Growth, optical and magnetic behavior of $YMn_{0.35}In_{0.65}O_3$ thin film

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The growth of $YMn_{0.35}In_{0.65}O_3$ thin films and their optical and magnetic behavior are reported. The $YMn_{0.35}In_{0.65}O_3$ thin film grows along the (0001) orientation with hexagonal structure similar to $YMnO_3$ on c-plane sapphire. The film shows paramagnetic behavior in the temperature range measured. The film exhibits a blue color due to the electronic transition in the red-green region of the visible spectrum. The development of such a relatively low cost, eco-friendly and highly stable chromophore can be used as a blue filter layer in color filter array.
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Naturally occurring pigments such as iron oxides (yellow to red) and lapis lazuli (blue) have been used by artists as colorants for centuries. The blue chromophores are well known from ancient times since the development of Egyptian blue.[1] The chromophore such as cobalt blue is used as color filters in ophthalmoscopes.[2] It is also known that the color filters play an important role in capturing color information while placing along with image sensors.[3] Even though there are many known blue chromophores, until now an eco-friendly, abundant in nature and highly durable chromophore still remains a challenge to find. Recently the substitution of indium ions to non-perovskite hexagonal $YMnO_3$ led to the discovery of a highly durable, new, blue inorganic pigment.[4] This discovery will potentially lead to the development of a relatively low cost, eco-friendly and highly stable chromophores.

The hexagonal manganites are an important material of research in the multiferroic family, especially $YMnO_3$.[5–7] The $YMnO_3$ has the tendency to crystallize in a hexagonal structure when made at high temperatures under atmospheric conditions. The perovskite-type $YMnO_3$ is only stable when prepared under high pressures. Nevertheless, only the hexagonal structure exhibits ferroelectricity and anti-ferromagnetism simultaneously. Hence, the growth of hexagonal manganite thin films has become the subject of interest for technological demands. Even though thin film growth techniques offer a platform to control crystal structure through substrate lattice pressure and growth conditions, the hexagonal manganite thin films grow in a very narrow range of condition.[8] In most cases it forms a polycrystalline film. In general, the substrate temperature range used for growth was 650-850 °C. Further post-deposition annealing seems to stabilize the growth along the c-axis. It is also known from the literature that the substrate temperature can be reduced to 700 °C by using a buffer layer to obtain the hexagonal structure.[9] Here we report the growth, optical and magnetic studies on the $YMn_{0.35}In_{0.65}O_3$ thin films grown on *c*-plane sapphire.

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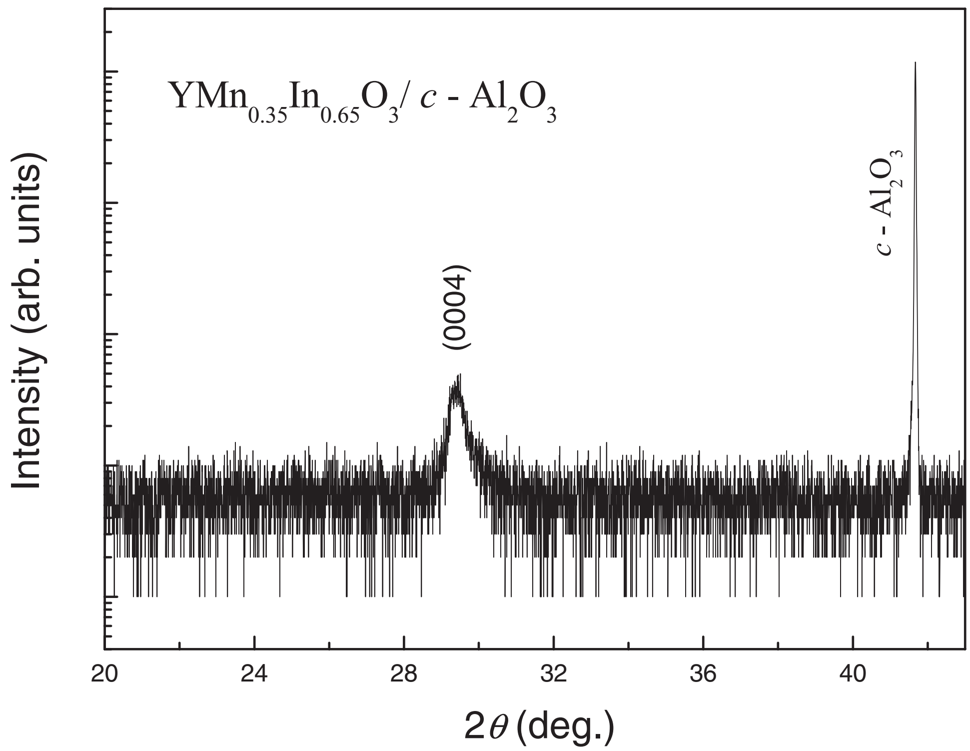

FIG. 1. X-ray diffraction pattern shows the *c*-oriented growth of $YMn_{0.35}In_{0.65}O_3$ thin film.

