CRYSTALLINE STRUCTURES AND COMPOSITIONAL DEPTH PROFILE OF LEAD-FREE $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ THIN FILMS AROUND THE MORPHOTROPIC PHASE BOUNDARY.

D. Pérez-Mezcua[1,2], R. Sirera[2], I. Bretos[1], J. Ricote[1], R. Jiménez[1], L.Fuentes-Cobas[3], R. Escobar-Galindo[1], D. Chateigner[4], L. Lutterotti[4] and M. L. Calzada[1]

1.Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC)
2.Universidad de Navarra
3.CIMAV- México
4.CRISMAT-ENSICAEN-France

Zaragoza, 20 de junio de 2013

1. Introduction
2. Experimental procedure
3. Results
4. Conclusions

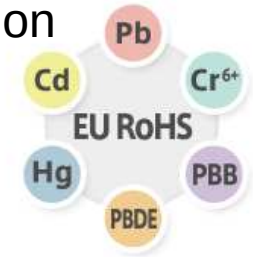
1. INTRODUCTION

1. INTRODUCTION

Actual trends in electronical devices

Lead free composition

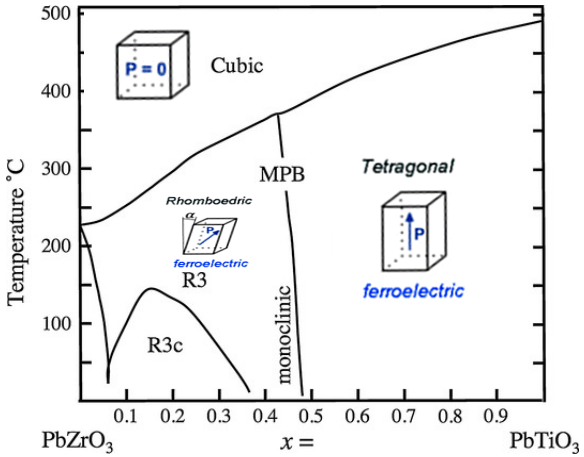
RoHS 2002/95/EC



Thin film

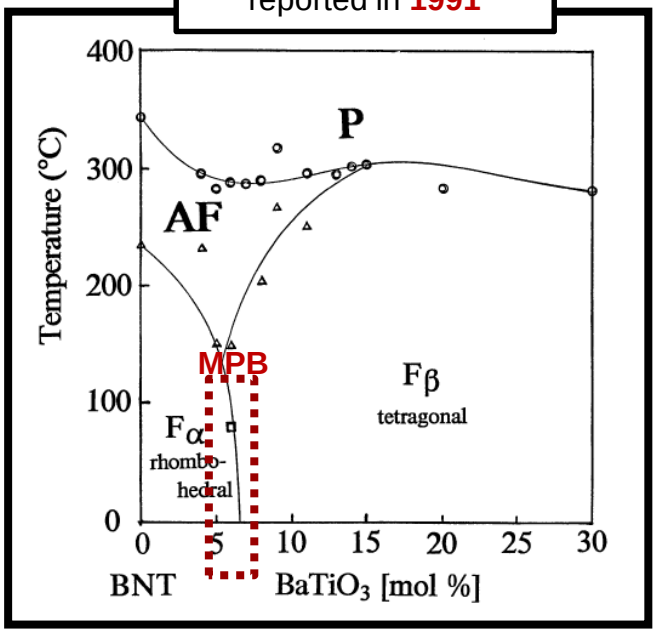
$(1-x)(Bi_{0.5}Na_{0.5})TiO_3$-$xBaTiO_3$ (BNBT)

$Pb(Zr,Ti)O_3$



The same as MPB-BNBT

BNBT phase diagram reported in **1991**



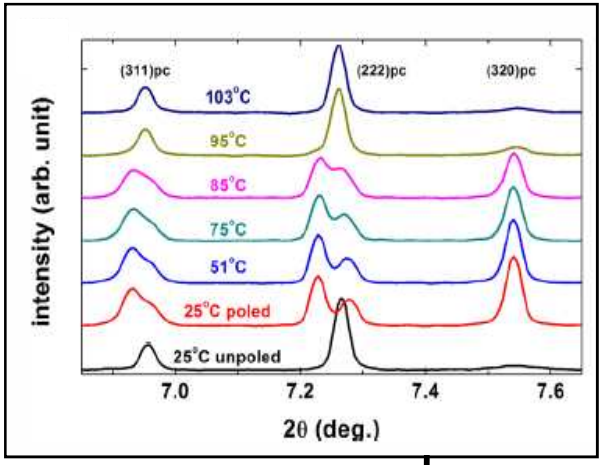
*Welberry et al, Metalll and Materials Trans ,**2010**, A 41, 1110-1118*
*Takenaka et al, Jpn J Appl Phys ,**1991,** 30, 2236-39*

Instituto de Ciencia de Materiales de Madrid ICMM
CSIC Consejo Superior de Investigaciones Científicas

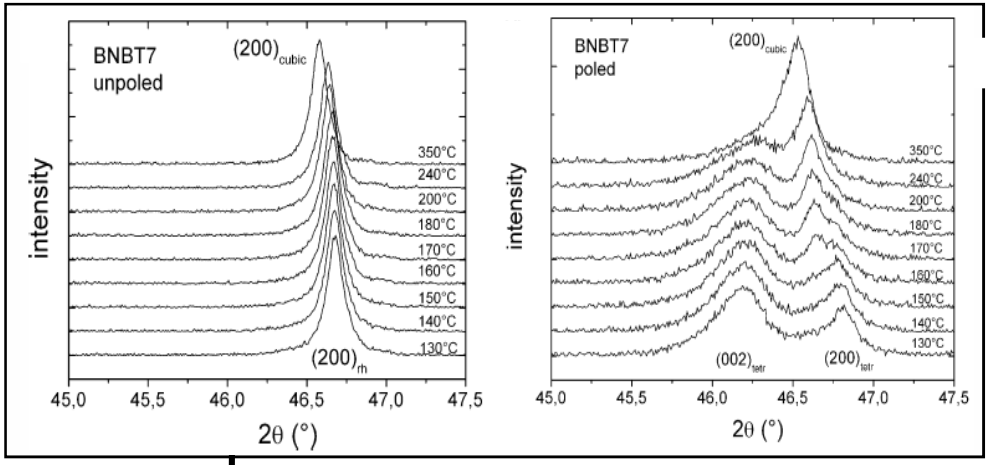
Morphotropic phase region in $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$-$xBaTiO_3$ (BNBT)

