SOLUTION DERIVED LEAD- FREE $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$ (BNBT) THIN FILMS IN THE PROXIMITY OF THE MORPHOTROPIC PHASE BOUNDARY (MPB)

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1. Objectives

- The main goal of this work is the study of lead-free ferroelectric oxides based on the **$(1\text{-}x)(Bi_{0.5}Na_{0.5})TiO_3\text{-}xBaTiO_3$ (BNBT)** system to replace the well known $Pb(Zr_xTi_{1-x})O_3$ (PZT) and the manufacturing of these materials as thin films for its integration in microelectronic devices.

1. Objectives

13.2.2003 | EN | Official Journal of the European Union | L 37/19

DIRECTIVE 2002/95/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 27 January 2003

on the restriction of the use of certain hazardous substances in electrical and electronic equipment

'ROHs' Directive

1. Member States shall ensure that, from 1 July 2006, new electrical and electronic equipment put on the market does not contain lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE). National measures restricting or prohibiting the use of

Applications of lead, mercury, cadmium and hexavalent chromium, which are exempted from the requirements

— lead in electronic ceramic parts (e.g. piezoelectronic devices).

Lead-free compositions to substitute lead based- on compositions (PZT)

Actual trends on the manufacturing of thin films

Integration of ferroelectric materials in the information technologies (ITRS 2011)

Preparation of thin films

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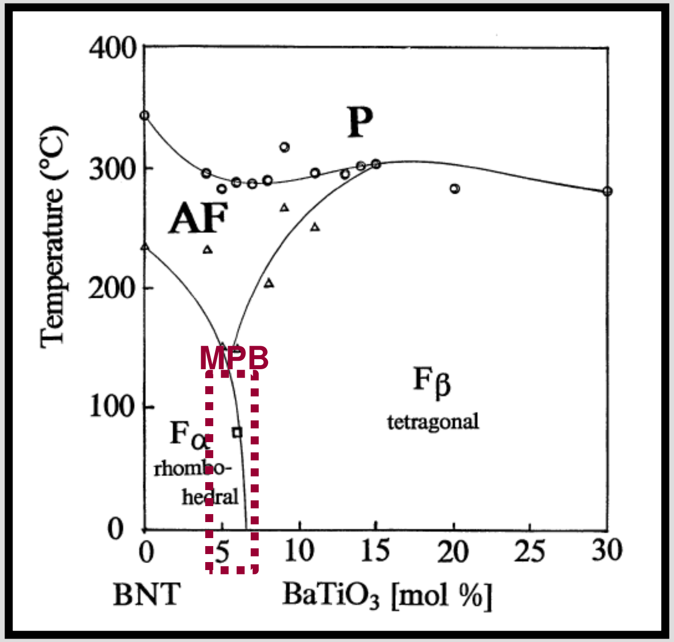
2. Introduction

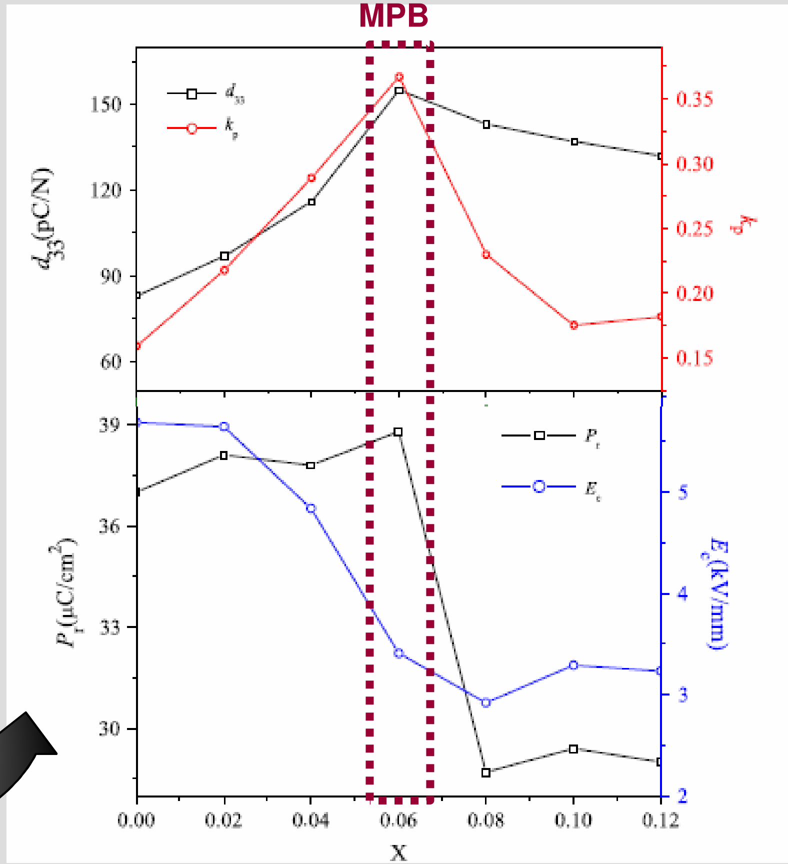
(1-x)$(Bi_{0.5}Na_{0.5})TiO_3$-x$BaTiO_3$ (BNBT)
Solid solution

