Raman Microscopy of La_2NiMnO_6 Thin Films

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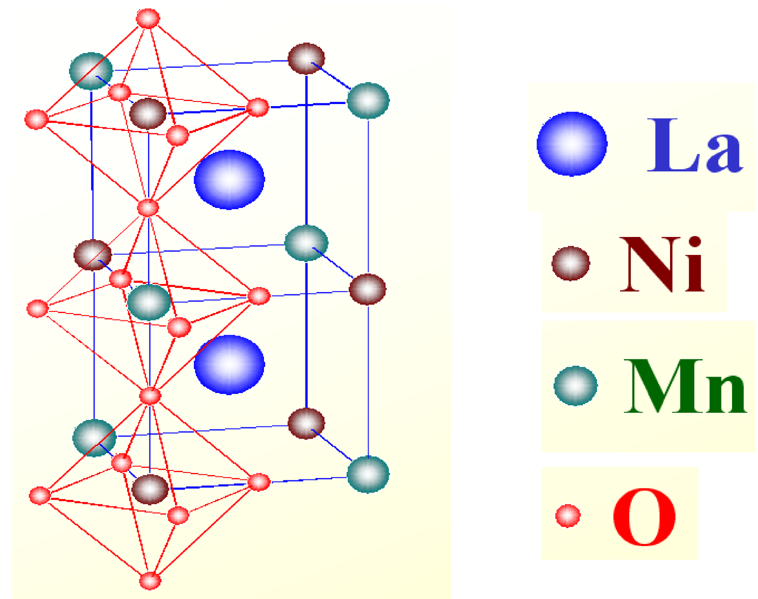
Motivation and Result

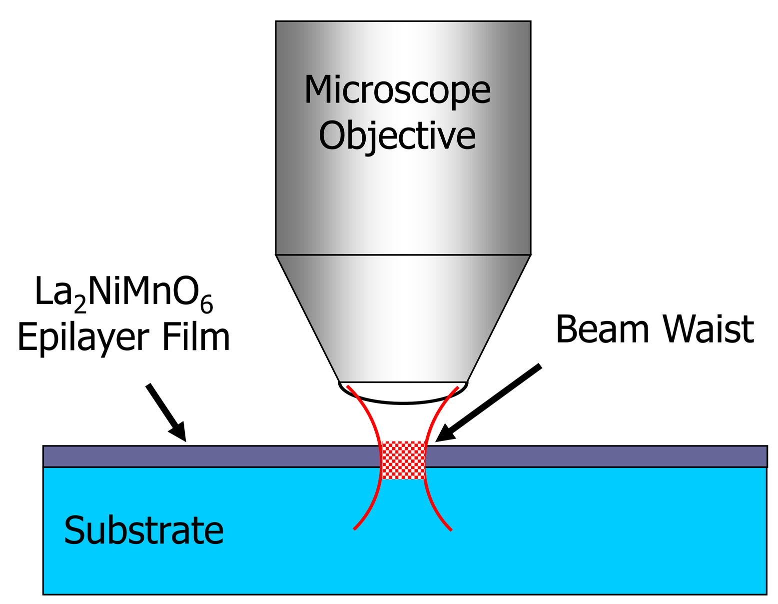
La_2NiMnO_6 has recently found to be multiferroic, having both magnetocapacitance and magnetoresistance below 270 K. These traits are linked to the structure of the perovskite. Confocal Raman microscopy is a very good probe of such structures as thin films deposited on various substrates. Raman can identify the strain in ultrathin (8 nm) epitaxial films where XRD features are not apparent. Raman can also confirm epitaxy in such ultrathin films.

