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Influence of substrate induced strain on B-site ordering and magnetic properties of Nd_2NiMnO_6 epitaxial thin films

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ABSTRACT

Epitaxial thin films of double perovskite Nd_2NiMnO_6 (NNMO) have been successfully grown on (001) oriented substrates of $(LaAlO_3)_{0.3}$-$(Sr_2AlTaO_6)_{0.7}$ (LSAT), $SrTiO_3$ (STO) and $LaAlO_3$ (LAO) by pulsed laser deposition under optimum growth conditions. X-Ray diffraction and reciprocal space maps of the asymmetric (103) peak reveal that the films deposited on LSAT and STO substrates are fully relaxed, while a large in- plane compressive strain has been observed in film grown on LAO. This results into the coexistence of anti-site disorder and orthorhombic phase in the film deposited on LAO, which is further confirmed from observed shift and broadening in the antisymmetric vibrations in the Raman spectra. The temperature dependent magnetization shows a ferromagnetic transition close to 200 K in all the three samples. However, film grown on LAO substrate shows an additional upturn transition at ~96 K (T'), which could be ascribed to the formation of antisite disorders further responsible for reduction of saturation magnetization (~1.8×10^5 A/m) in hysteresis curve of the sample. The ordered structure obtained on LSAT and STO exhibit in-plane easy axis with a large coercivity of ~0.2 T, while, the film deposited on LAO does not show any preferred anisotropic direction.

1. Introduction

Multifunctional double perovskite oxides ($A_2BB'O_6$), which possess co-existing electric and magnetic orderings have become an area of prime interest for research and are driven on a large scale by the constantly increasing demand for reduced power consumption, higher speed and additional functionality for next–generation electronic devices [1–4].The magnetic and electrical properties of these compounds depend on A and B/B′. For instance, Sr_2MoFeO_6 is a half metallic ferromagnet (T_c ~ 400 K) which also shows giant tunnelling magnetoresistance, while La_2NiMnO_6 is a ferromagnetic semiconductor (T_c ~ 280 K) [5,6]. The degree of the B/B′ cationic ordering affects the magnetic and electrical properties of the double perovskites. In the perfectly ordered monoclinic structure, the B and B′ transition metal ions are arranged alternately in the 2c (0 ½ 0) and 2d (½ 0 0) Wyckoff positions. However, experimentally it has been found that, the B and B′ atoms get interchanged resulting into formation of anti-site disorders [7]. The role of anti-site disorders in low temperature magnetic behaviour has been studied in detail [1,7,8]. A second kind of disorder also arises when the material crystallizes in the orthorhombic *Pbnm* structure, where, B and B′ ions arrange randomly at the *4b* site [9]. In such a scenario, the materials are described by the molecular formula $AB_{0.5}B'_{0.5}O_3$. Most of the double perovskites are found to coexist in a mixture of pre-dominant $P2_1/n$ phase with a significant fraction of *Pbnm* phase [9–11].

Among the double perovskites, R_2NiMnO_6 (RNMO, R = rare earth element) have received much attention owing to their rich physics and potential applications in spintronics, such as, multiple state logic devices, tunnel junctions and magnetoelectric sensors [12–15]. In particular, La_2NiMnO_6 (LNMO) is the most studied compound both as bulk and thin film. Bulk LNMO shows a near room temperature ferromagnetic transition, accompanied by large magneto-capacitance and magnetoresistance effects [1,12,15].The ferromagnetism originates from the nearest neighbour Ni^{2+}-O-Mn^{4+} super-exchange interaction between the unequal spin states of Ni^{2+} (S = 1) and Mn^{4+} (S = 3/2) [10]. However, presence of anti-site disorders result in antiferromagnetic coupling due to superexchange interactions between Ni^{2+}-O-Ni^{2+} and Mn^{4+}-O-Mn^{4+} ions [10,16]. In the B/B′ disordered orthorhombic phase, both Ni and Mn ions are present in 3+ valence state. Due to their (B and B′) random distribution, nearest neighbour Ni^{3+}(Mn^{3+})-O-Ni^{3+}(Mn^{3+}) antiferromagnetic interactions occur along with Ni^{3+}-O-Mn^{3+} ferromagnetic interactions. One of the greatest challenges is to control the ordering of the *B*-site cations. In this regard, considerable success has been achieved in preparing highly ordered both, bulk and thin films of LNMO [10,13,17,18]. A single magnetic transition seen in single

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crystals by Iliev et al. [18] is an ideal bench mark for minimal disorder. On the other hand, interesting properties like magnetodielectricity and glassy behaviour are observed in partially disordered LNMO [1]. The degree of order/disorder is manifested in various properties like dielectric relaxation and anomalous spin-phonon coupling as seen from Raman spectra [1,19,20].