BNT-BT
Phase diagram

Morphotropic phase boundary(MPB)



*Takenaka et al. Jpn J Appl Phys **1991**; 30: 2236-39*



*Thomas et al. Solid State Sci **2008**; 10:934-940*

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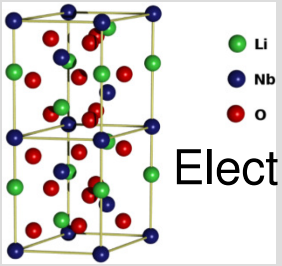
Towards the miniaturization of ferroelectric materials and their integration into microelectronic devices

1 mm	100 µm	10 µm	1 µm	100 nm	1 nm

Bulk ceramics → Thin plates → Thick films → Thin films → Ultra- thin films → Nano-sozed systems

1950	1970	1990	>2000



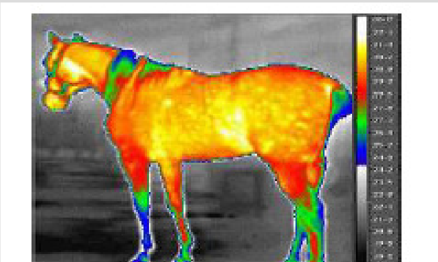
Electro-optic activity

High permitivity

DRAMs

Ferroelectric films

Pyroelectricity



Infrared sensor

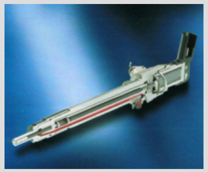
Ferroelectricity

NVFRAMs

Piezoelectricity

Sensors

Actuators



Bretos. Ph. D Thesis UAM ***2006***

2. Introduction

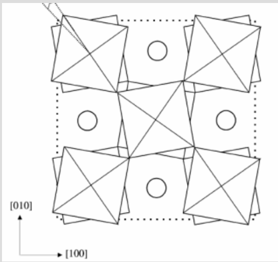
Bulk ceramic $Bi_{0.5}Na_{0.5}TiO_3$

Increasing temperature

Rhombohedral phase → Tetragonal phase → Cubic phase

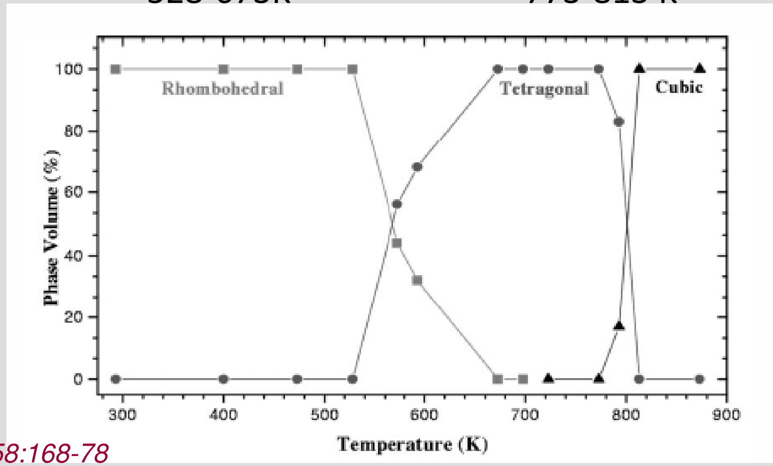
528-673K | 773-813 K

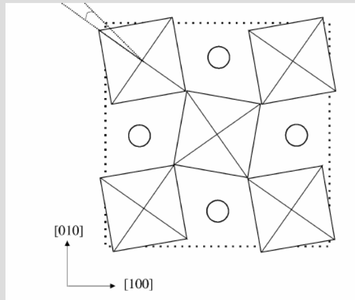
*Thomas et al.Solid State Science **2010**; 12: 311-17*



Rhombohedral

*Jones et al. Acta Crystallogr B **2002**; B58:168-78*





Tetragonal

*Jones et al. Acta Crystallogr B **2000**; B56:426-30*

Single-crystal X-ray diffraction

- $Bi_{0.5}Na_{0.5}TiO_3$ → Rhombohedral phase with tetragonal inclusions — *Thomas et al.Solid State Science **2010**; 12: 311-17*
- $0.89Bi_{0.5}Na_{0.5}TiO_3$-$0.11BaTiO_3$ → Tetragonal

Thin film

- $0.90Bi_{0.5}Na_{0.5}TiO_3$-$0.10BaTiO_3$ → Displacement of the MPB composition — *The reason could be* → Structural effects

*Cheng et al. Appl Phys Lett **2004;** 85: 2319-21*