Structure of La_2NiMnO_6



Rogado *et al.*, Adv. Matter. 12, 36 (2005)

Schematic of Raman Microscope Set-Up



Raman and Strain:

When a lattice is strained due to epitaxial mismatch, the vibrational modes will shift due to increased/decreased bond lengths. This is reflected in the following equation:

$$\Delta \nu = a\,\frac{a_{bulk}-a_{epi}}{a_{epi}} = a\varepsilon_{xx}$$

$a_{||}$ = lattice parameter substrate

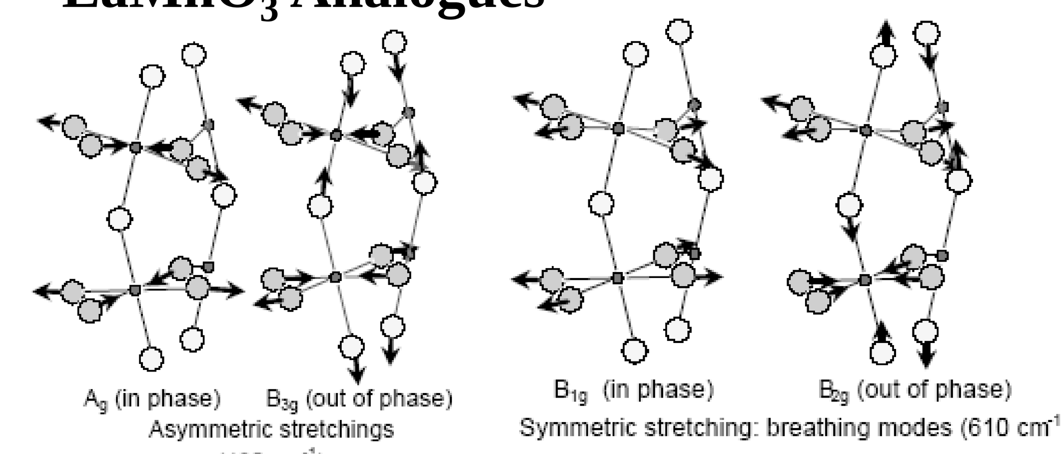
a_{epi} = lattice parameter epilayer

a = strain-shift coefficient

Mode Descriptions

Raman Shift	Mode	Vibration
533 cm^{-1}	A_g (AS)	Asymmetric stretch of octahedra
678 cm^{-1}	B_g (SS)	Symmetric stretch of octahedra

