EUROPEAN SYNCHROTRON RADIATION FACILITY
ESRF User Office
CS 40220, F-38043 GRENOBLE Cedex 9, France
Delivery address: 71 avenue des Martyrs, 38000 GRENOBLE, France
Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: useroff@esrf.fr; web: http://www.esrf.fr
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MA5329 : Experiment Report

Aims of Experiment:

$NiTiO_3$ compounds can crystallize in three structures displaying different cationic distributions: ordered **ilmenite-type** (**IL**, *R-3, space group 148*) and **$LiNbO_3$-type** (**LN,** *R3c, space group 161*), and disordered **corundum-type** (**CR**, *R-3c, space group 167*). Conversely to the centrosymmetric IL and CR structures, LN is a non-centrosymmetric structure that can be stabilized under high pressure conditions allowing the coexistence of antiferromagnetic and ferroelectric orders. Structuration of materials in thin films represents a valuable approach to access to high pressure states, by applying and maintaining after synthesis, strongly stressed structures (residual or epitaxial stress).

While conventional X-ray diffraction analyses enable to identify IL structure, it cannot distinguish between the polar LN structure and the non-polar CR one. The aims of MA5329 Experiment is to use synchrotron source for the analysis of $NiTiO_3$ thin films by **REsonant X-ray Spectroscopy** (**REXS**) in order to characterize the (Ni,Ti) distribution in the cationic network along with the oxygen position and to discriminate the CR or LN structures.

Sample details, experimental technique(s), measurement set-up:

The samples analyzed during the MA5329 Experiment were $NiTiO_3$ (**NTO**) thin films of different thicknesses deposited on two types of Al_2O_3 (**ALO**) single crystal substrates leading to different epitaxial relations and stress conditions. Samples are listed in the following **TAB. 1**.

Sample name	Composition	Thickness (nm)	Deposition Temperature (°C)	Substrate
MCNT221-2	$NiTiO_3$	80	650	(001) C-sapphire
MCNT222-1	$NiTiO_3$	40	650	(001) C-sapphire
MCNT161	$NiTiO_3$	80	600	(001) C-sapphire
MCNT211-1	$NiTiO_3$	80	650	(100) M-sapphire
MCNT221-3	$NiTiO_3$	40	650	(100) M-sapphire

TAB. 1. List of studied samples

Thin films deposited on C-sapphire present an epitaxial-like growth with two variants tilted by 60° in the plane of the substrate and described by the following epitaxial relations: $(001)_{NTO}$ // $(001)_{ALO}$, $[001]_{NTO}$ // $[001]_{ALO}$ and $[100]_{NTO}$ // $[100]_{ALO}$ for variant 1, and $(001)_{NTO}$ // $(001)_{ALO}$, $[001]_{NTO}$ // $[001]_{ALO}$ and $[100]_{NTO}$ // $[110]_{ALO}$ for variant 2. On M-sapphire, NTO thin films present an epitaxial-like growth of the films with the epitaxial relations: $(100)_{NTO}$ // $(100)_{ALO}$, $[210]_{NTO}$ // $[210]_{ALO}$ and $[001]_{NTO}$ // $[001]_{ALO}$. A sketch of the $NiTiO_3$ thin film growth is displayed in **FIG. 1**.

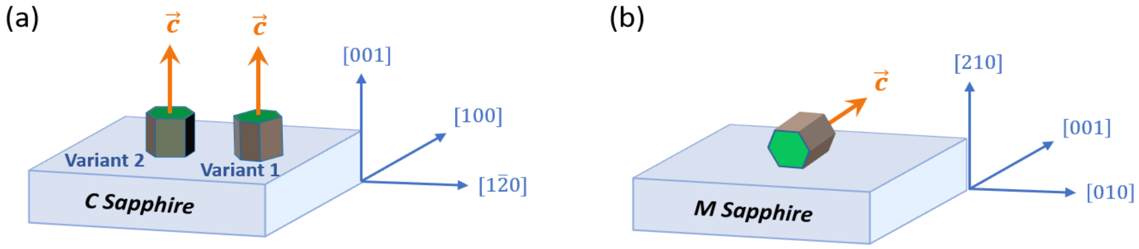

FIG. 1. Sketch of the $NiTiO_3$ thin film growth on (a) C sapphire and (b) for M sapphire substrates