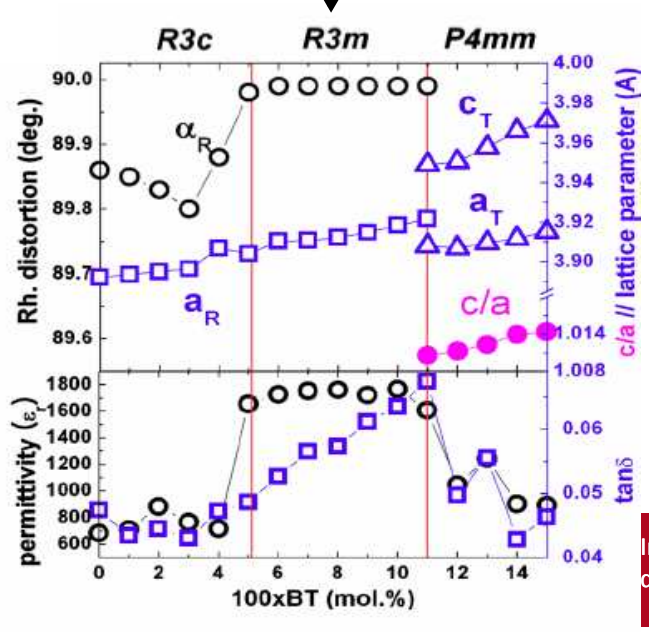
Bulk ceramics

BNBT6.0



BNBT7.0





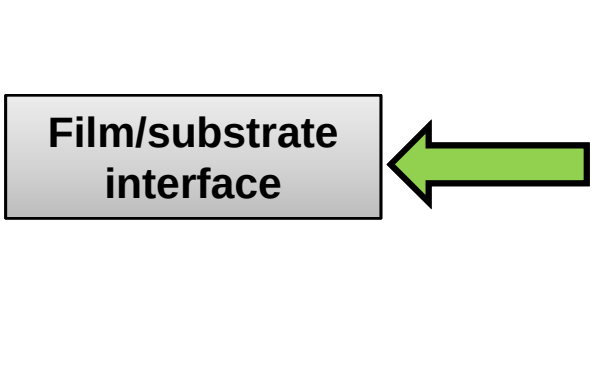
Pitch et al, J. Eur. Ceram. Soc., ***2010,*** *30, 3445-3453*
W. Jo et al, *J. Appl. Phys*. **2011**, 109, 014110
W. Jo et al, *Appl Phys Lett*, **2013**, 102, 192903