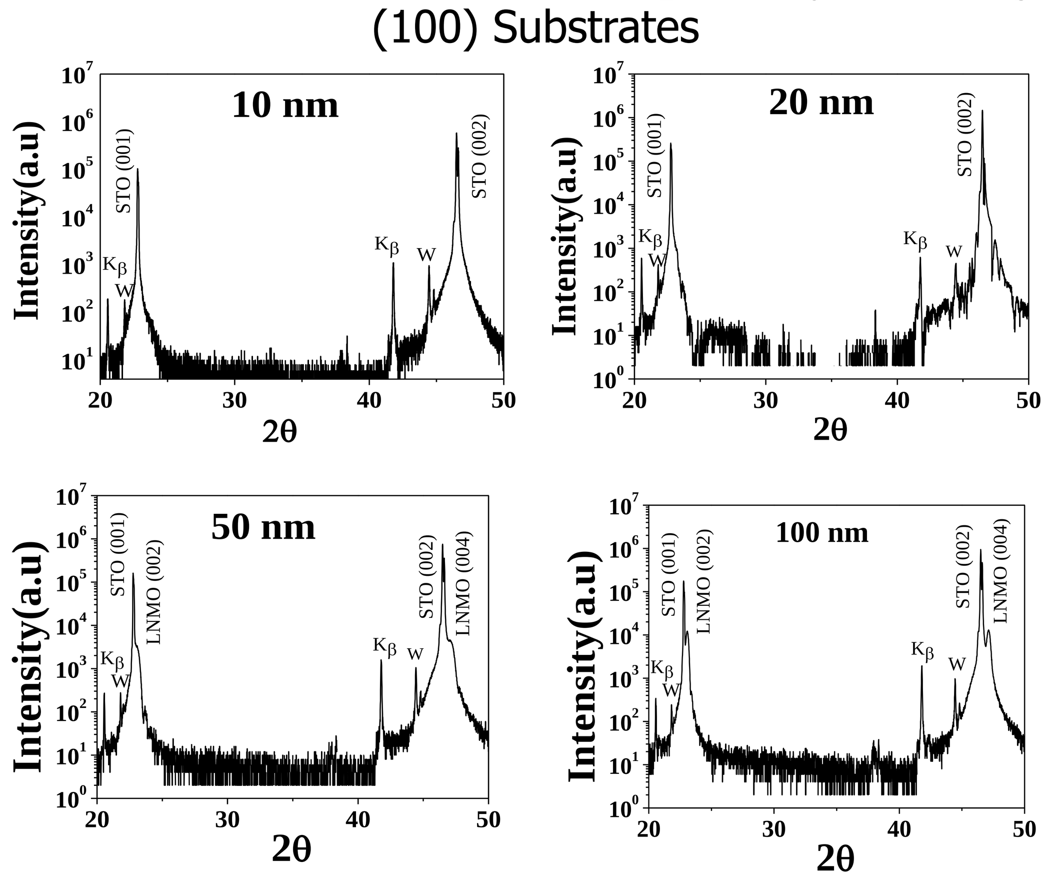
$LaMnO_3$ Analogues



L. Martín-Carrón and A. de Andrés Eur. Phys. J. B 22, 11-16 (2001)

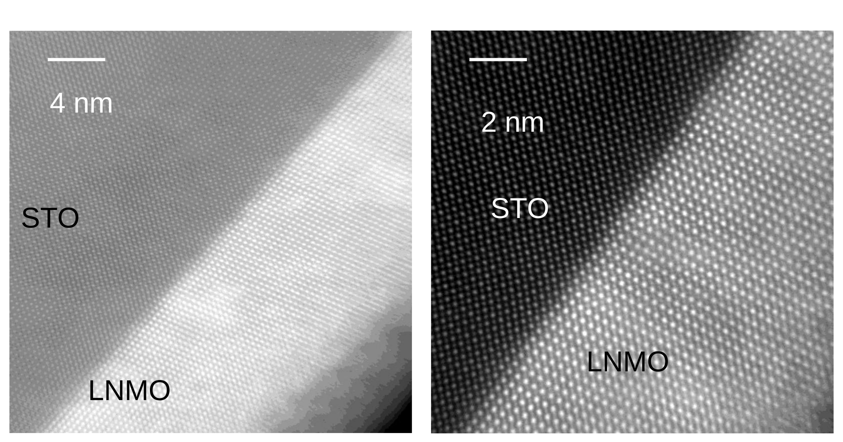
Other Techniques Used to Examine Structures

X-Ray Diffraction Patterns of La_2NiMnO_6 on $LaAlO_3$ (100) Substrates



XRD patterns of La_2NiMnO_6 (LNMO) films on $LaAlO_3$ (100) substrate. The peak for the LNMO film does not begin to appear until 50 nm. As seen by Raman, by that point the film structure has relaxed greatly from its configuration at the interface with the substrate.

High Resolution Transmission Electron Micrograph of LNMO on $SrTiO_3$ (100) Substrate

