lower deposition temperatures. As the contribution of the surface energy is inversely dependent on the thickness, the stabilizing effect can only be observed for the films of limited thickness.[6] Already, $GdMnO_3$ thin films do not crystallize completely in a pure hexagonal phase; the upper layer is indeed of perovskite structure. This tendency is even more pronounced for $EuMnO_3$.

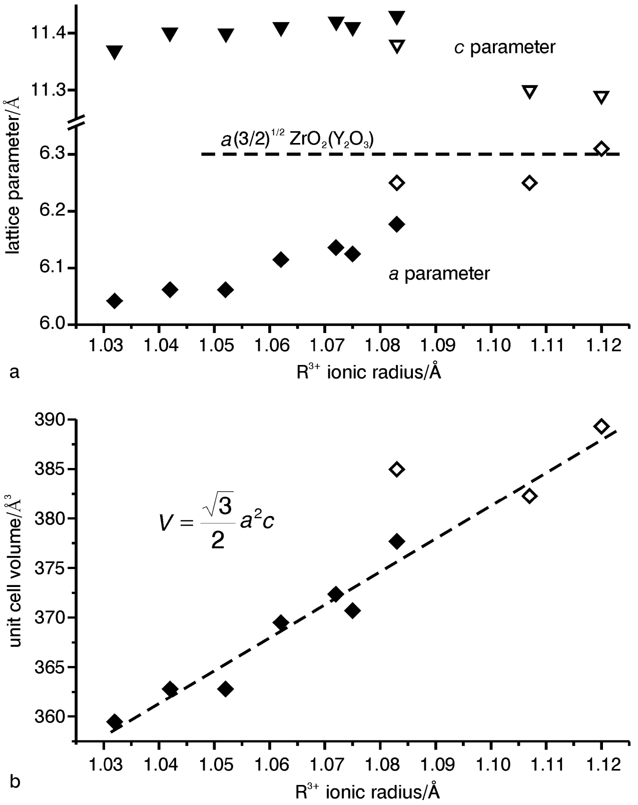

Fig. 4 (a) Lattice parameters and (b) unit cell volumes for hexagonal phases: closed symbols for bulk samples (JCPDS database), open symbols for thin films (experiment).

In conclusion, we have succeeded in the preparation of epitaxial films of hexagonal $RMnO_3$ (R = Dy, Gd, Eu) by low pressure MOCVD. For Gd and Eu these phases were not known before and apparently cannot exist as the bulk phase. For Dy, the decrease of the hexagonal phase formation temperature is *ca.* 700 °C (900 °C for the thin film instead of 1600 °C for the bulk phase). These phases can be formed with the hexagonal structure (instead of the stable perovskite structure) because of epitaxial stabilization of the phases on fluorite substrates of the proper orientation (111).

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