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Epitaxial stabilization of rare-earth garnets $(La_{1-x}Nd_x)_3Fe_5O_{12}$ and perovskites $RInO_3$ (R = Sm–Tm)

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The new unstable phases of garnets and perovskites were observed using the effect of epitaxial stabilization.

Epitaxial stabilization is based on a free energy gain due to structural coherence at the film/substrate interface, and it can be effectively used to enlarge the spectrum of new functional materials.

The phase composition of thin films on single crystal substrates disagrees very often with equilibrium phase diagrams of corresponding bulk systems; the origin of this phenomenon can be of kinetic or thermodynamic nature. At a high deposition temperature (700–900 °C), which is typical of metal-organic chemical vapour deposition (MOCVD) of oxide films, there are no kinetic limitations for heterogeneous processes at vapour/substrate interfaces. Due to this, the phase composition of a crystalline deposit at the substrate corresponds to the global minimum of free energy of the system. In such a case, the above disagreements with phase diagrams, if observed, are manifestations of the change of equilibrium relationships because of oriented crystallization of the film on the substrate. The changes of phase relations in thin films of binary and more complex oxides (in particular, HTSC and CMR manganites) and also the formation of unexpected polymorphs, or unusual oxidation states, were found[1,2] to be caused by epitaxy on the substrate or on the crystalline surface of another phase (matrix).

The free energy gain of the epitaxial phase allowed us to formulate epitaxial stabilization as the enlargement of the P–T–X space of the thermodynamically stable existence of an epitaxial phase compared to a free bulk state of the phase.

We found that $(La_{1-x}Nd_x)_3Fe_5O_{12}$ (x = 0.3–1) and $RInO_3$ (R = Sm–Tm) can be obtained as thin epitaxial films in spite of the thermodynamic instability of corresponding bulk materials under film deposition conditions.

Epitaxial stabilization can be a tool for the synthesis of unstable compounds in the state of epitaxial films. The latter can be used as an alternative to the lacking single crystal samples for the study of fundamental physical properties or as thin film materials for practical applications.

The thin films were obtained by the MOCVD technique[3] using 2,2,6,6-tetramethylheptane-3,5-dionato chelates of corresponding metals as volatile precursors. The deposition temperature was 850–1000 °C, the oxygen pressure was 4 mbar, the total pressure was 13 mbar, and the deposition rate was ≈ 3 nm/pulse. Polished single-crystalline substrates of perovskite type (001) $SrTiO_3$, garnet type (111) and (210) $Gd_3Ga_5O_{12}$ and $Nd_3Ga_5O_{12}$ were used.

A solution of $M(thd)_3$ (M = La–Lu, In, Fe) in benzene was dripped in separate small droplets (1 μl) on a glass fibber carrier band heated to 140 °C, the solvent being instantaneously evaporated and the dry small specks of precursors were thus formed. One by one evaporation of the precursors specks by a hot carrier gas flow (argon) was performed in a specially designed vacuum chamber. One speck is evaporated during 6 s, the pulses of the precursor vapors are evolved by the carrier gas to a hot wall horizontal reactor where the deposition takes place. The deposition rate in a pulse process is easily regulated by the amount of the precursor in one speck. The films were characterised by XRD, SEM, EDX and HREM (cross-section mode) techniques.

In the $RInO_3$ series the perovskite phases are known in the bulk state for La–Dy members, but Eu–Dy members can be prepared only at a pressure of 65 kbar. Normal pressure phases for Sm–Ho have a hexagonal structure, and Er–Lu ones are of a fluorite structure. As $SrTiO_3$ shows the best match of the unit cell with the perovskite $RInO_3$, this substrate was chosen for the stabilization. As it can be seen in Figure 1, we succeeded in obtaining epitaxial perovskite $RInO_3$ films for Eu–Lu members. The decrease of the stabilised perovskite (002) reflection intensity with decreasing ionic radius of R^{3+} corresponds to the above decrease of h_c with increasing perovskite instability. These new rare earth indates in a pure or doped state are interesting as gas sensor materials.