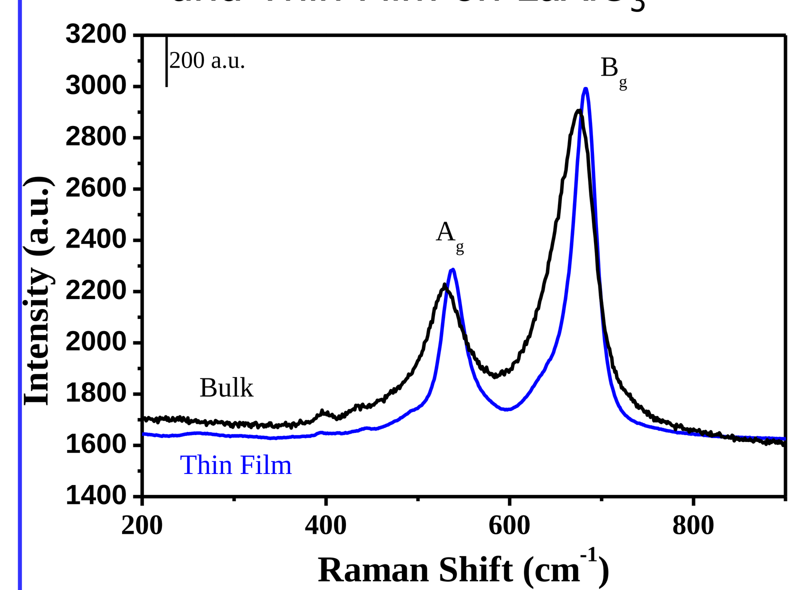


Images courtesy of M. Varela and S. Pennycook, Oak Ridge National Lab

HR-TEM image of La_2NiMnO_6 (LNMO) films on $SrTiO_3$ (100) (STO) substrate. There is a excellent heteroepitaxial match with the LNMO film and the STO substrate at the interface.

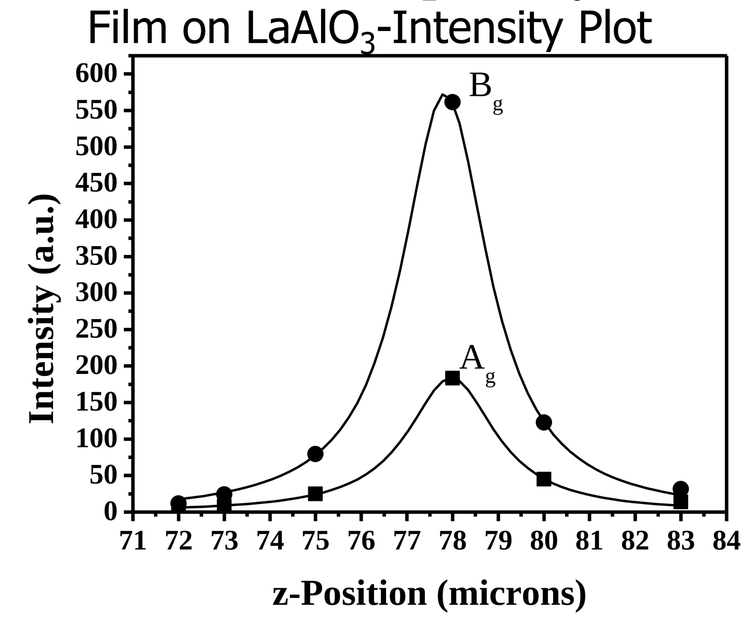
Raman of La_2NiMnO_6 Depth Profiles and Film Thickness on $LaAlO_3$ (100) Substrate

Raman Spectra of La_2NiMnO_6 Bulk and Thin Film on $LaAlO_3$



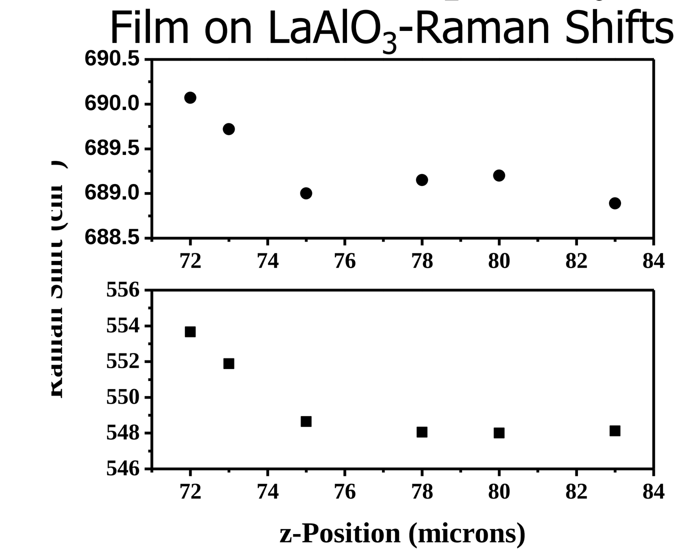
Raman spectrum of bulk (black) is slightly broader than the thin film (blue), indicating that the thin film is more ordered. The thin film also blue shifts by 8 cm^{-1}.