1. INTRODUCTION

$(1-x)(Bi_{0.5}Na_{0.5})TiO_3$-$xBaTiO_3$ (BNBT) thin films

Easy volatilization of high vapour pressure elements

Excesses of these elemens: Bi^{3+} and Na^{+}



Film/substrate interface

Drawbacks of the excesses incorporation

Reaction interface

Cross contamination

Stresses development during the thermal treatments

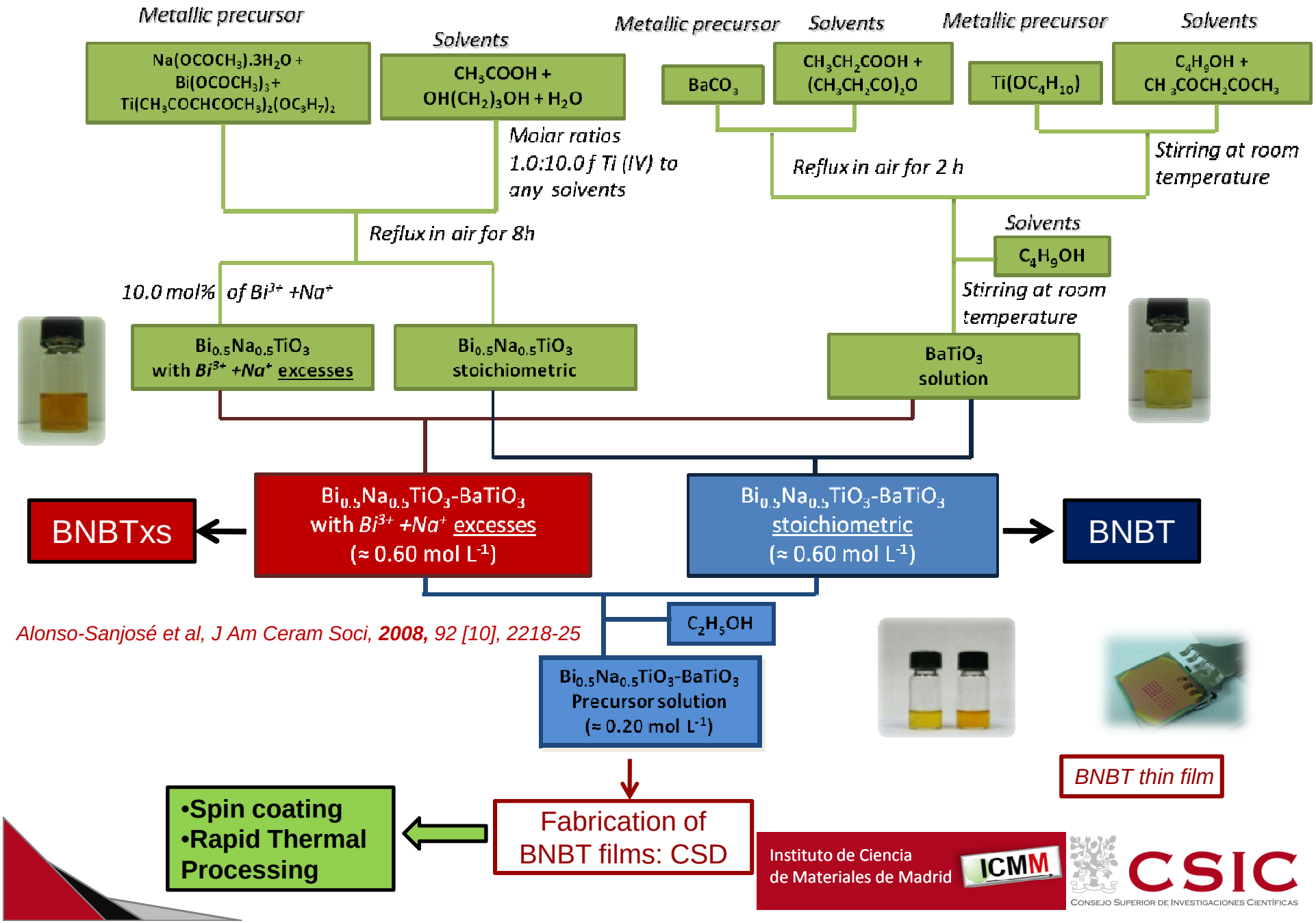
Change of the cell parameters

A shift of the MPB in thin film with respect to the bulk ceramic

*C. Dragoi et al, Appl Surf Sci, **2011**, 257, 9600-05*
*I. Bretos et al, Mater Lett, **2011**, 65, 2714-16*
*N. Scarisoreanu et al, Appl Surf Sci, **2007**, 2544, 1292-1297*
*H. W. Cheng et al, Appl Phys Lett, **2004**, 85, 2319-21*

2. EXPERIMENTAL PROCEDURE

2. EXPERIMENTAL PROCEDURE

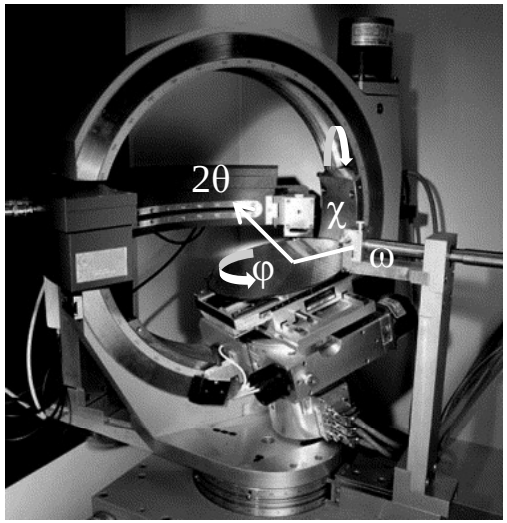


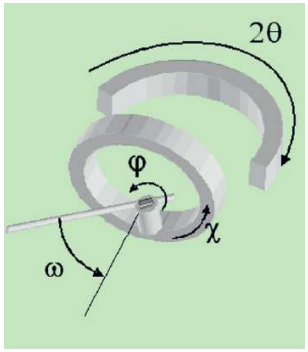
Instituto de Ciencia de Materiales de Madrid ICMM CSIC Consejo Superior de Investigaciones Científicas

2. EXPERIMENTAL PROCEDURE

Structural study: X-ray diffraction

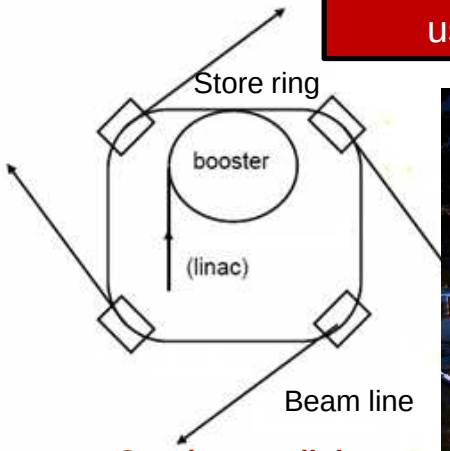
Four-circle XRD diffractometer





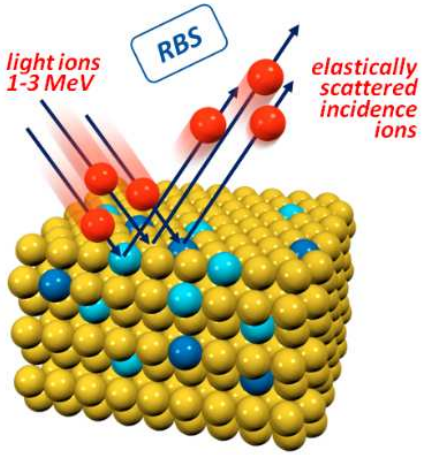
CRISMAT-ENISCAEN
France

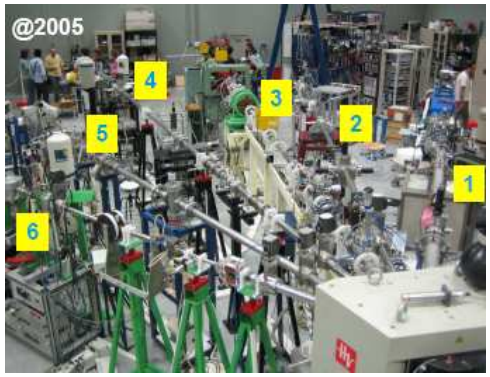
Grazing Incidence X-ray diffraction using Synchrotron radiation



Synchrotron light
λ=0.97354 Å

Compositional study: Rutherford backscattering spectroscopy (RBS)





UAM
UNIVERSIDAD AUTONOMA
DE MADRID
CMAM

W. K. Chu et al, "Backscattering Spectrometry",1978 Academic Press, New York

Instituto de Ciencia
de Materiales de Madrid
ICMM
CSIC
Consejo Superior de Investigaciones Científicas