In R_2NiMnO_6 family, when La is replaced by Nd, the average Ni—O bond length increases while the Mn—O bond length reduces. The decrease in ⟨Ni—O—Mn⟩ bond angles causes a decrease in ferromagnetic transition temperature from 280 K to 194 K [21]. Bulk Nd_2NiMnO_6 (NNMO) have been synthesised by various groups with varying degree of disorder as found from their magnetic studies. Booth et al. [21] have synthesised ordered bulk NNMO which shows only a single transition near 194 K. However, samples with an amount of disorder show an additional magnetic transition near 100 K [22,23]. The precise nature of the second transition is sensitive to synthesis conditions and varied in reports, which are available in literature. Shi et al. [22] have observed a secondary transition in their zero field cooled magnetization below 75 K indicating a prominent role of the antiferromagnetic phase due to the mixed valence nature of B/B′ site cations. Yadav et al. [23] have observed a re-entrant spin glass like behaviour below the secondary transition while in our recent report [24] no spin glass like phase has been detected for secondary transition in the *ac* susceptibility measurements. Compared to bulk, a greater degree of cationic ordering and crystallinity could be achieved in thin films of double perovskites [13,17,25,26]. The growth of epitaxial films of double perovskites with fewer grain boundaries is favourable for device perspective. The extent of cationic ordering is controlled by variation of oxygen partial pressure and temperature [2,17]. In addition, we found that the selection of underlying substrates also play an important role in achieving B-site ordering and controlling the nature of magnetic anisotropy [2,17,26,27] which is essential in development of magnetic heterostructures.

Unlike LNMO, properties of thin films of NNMO have not been reported yet. As the properties of thin films are found to be crucially dependent on the choice of substrate, in the present work, effect of substrate on structural and magnetic properties have been discussed in detail. An interesting aspect of double perovskite thin films is that, depending on substrate, the extent of disorder can be altered due to varying degree of lattice mismatch between film and substrate. In this study, we have prepared NNMO thin films on three different substrates with pseudo-cubic structure viz. LSAT, STO and LAO.

2. Experimental details

Epitaxial thin films of NNMO were deposited onto (001) oriented LSAT, STO and LAO substrates (with NNMO films denoted by NNMO/LSAT, NNMO/STO and NNMO/LAO, respectively, from now onwards) by pulsed laser deposition technique using a KrF excimer Laser ($\lambda = 248$ nm). The stoichiometric target of NNMO used for the deposition was prepared using conventional solid state reaction method whose details are reported elsewhere [24]. Epitaxial thin films were grown at fixed substrate temperature of 750 °C and the laser repetition rate of 5 Hz was used for the ablation. The target to substrate distance was fixed at 5 cm for all the samples. The laser energy density on the target surface was ~2 J/cm^2 and the number of laser shots was 5000 for each deposition on different substrates. To avoid the oxygen inadequacy in the thin films, high oxygen partial pressure of 106 Pa was maintained during the deposition of the films. After deposition, in-situ annealing of the films has been done for an hour in 101 kPa oxygen pressure at 750 °C, and then slowly cooled down to room temperature. The thickness of films was determined using field emission scanning electron microscope (FE-SEM). The crystal structure of the samples was examined using X-ray diffractometer (Bruker D8 advance) operated in the $\theta/2\theta$ scan mode. The Raman spectra (Renishaw, United Kingdom) were measured for all the samples using 514.5 nm Ar$^+$ Laser for excitation. The magnetic properties were investigated using Quantum Design's Superconducting Quantum Interference Device magnetometer (MPMS XL Evercool).