The twinning of stabilised highly orthorhombically distorted perovskites was found using an HREM technique. Growth

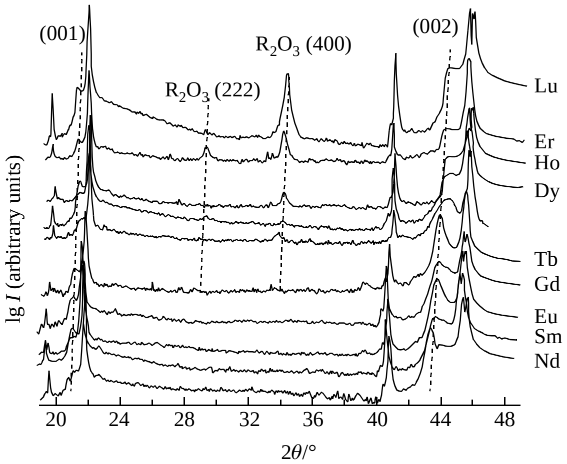

Figure 1 XRD patterns of $RInO_3$ thin films on a (001) $SrTiO_3$ substrate.

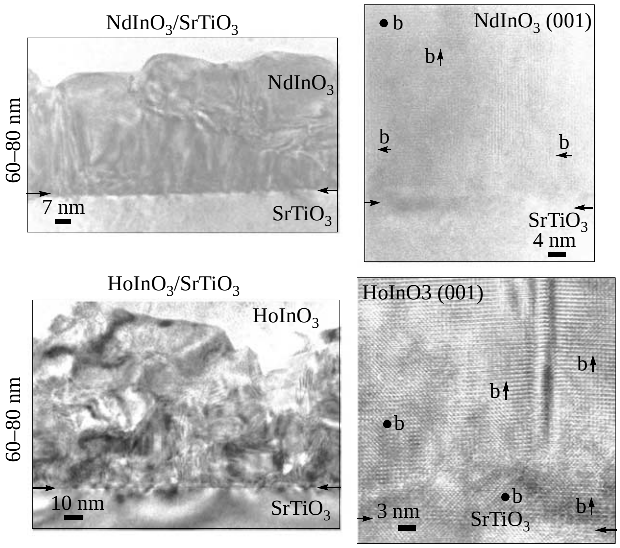

Figure 2 TEM images (cross-section) of $RInO_3$ films.

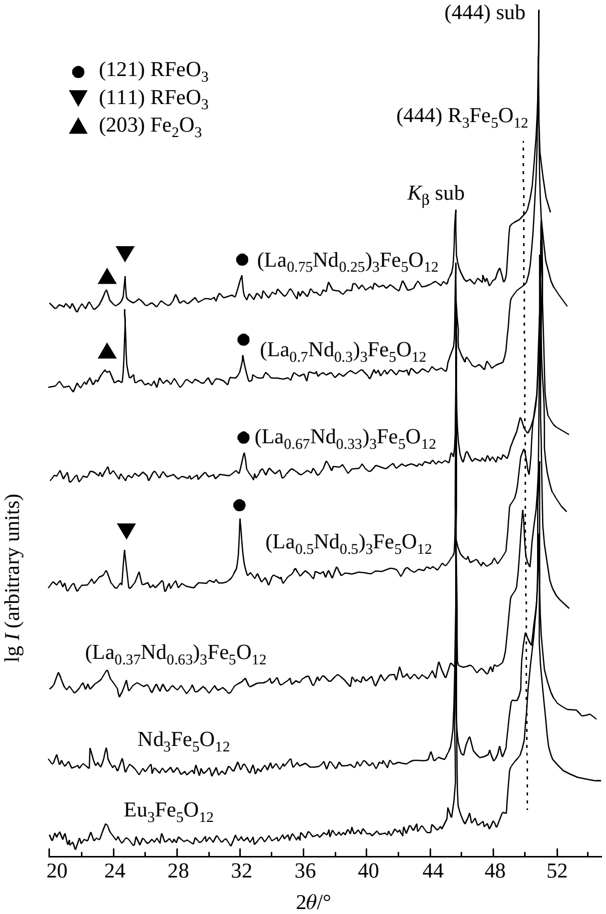

Figure 3 XRD patterns of $(La_{1-x}Nd_x)_3Fe_5O_{12}$ films. The growth of garnet phases was observed for $0.3 \le x \le 1$.