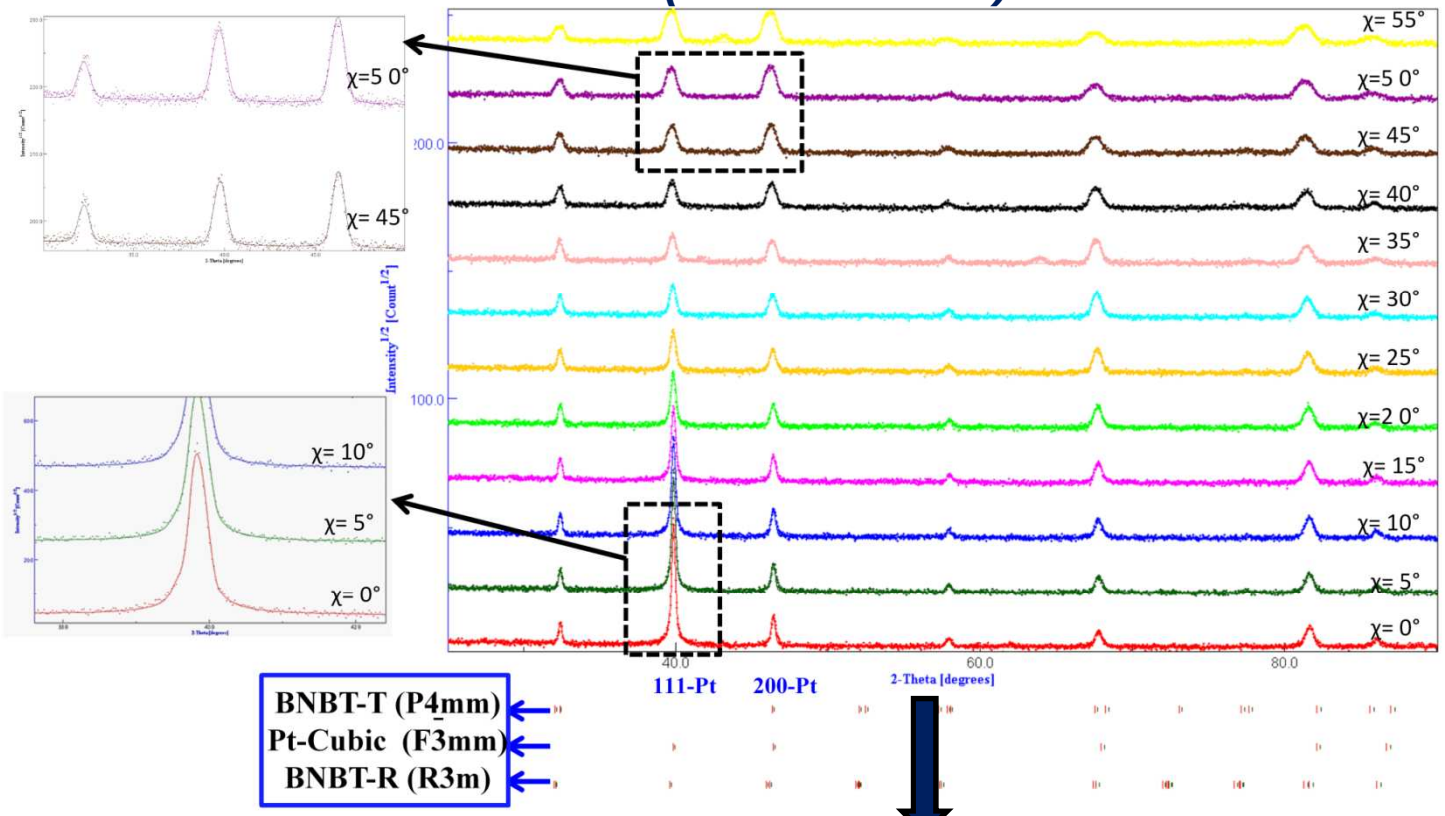
3. RESULTS AND DISCUSSION

3. RESULTS

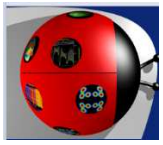
Structural study

Rietveld refinement

BNBT5.5 thin film (Stoichiometric)



	BNBT3.5	BNBT5.5		BNBT10.0
Crystal system	Rhombohedral	Rhombohedral	Tetragonal	Tetragonal
Space group	R3m	R3m	P4mm	P4mm
a_R(Å) / a_T (Å)	3.817	3.857	3.871	3.868
α_R(º) / c_T(Å)	89.861	89.460	3.890	3.891
Volume fraction (%)	99.9	71.0	28.9	95.3
χ^2	1.083	1.153		1.165