3. Results and discussion

3.1. Structural properties

The thickness of the NNMO films (~300 nm) has been determined from cross sectional image using FE-SEM. The X-ray diffraction (θ-2θ) scans and rocking curve measurements of NNMO films on LSAT, STO and LAO substrates are shown in Figs. 1(a)–1(c), respectively. The existence of only the diffraction peaks corresponding to NNMO (00*l*) reflections and substrate confirms that the films are highly oriented along the c-axis. The additional two peaks in the XRD patterns of all the films correspond to (00*l*) K_β and the other two peaks (W) result from the wavelength in the X-ray beam induced by tungsten impurities. The XRD pattern of NNMO film on STO substrate (Fig. 1(b)) shows additional two peaks (marked as *) which were also present in the XRD pattern of bare STO substrate. From the rocking curves (inset of Fig. 1(a)–(c)), we have obtained the full width at half maximum (FWHM) values of 0.08°, 0.2° and 0.6° for NNMO/LSAT, NNMO/STO and NNMO/LAO, respectively. The small FWHM values suggest that the as-grown NNMO films have good crystallinity, particularly in NNMO on LSAT and STO substrates. The presence of single peak with small FWHM confirms that the films are grown in a single phase, coherent and epitaxial manner in pseudo-cubic (001) direction. The XRD Φ scan of in-plane (200) reflection of the NNMO film on STO substrate is shown in Fig. 1(d). The observation of peaks at an interval of 90̊, clearly demonstrate the epitaxial growth of the NNMO film. The pseudo-cubic out of plane lattice parameters of NNMO/LSAT and NNMO/STO are $c = 3.826$ Å and 3.8314 Å, respectively, which are smaller than the corresponding substrate lattice parameters of 3.8712 Å and 3.9082 Å, respectively. NNMO/LAO have a larger out of plane lattice parameter ($c = 3.8962$ Å) than the substrate lattice parameter (3.789 Å). The pseudo-cubic lattice parameters of bulk NNMO (a_{bulk} ~ 3.8359 Å, c_{bulk} ~ 3.8568 Å) are smaller than LSAT and STO but larger than LAO substrate, where a_{bulk} and c_{bulk} are the in-plane and out of plane lattice parameter of bulk, respectively. Defining the out of plane bulk mismatch as $(c_{film}\text{-}c_{bulk})/c_{bulk}$ [28], we find that for NNMO/LSAT and NNMO/STO, there occurs a compression factor of −0.78% and −0.65%, respectively. On the other hand, NNMO/LAO undergoes an elongation of 1.021% with respect to bulk NNMO along the *c* axis. The larger in-plane lattice parameters of LSAT and STO substrates compared to a_{bulk} causes in plane tensile strain on the films. Assuming that the deposited NNMO films attain the same in-plane lattice parameters as the substrate during initial stages of growth, we define the in-plane bulk mismatch as $(a_{subs}\text{-}a_{bulk})/a_{bulk}$ [28]. This should give rise to in-plane bulk mismatch of +0.9% and 1.8% in case of NNMO/LSAT and NNMO/STO, respectively, while in the case of NNMO/LAO we expect an in-plane bulk lattice mismatch of a_{bulk} by −0.9%.

The true in-plane lattice parameters of all the NNMO films along with the corresponding strain were obtained from the asymmetric reciprocal space mapping (RSM) of the (103) peak as shown in Fig. 2. The vertical axis corresponds to out of plane q_z [001] direction and the horizontal axis corresponds to the in-plane q_x [100] direction. The nature of strain on the grown films is decided by the position of maximum intensity region of film with respect to that of the substrate, indicated by arrows in Fig. 2 (a–c). Let, (q_{xf},q_{zf}) correspond to the maximum intensity point of film and (q_{xs},q_{zs}) denote the coordinates of the maximum intensity point of the corresponding substrate. In all the three samples, we find neither of (q_{xf},q_{zf}) exactly coincides with that of (q_{xs},q_{zs}). NNMO/LSAT and NNMO/STO show uniform shift (Fig. 2(a) and Fig.2(b)) in (q_{xf}, q_{zf}) with respect to (q_{xs},q_{zs}). From $q_{xf,}$ the in-plane lattice parameters are found to be 3.8215 Å and 3.8433 Å for NNMO/LSAT and NNMO/STO, respectively, which are closer to the in-plane lattice parameter of pseudo-cubic bulk NNMO (a_{bulk}). Thus, NNMO/LSAT and NNMO/