Depth Profile of La_2NiMnO_6 Thin Film on $LaAlO_3$-Intensity Plot



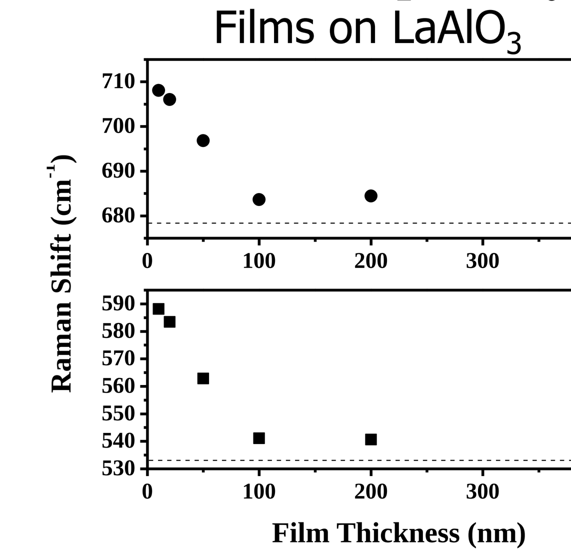
Intensity profile of the A_g (squares) and B_g (circles) modes as a function of position of microscope to sample. The depth resolution for this sample is 2.3 μm.

Depth Profile of La_2NiMnO_6 Thin Film on $LaAlO_3$-Raman Shifts



Peak positions of the A_g (squares) and B_g (circles) modes as a function of position of microscope to sample. The focal point (where highest intensity occurs) is at 78 microns. The shifts indicates that there is strain at the interface that relaxes as one moves away from the interface

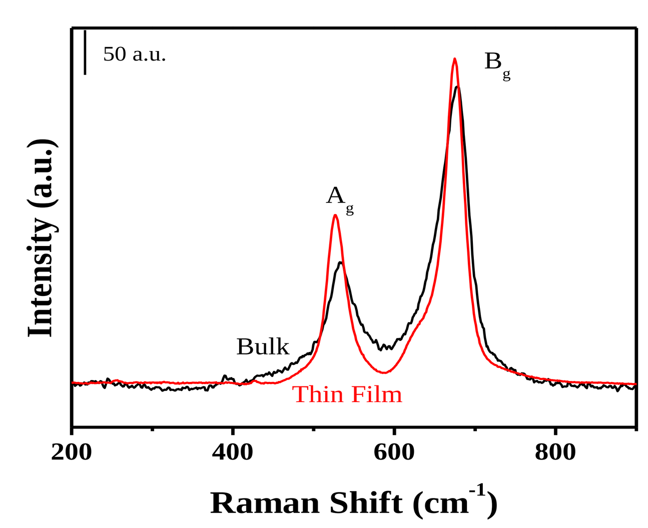
Raman Shifts La_2NiMnO_6 Thin Films on $LaAlO_3$



Peak positions of the A_g (squares) and B_g (circles) modes as a function of thickness of deposited films (8-400 nm). The shifts indicate that there is strain at the interface that relaxes as the film gets thicker.

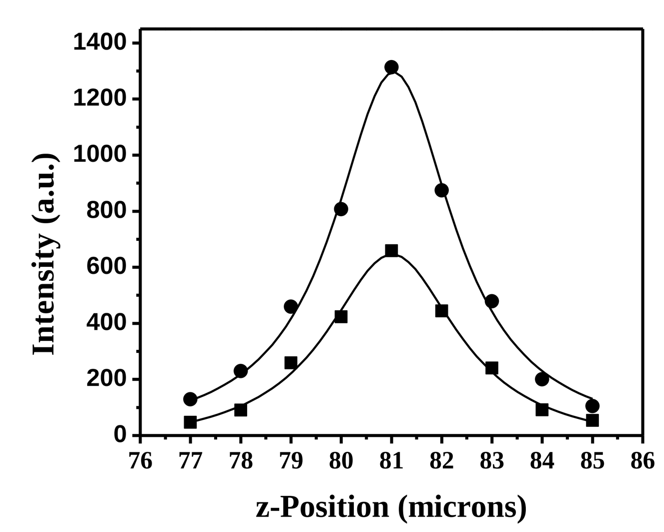
Raman of La_2NiMnO_6 Depth Profiles and Film Thickness on $SrTiO_3$ (100) Substrate