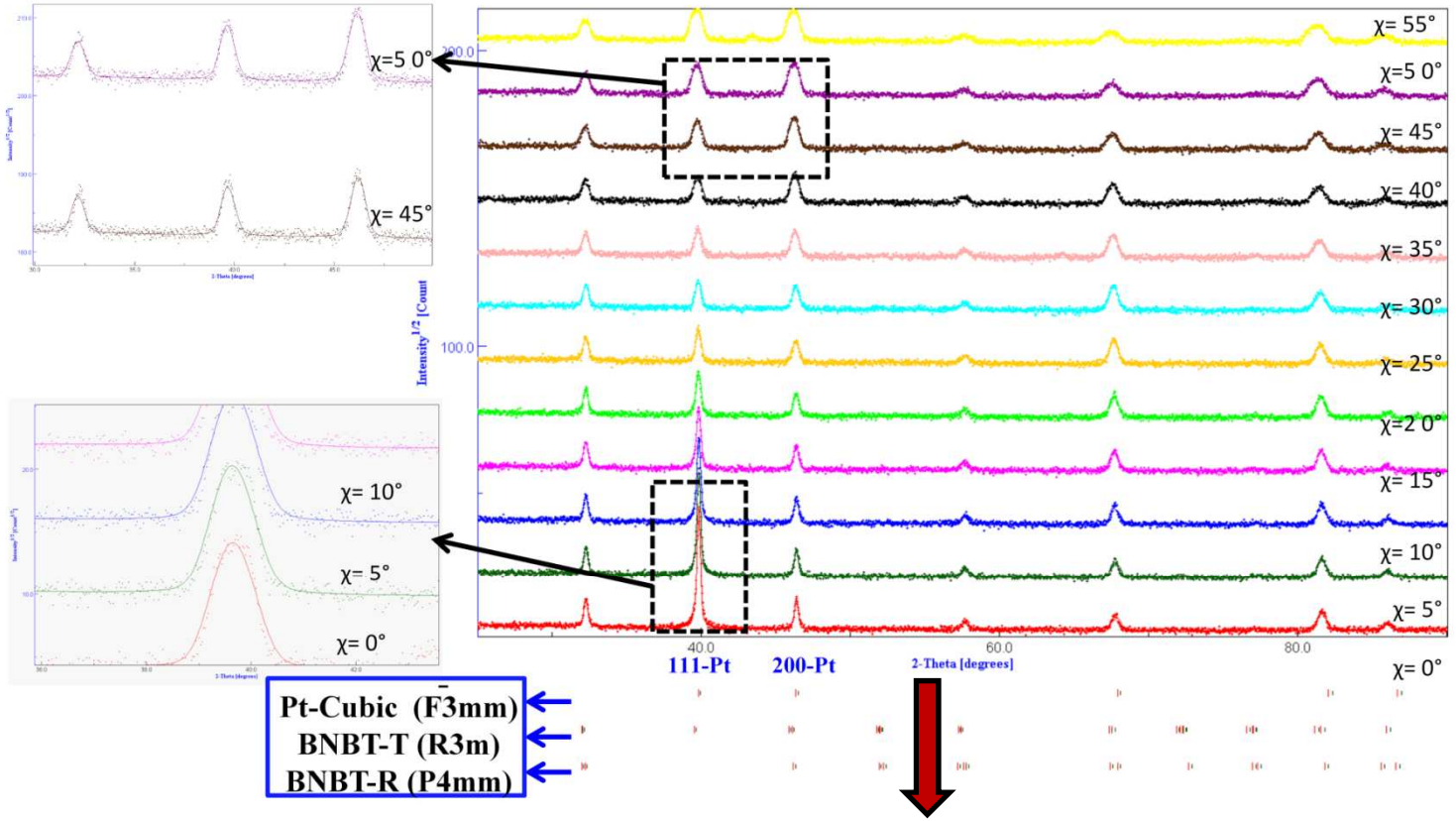
Maud - Materials Analysis Using Diffraction
http://www.ing.unitn.it/~maud/

3. RESULTS

Structural study

Rietveld refinement

BNBT10.0xs thin film (Excesses)



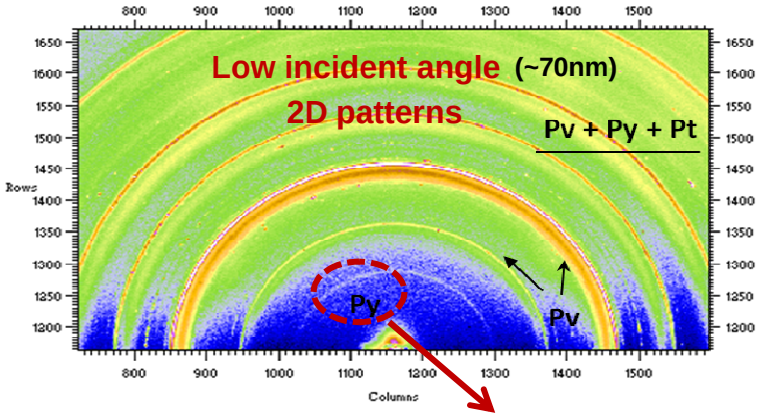
	BNBT5.5xs	BNBT10.0xs		BNBT15.0xs
Crystal system	Rhombohedral	Rhombohedral	Tetragonal	Tetragonal
Space group	R3m	R3m	P4mm	P4mm
a_R(Å) / a_T (Å)	3.863	3.868	3.873	3.869
α_R(º) / c_T(Å)	89.499	89.616	3.895	3.889
Volume fraction (%)	96.4	82.4	17.(5)	95.7
χ^2	1.177	1.162		1.149