The diffracted intensity has been collected on selected reflections on a continuous energy range (-50 eV to +200 eV) at the Ni-K edge (at 8333 eV) with an energy resolution of 1 eV. The $\{h\ k\ l\}$ reflections recorded for each variant of each sample are listed in the following table **TAB. 2**.

{*h k l*}	MCNT221-2	MCNT222-1	MCNT161	MCNT211-1	MCNT211-3
{0 0 6}	X	X	X		
{0 0 12}	X	X	X		
{3 0 0}				X	X
{0 1 2}	X	X	X	X	X
{0 4 2}	X	X		X	
{1 0 4}					X
{1 1 6}	X	X	X	X	X
{1 1 9}	X			X	
{1 1 3}	X	X	X	X	X
{2 2 6}	X	X	X	X	X
{1 2 2}	X	X	X	X	
{1 2 8}	X	X	X	X	
{2 0 8}	X	X	X	X	X
{2 1 1}	X		X	X	
{3 0 6}	X	X	X	X	
{3 1 2}	X	X	X	X	X
{1 1 10}					X
{1 1 12}	X			X	

TAB. 2. List of recorded reflections on each variant of the studied samples

Report on preliminary results:

As example of first results for thin film on C-sapphire substrates, **FIG. 2** and **FIG. 3** present for each variant the experimental spectra recorded on 226 and 112 reflections, respectively. In these figures, the simulated spectra for CR or LN structures are also presented for a qualitative comparison. The spectra recorded on 226 reflection for each variant look similar to those simulated for CR structure (**FIG. 2.**). Nonetheless, this trend is not systematically observed for every reflection. For example, the different variants in the plane of the substrate do not present similar spectra for 122 reflection (**FIG. 3.**). This result suggests that the different variants could present either different structures or differences in cationic *z* displacement in relation with a potential structuration in ferroelectric domains.

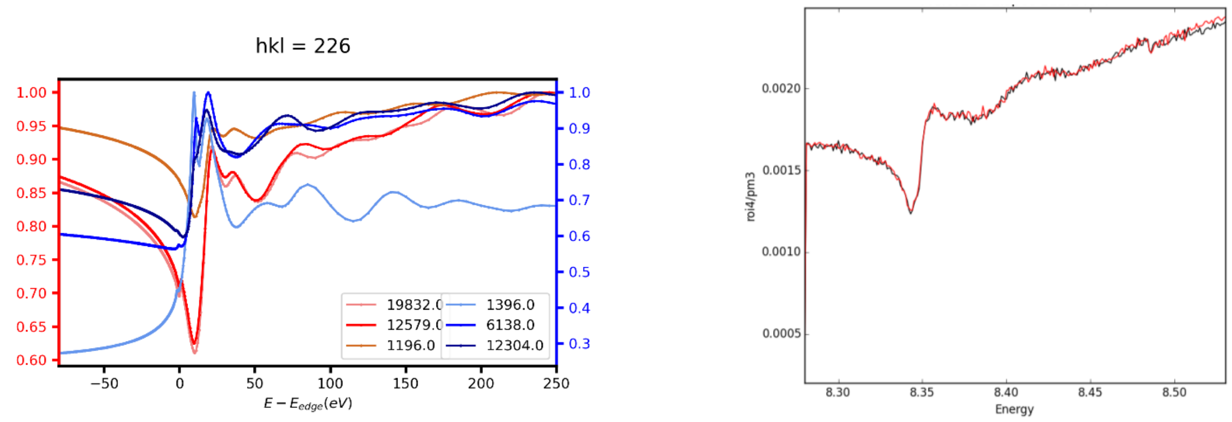

FIG. 2. ***Left:*** *Simulated spectra of 226 reflection for CR (red) and LN (blue) structures with different z positions in the lattice, 0 eV corresponds to Ni-K edge (at 8333 eV);* ***Right:*** *Experimental spectra of 226 reflection for variant 1 (in red) and variant 2 (in black) for MCNT221-2 sample (80 nm / C sapphire) - Energy is plotted in keV*