orientation $(001)_{SrTiO_3}||(110)_{RInO_3}$, $[010]_{SrTiO_3}||[110]_{RInO_3}$ was observed for the thin films of Nd–Dy phases, while the films formed by rare earths of a smaller radius, Dy–Tm, consisted of domains with two different orientations: $(001)_{SrTiO_3}||(110)_{RInO_3}$, $[010]_{SrTiO_3}||[110]_{RInO_3}$ and $(001)_{SrTiO_3}||(001)_{RInO_3}$, $[010]_{SrTiO_3}||[010]_{RInO_3}$ (Figure 2). In the sequence of $R_3Fe_5O_{12}$ compounds the garnet phases do not exist under ambient pressure for the rare earth elements of large ionic radii (R = La–Nd). At the normal pressure only perovskite phases occur in these $R_2O_3 + Fe_2O_3$ systems. By MOCVD $R_3Fe_5O_{12}$ thin films were grown on garnet substrates $Gd_3Ga_5O_{12}$, $Nd_3Ga_5O_{12}$ and $(Y_{0.8}Ca_{0.9}Tm_{0.7}Sm_{0.6})(Ge_{0.2}Fe_{0.8})_5O_{12}$. On MgO and $SrTiO_3$ substrates with other structures the films consisting of a mixture of perovskite with Fe_2O_3 were grown. The epitaxial stabilization of garnets $(La_{1-x}Nd_x)_3Fe_5O_{12}$ ($x = 0.3$–1) was found only on garnet substrates. The XRD patterns of $(La_{1-x}Nd_x)_3Fe_5O_{12}$ had the peaks of the garnet structure only in case of $x > 0.3$ (Figure 3).

For $x < 0{,}3$ the growth of garnet phases was not observed. This conclusion was confirmed by HREM [Figure 4(*a*)]. The atomically flat coherent interfaces without misfit dislocations between $(La_{1-x}Nd_x)_3Fe_5O_{12}$ ($x = 0.3$–1) and substrates were observed by HREM. A clear correlation between the free energy of garnet formation and the critical thickness of the layer was demonstrated [Figure 4(*b*),(*c*)].

The epitaxially stabilised phases of garnets and perovskites considered above grow under conditions different from those required for bulk phase formation because the epitaxy changes remarkably their thermodynamic properties, but not because surface reaction kinetics hinders the attainment of a free energy minimum during film growth.[1]

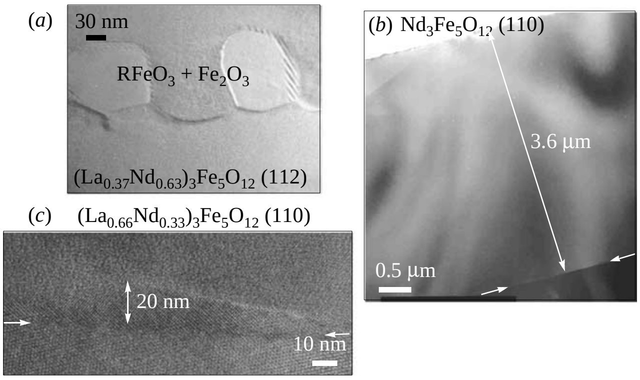

Figure 4 TEM images (cross-section) of (*a*) $(La_{0.37}Nd_{0.63})_3Fe_5O_{12}$, (*b*) $Nd_3Fe_5O_{12}$ and (*c*) $(La_{0.66}Nd_{0.33})_3Fe_5O_{12}$ films.

No doubt, this versatile synthetic approach used with a variety of synthetic single crystal substrates will result in new epitaxially stabilised materials with interesting functional properties.

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