Maud - Materials Analysis Using Diffraction
http://www.ing.unitn.it/~maud/

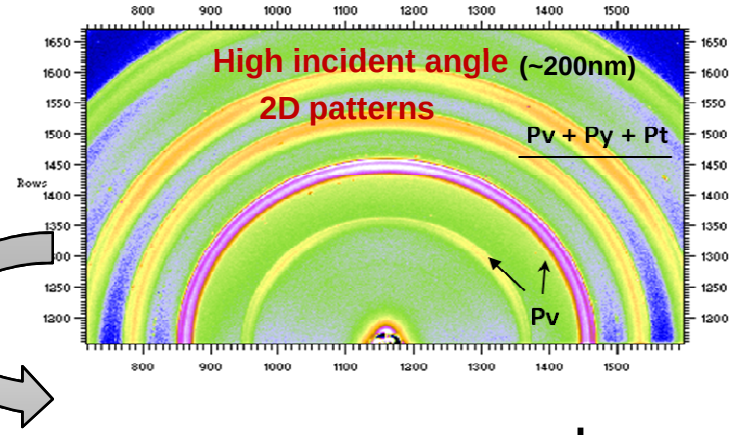
3. RESULTS

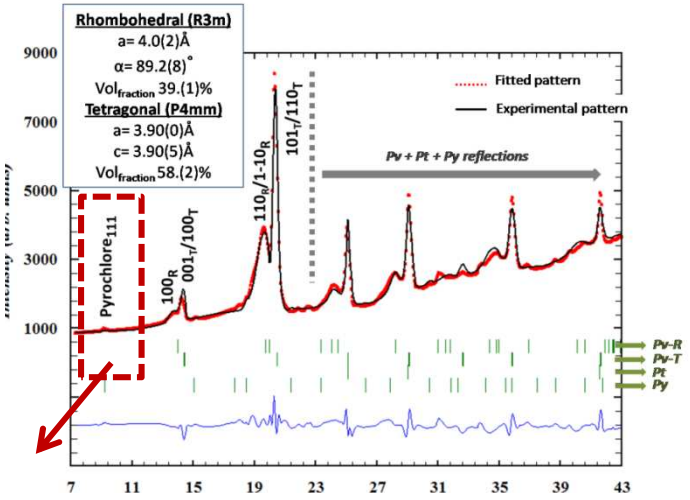
Structural study

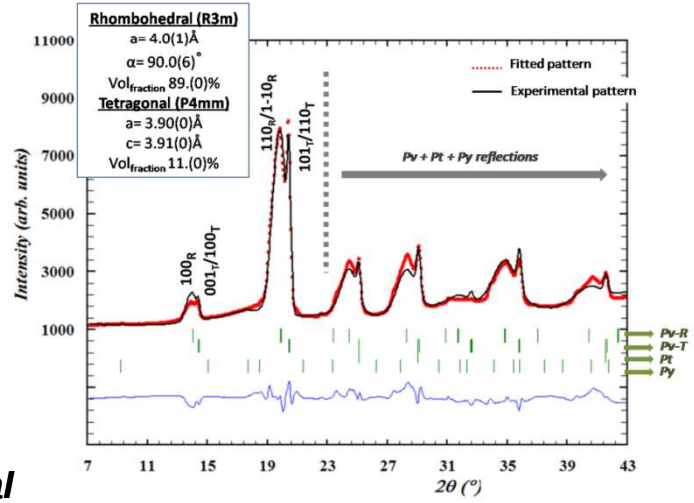
Grazing incidence X-ray synchotron Radiation:BNBT10.0xs

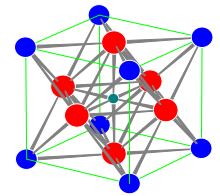


Secondary phase

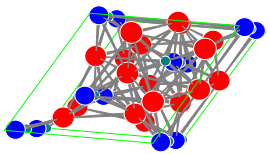




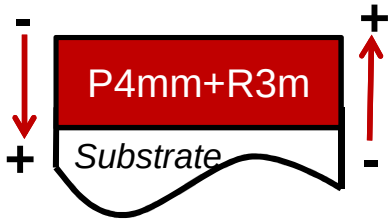




P4mm



R3m



Rhombohedral volume fraction

Tetragonal volume fraction

http://www.esrf.eu/computing/scientific/ANAELU/Anelu_Page.htm

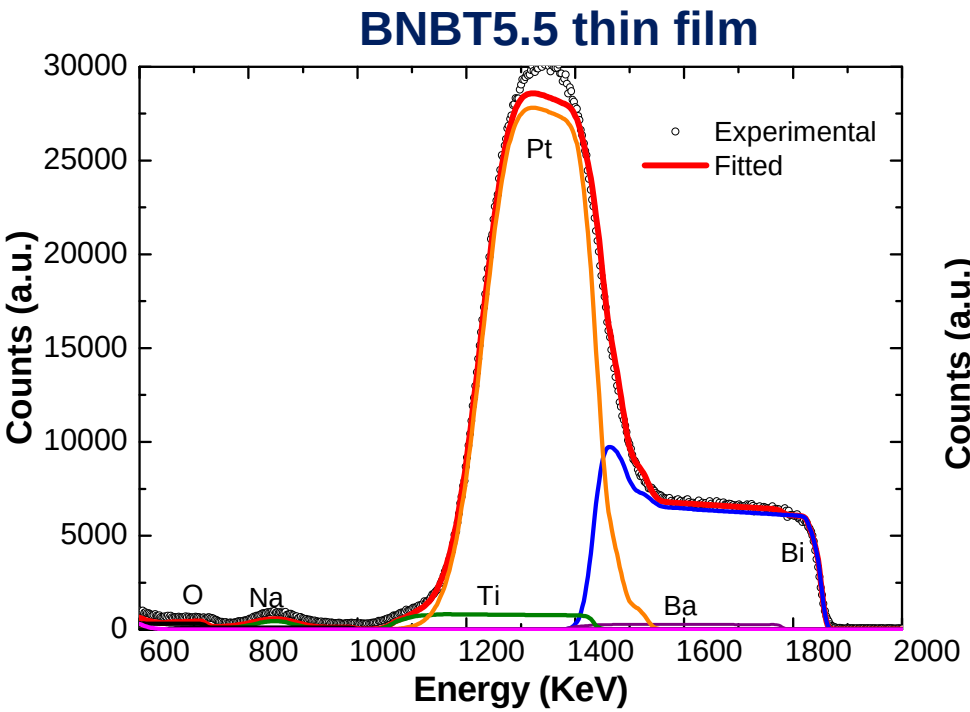
*L. Fuentes-Montero et al, In: SSRL/LCLS User's conference**, 2009***

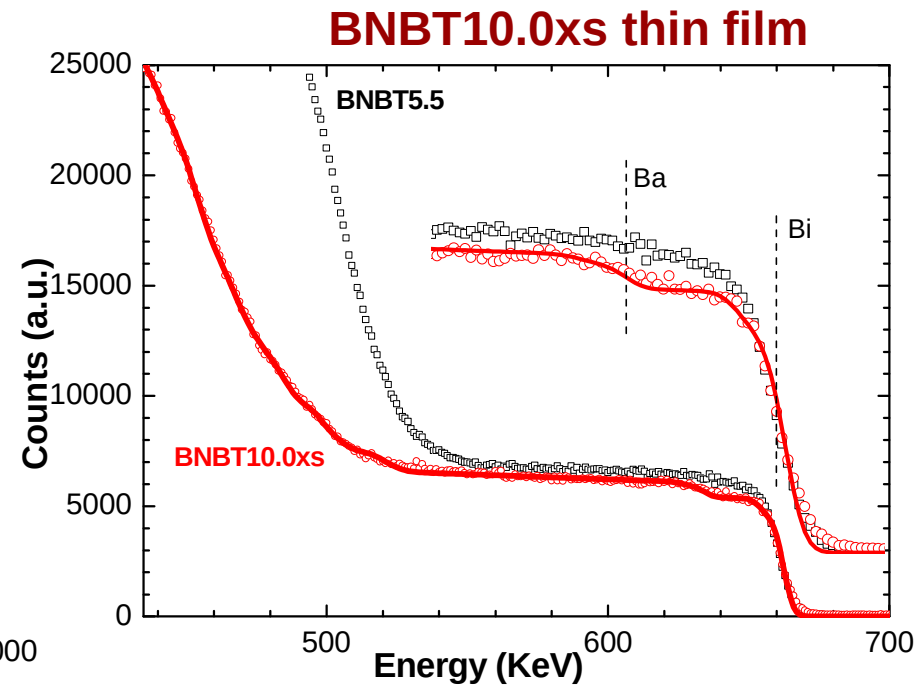
Instituto de Ciencia de Materiales de Madrid ICMM