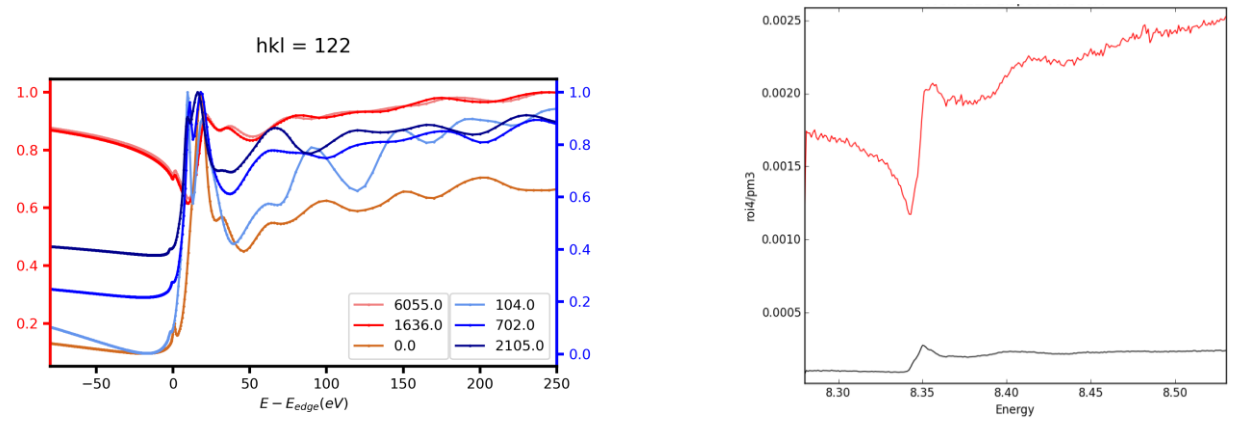

FIG. 3. ***Left:*** *Simulated spectra of 122 reflection for CR (red) and LN (blue) structures with different z positions in the lattice, 0 eV corresponds to Ni-K edge (at 8333 eV);* ***Right:*** *Experimental spectra of 122 reflection for variant 1 (in red) and variant 2 (in black) for MCNT221-2 sample (80 nm / C sapphire) - Energy is plotted in keV*

As example of first results for thin film on M-sapphire substrates, **FIG. 4** and **FIG. 5** present the experimental spectra recorded on 226 and 112 reflections, respectively. In these figures, the simulated spectra for CR or LN structures are also presented for a qualitative comparison. For 226 and 112 reflections, experimental spectra are appreciably close to simulated spectra for CR structure, supporting that $NiTiO_3$ adopts this structure on M-plane sapphire.