The single phase hexagonal $YMn_{0.35}In_{0.65}O_3$ target was prepared by conventional solid state reaction from the stoichiometric mixture of Y_2O_3, In_2O_3 and Mn_2O_3. The preparation conditions were reported elsewhere.[4] The Y(In,Mn)O_3 thin film was grown on *c* - plane Al_2O_3 (0001) substrates (CrysTec, Germany) at 800 °C with an oxygen pressure of 20 mTorr by a pulsed laser deposition technique using KrF excimer laser (λ = 248 nm, 3 Hz). The as-grown thin film (typically 180 Å thick) was annealed in-situ after deposition at the same substrate temperature with 100 mTorr of oxygen pressure for ten minutes. The crystalline nature of the film was studied using x-ray diffraction ($\lambda = 1.5406$ Å) technique. The composition of the film was checked by Energy Dispersive Scattering analysis, and corresponds to the target within the experimental error. The magnetization measurements were carried out as a function of temperature using a superconducting quantum inference device based magnetometer (MPMS, Quantum Design, USA) with a magnetic field of 1000 Oe parallel to the substrate plane. The reflective optical measurements were carried out using UV-Visible spectrometer at room temperature.

The θ-2θ x-ray diffraction pattern (Fig. 1) reveals that the film is highly oriented and no alternate phases or extra orientations were detected. The $YMn_{0.37}In_{0.63}O_3$ ceramic reported to crystallize in $P6_3cm$ space group with lattice parameters $a = 6.17$ Å and $c = 11.770$ Å. The lattice parameters of hexagonal $YMnO_3$ and $YInO_3$ are $a = 6.12$ Å and $c = 11.4$ Å and $a = 6.26$ Å & $c = 12.2$ Å respectively. The deposited film grows along *c*-orientation with (0001) reflection similar to that of $YMnO_3$ thin film known in literature[8] indicating that the film may have the same hexagonal phase. The grown thin film has an out-of-plane lattice parameter value, estimated from the position of the (0004) peak, of 12.1396 Å. It is known from the literature that hexagonal $YMnO_3$ thin films tend to have a larger c value even in the presence of the in-plane tensile stress (35% mismatch) and it is attributed to the weakening of inter plane and intra plane ionic bond strength due to the in-plane tensile stress.[8] Note that the substrate temperature and post deposition annealing seems to be important for the formation of the hexagonal phase, since for example the hexagonal phase does not form at a substrate temperature below 800 °C.

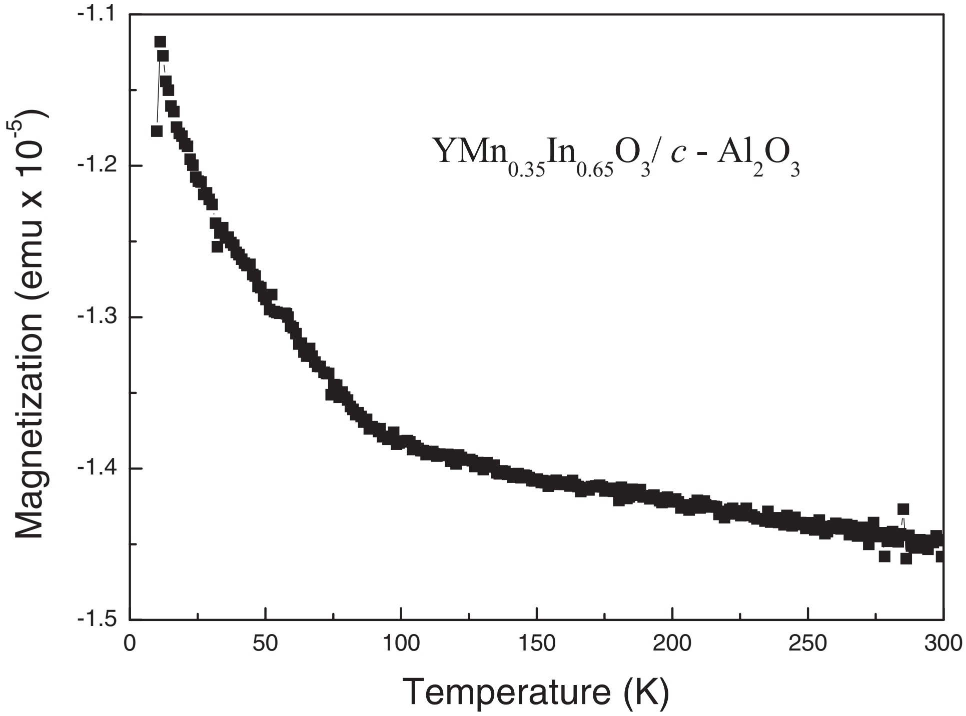

FIG. 2. Field cool magnetic moment as a function of temperature with a magnetic field of 1 kOe.