CSIC Consejo Superior de Investigaciones Científicas

Compositional study

Rutherford Backscattering **(RBS)** experiments





Experimental and fitted spectra of the BNBT5.5 thin film

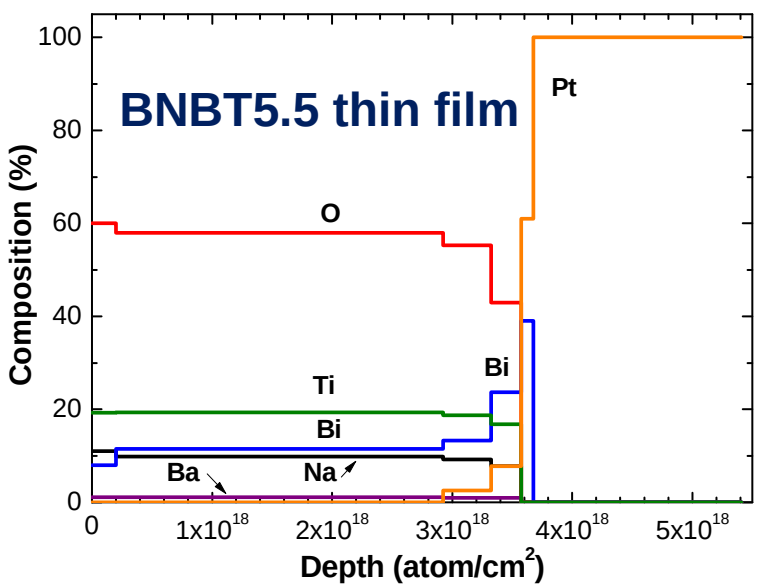
Larger thickness and thicker interface for the BNBT10.0xs thin film

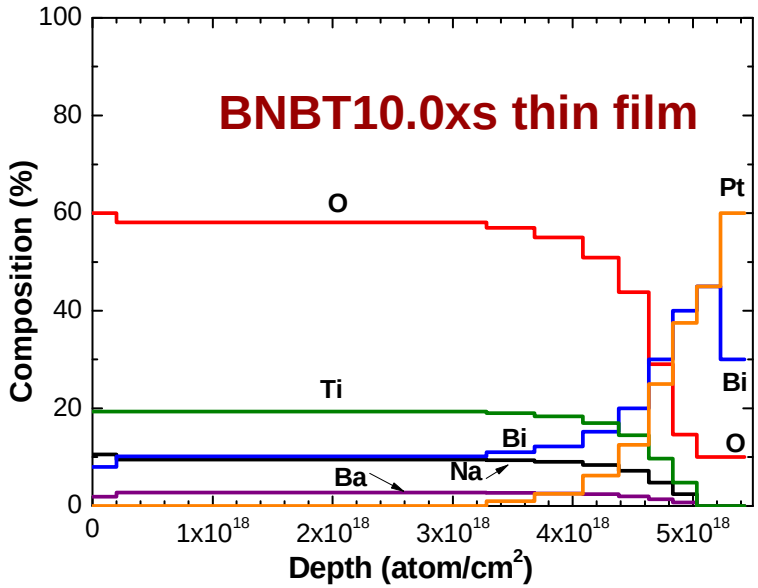
*.Kotai, Nucl Instrum Methods, **1994, B 85**, 588–96,*
*M. Mayer, "SIMNRA User's Guide", **1997***

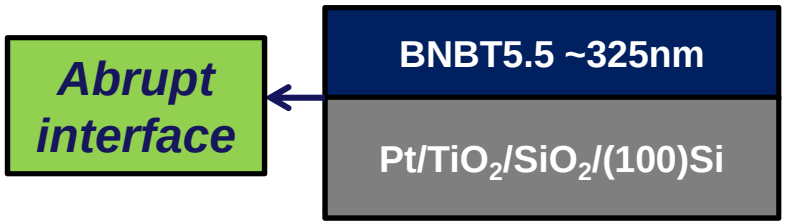
3. RESULTS

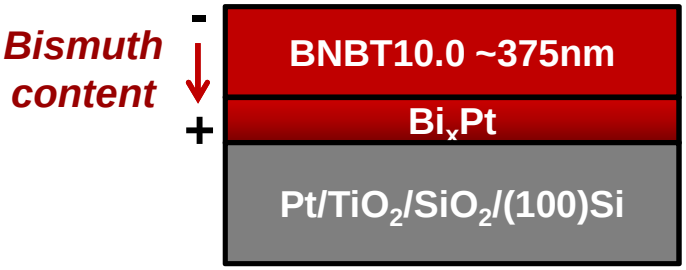
Compositional study

Compositional depth profile







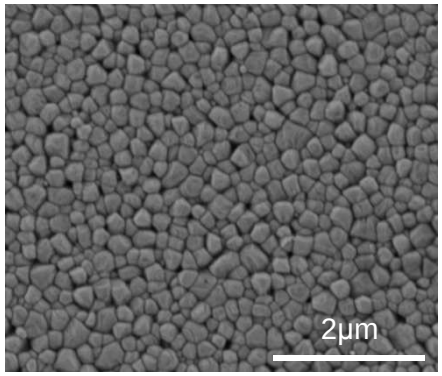


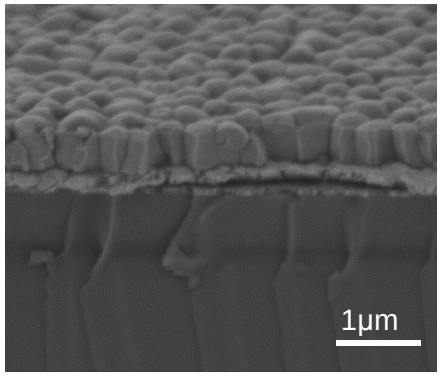
.Kotai, Nucl Instrum Methods, **1994, B 85**, 588–96,
M. Mayer, "SIMNRA User's Guide", **1997**