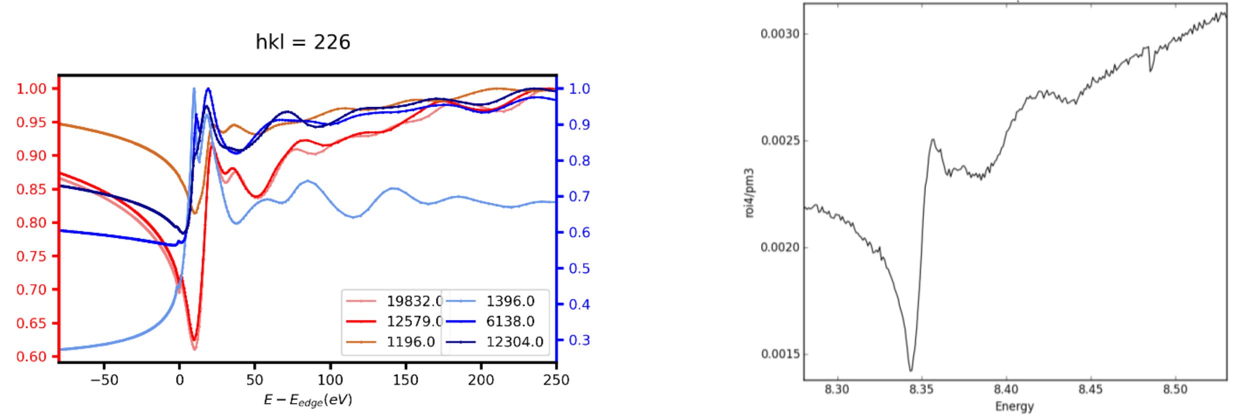

FIG. 4. ***Left:*** *Simulated spectra of 226 reflection for CR (red) and LN (blue) structures with different z positions in the lattice, 0 eV corresponds to Ni-K edge (at 8333 eV);* ***Right:*** *Experimental spectra of 226 reflection for MCNT211-1 sample (80 nm / M sapphire) - Energy is plotted in keV*

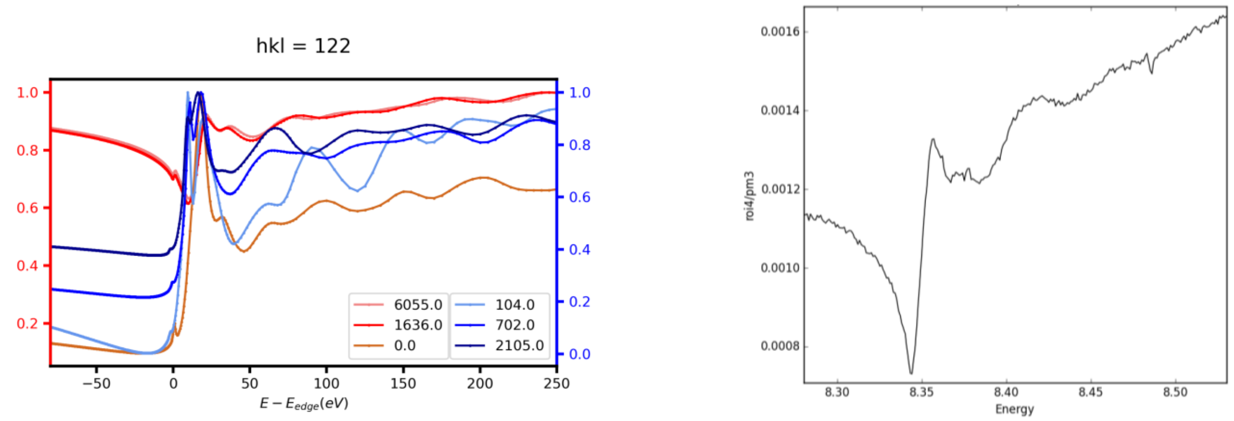

FIG. 5. ***Left:*** *Simulated spectra of 112 reflection for CR (red) and LN (blue) structures with different z positions in the lattice, 0 eV corresponds to Ni-K edge (at 8333 eV);* ***Right:*** *Experimental spectra of 112 reflection for MCNT211-1 sample (80 nm / M sapphire) - Energy is plotted in keV*

In conclusion, a qualitative comparison between simulated spectra and raw experimental spectra suggests that the structure of $NiTiO_3$ thin films could correspond to the CR structure whatever the substrate orientation and film thickness are. Nonetheless, this trend is not observed for every reflection and further data processing is required in order to properly identify the obtained structures. Especially, some corrections of the raw spectra need to be performed such as fluorescence corrections, re-centering of Region Of Interest (ROI) position, elimination of aberrant measurement points. This post-treated set of data will be then used for structural refinement taking in consideration all the recorded reflections to identify the space group of the thin film's structure and discriminate the CR or LN structures.