The temperature dependent magnetic measurement shows the paramagnetic behavior and the absence of an antiferromagnetic transition in the measured temperature range. The antiferromagnetic transition temperature of 72 K for $YMnO_3$ is reported to shift towards a lower temperature with In^{3+} ion substitution.[10] For $YMn_{0.75}In_{0.25}O_3$ composition, the antiferromagnetic transition is reported to be 42 K.[10] In literature, Dixit *et. al*. suggested that the antiferromagnetic transition temperature for $YMn_{1-x}In_xO_3$ ($x \geq 0.5$) samples might have lowered below 20 K where the paramagnetic tail obscures the magnetic data at that temperature range.[10] For $YMn_{0.35}In_{0.65}O_3$ thin films, there was no such behavior until 10 K (See Figure 2). Hence the T_N might has been suppressed for this composition or is lowered than 10 K. Another possible reason can be due to low film thickness, the diamagnetic nature of substrate might dominate.

The color of the $YMn_{0.35}In_{0.65}O_3$ film is blue in nature similar to the bulk (See Figure 3). Theoretical calculations reported that the observed blue color is due to the electronic transition between Mn $3d_{x^2-y^2,xy}$ orbital states to a Mn $3d_{z^2}$ state. This electronic transition occurs only in the hexagonal environment as it is a symmetry allowed transition whereas in the case of octahedral environment, this d′-d′ transition becomes symmetry forbidden. Hence the blue color of the thin film occurs as it has hexagonal structure. The optical study shows that this d-d transition occurs approximately at 1.85 eV. Hence the absorption is in the red-green region and also shows the absence of absorption in the blue region of the visible spectrum attribute to the blue color of the film.

In conclusion, $YMn_{0.35}In_{0.65}O_3$ thin films were grown on c-plane sapphire. The films grow along the (0001) orientation, with a hexagonal structure similar to $YMnO_3$. The film shows paramagnetic behavior for the temperature range measured. The film exhibits blue color due to the electronic transition in the red-green region of the visible spectrum. The development of such a relatively low cost, eco-friendly and highly stable metal oxide chromophore can be used as a blue filter layer in color filter array.

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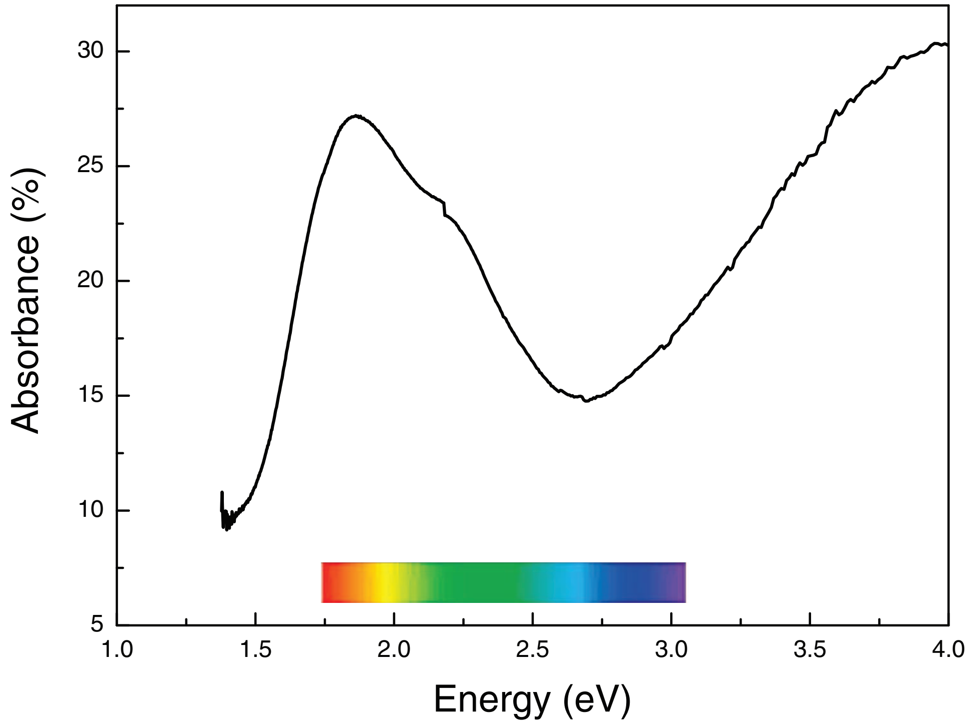

FIG. 3. Absorbance spectrum of $YMn_{0.35}In_{0.65}O_3$ film in the visible region.

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