Instituto de Ciencia de Materiales de Madrid
ICMM
CSIC
Consejo Superior de Investigaciones Científicas

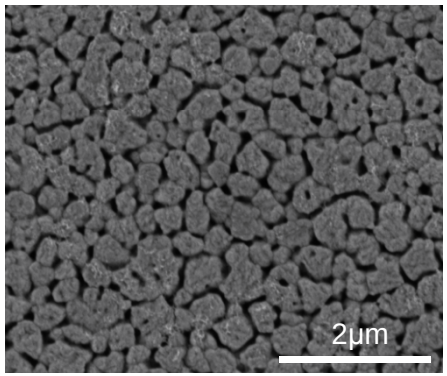
FEG-SEM micrographs

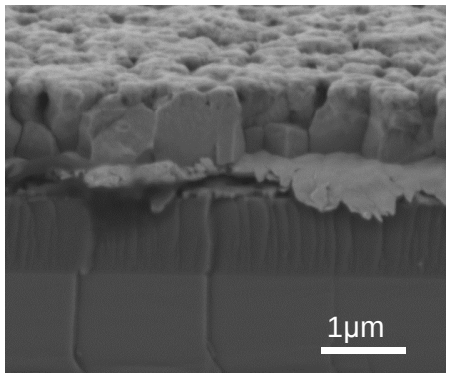
BNBT5.5 thin film





BNBT10.0xs thin film



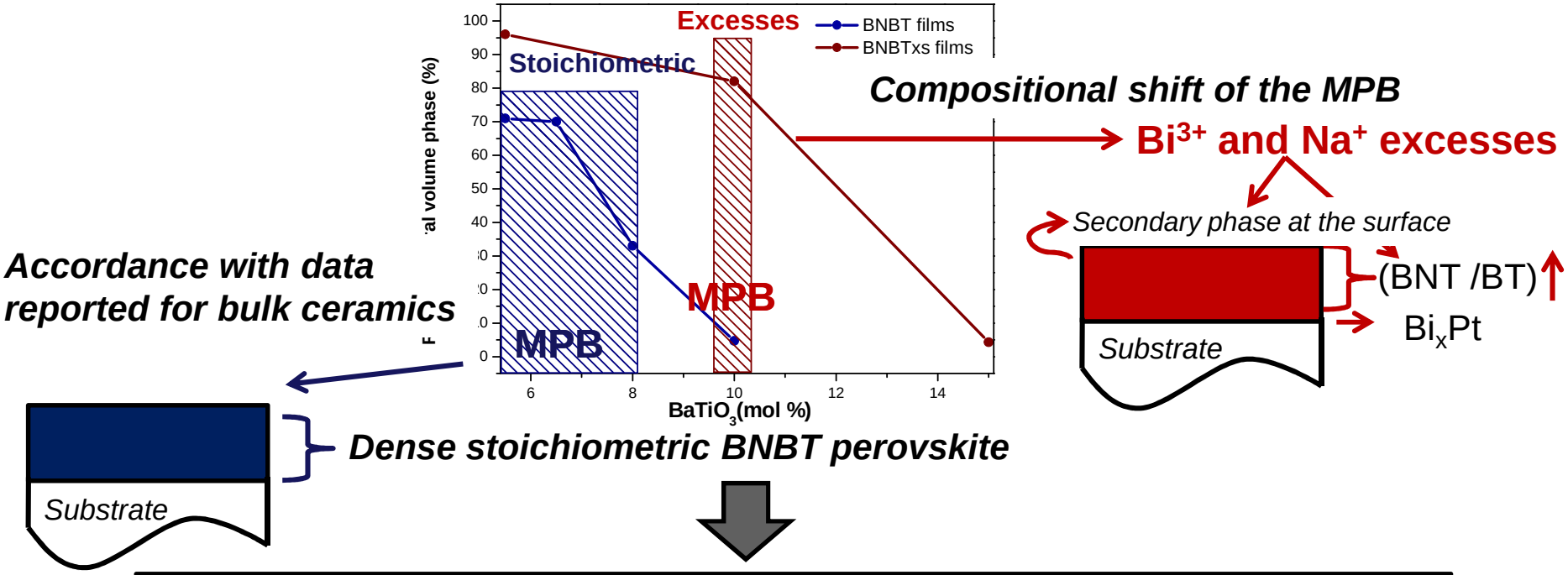


Thickness	by SEM	by RBS
BNBT5.5	~340 nm	~325 nm
BNBT10.0xs	~550 nm	~375 nm

Taking into account, the **theoretical density** of the BNBT (5.96 g cm^{-3})

4. CONCLUSIONS

4. CONCLUSIONS



• The morphotropic phase boundary (MPB) of the **BNBT stoichiometric thin films** is placed at x ~0.055-0.080. This is the MPB region also found for **bulk ceramics**.

• For the BNBTxs films, the MPB is located close to x ~0.100. This suggests that the Bi^{3+} and Na^{+} excesses remain in the bulk film, as second phases or incorporating to the A-sites of the perovskite.

• **Bi^{3+} and Na^{+} excesses** are not required to obtain MPB-BNBT perovskite thin films with homogenous compositional depth profiles.

• These structural and compositional characteristics suggest that these films would have an appropriate functionality for applications in microelectronic devices.

Acknowledgements

This work has been supported by the Spanish Project MAT2010-15365
D. Pérez-Mezcua acknowledges the financial support of the FPU Spanish Program
Dr. I. Bretos acknowledges the financial support of the Juan de la Cierva Program
Dr. R. Escobar-Galindo acknowledges the financial support of the Ramon y Cajal Program

εC XI ZARAGOZA 2013
XI Reunión Nacional de Electrocerámica

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Instituto de Ciencia de Materiales de Madrid ICMM
CSIC Consejo Superior de Investigaciones Científicas