Raman Spectra of La_2NiMnO_6 Bulk and Thin Film on $SrTiO_3$



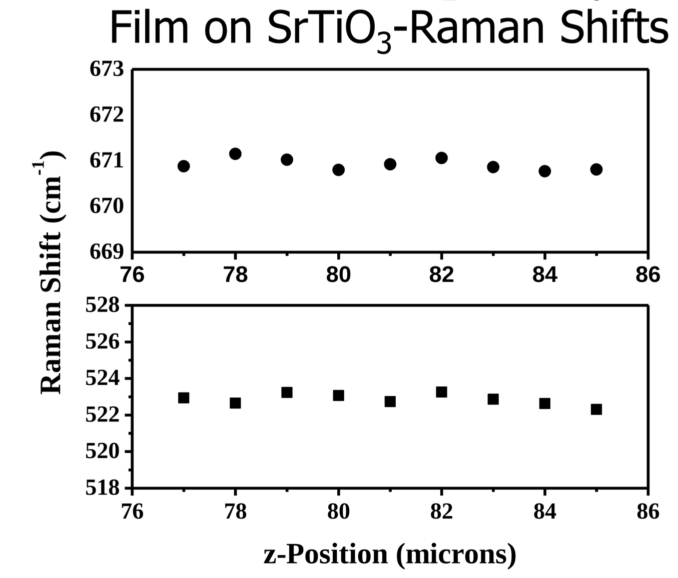
Raman spectrum of bulk (black) is slightly broader than the thin film (red), indicating that the thin film is more ordered. The thin film also red shifts by 4 cm^{-1}.

Depth Profile of La_2NiMnO_6 Thin Film on $SrTiO_3$-Intensity Plot



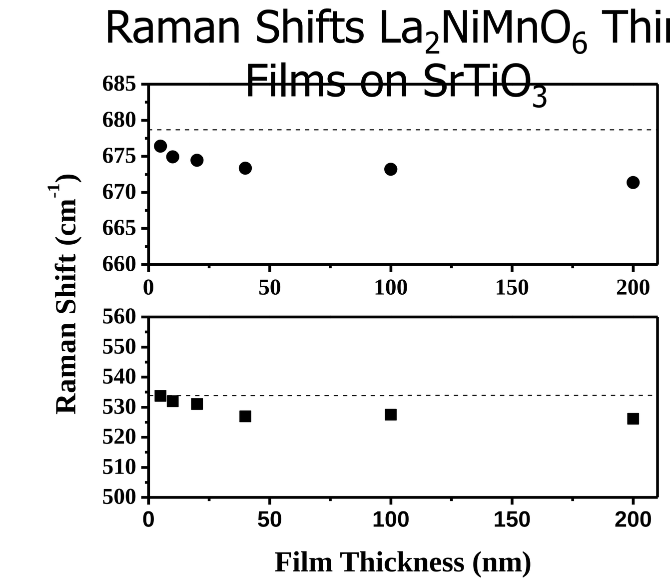
Intensity profile of the A_g (squares) and B_g (circles) modes as a function of position of microscope to sample. The depth resolution for this sample is 2.9 μm.

Depth Profile of La_2NiMnO_6 Thin Film on $SrTiO_3$-Raman Shifts



Peak positions of the A_g (squares) and B_g (circles) modes as a function of position of microscope to sample. The focal point (where highest intensity occurs) is at 81 microns. There is no appreciable shift in the modes of the film, indicating uniformity.

Raman Shifts La_2NiMnO_6 Thin Films on $SrTiO_3$



Peak positions of the A_g (squares) and B_g (circles) modes as a function of thickness of deposited films (8-200 nm). There is very little shift at the interface.

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