*Bretos et al. Mater Lett **2011**; 65:2714-2716*

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3. Experimental Procedure

3. Experimental procedure

Metallic precursor

$Na(OCOCH_3).3H_2O$ + $Bi(OCOCH_3)_3$ + $Ti(CH_3COCHCOCH_3)_2(OC_3H_7)_2$

Solvents

CH_3COOH + $OH(CH_2)_3OH$ + H_2O

10.0 mol% of Bi(III) excess + 10.0 mol% of Na(I) excess

Molar ratios 1.0:10.0 f Ti (IV) to any solvents

Reflux in air for 8h

$Bi_{0.5}Na_{0.5}TiO_3$ Precursor sol (≈0.60 mol L^{-1})

*Alonso et al. J Am Ceram Soci **2008**; 92 [10]: 2218-25*

Metallic precursor

$BaCO_3$

Solvents

CH_3CH_2COOH + $(CH_3CH_2CO)_2O$

Reflux in air for 2 h

Metallic precursor

$Ti(OC_4H_{10})$

Solvents

C_4H_9OH + $CH_3COCH_2COCH_3$

Stirring at room temperature

Solvents

C_4H_9OH

Stirring at room temperature

$BaTiO_3$ Precursor solution (≈ 0.30 mol L^{-1})

*Hoffmann el al. J Eur Ceram Soci **1999**: 19 ;1339-1343*

$Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ Precursor solution (≈ 0.60 mol L^{-1})

Solvent

C_2H_5OH

$Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ Precursor solution (≈ 0.20 mol L^{-1})

3. Experimental procedure

Composition in the vicinity of the MPB

$Bi_{0.5}Na_{0.5}TiO_3$
Precursor sol
(BNTs)

$BaTiO_3$
Precursor solution
(BT)

$Bi_{0.5}Na_{0.5}TiO_3$
Precursor sol
(10%mol.exc. Bi_2O_3+10% mol. exc. NaO)

Stirring at room temperature(72 h)

BNBTs5.5
BNBTs6.5
BNBTs8.0
BNBTs10.0

Stoichiometric

BNBT5.5
BNBT10.0
BNBT15.0

10% mol. Bi(III) and Na(I) excesses

Dried ethanol

Annealed at 900ºC(1h)

Heat shock

Slow cooling

Crystalline powders

Diluted solution to prepare the films by CSD

Crystallization: RTP

*Schwartz Cr Chim **2004**; 7 :433-461*

25ºC/ 60s Vacuum

25ºC/ 120s Oxygen

22s

650ºC/60s

22s

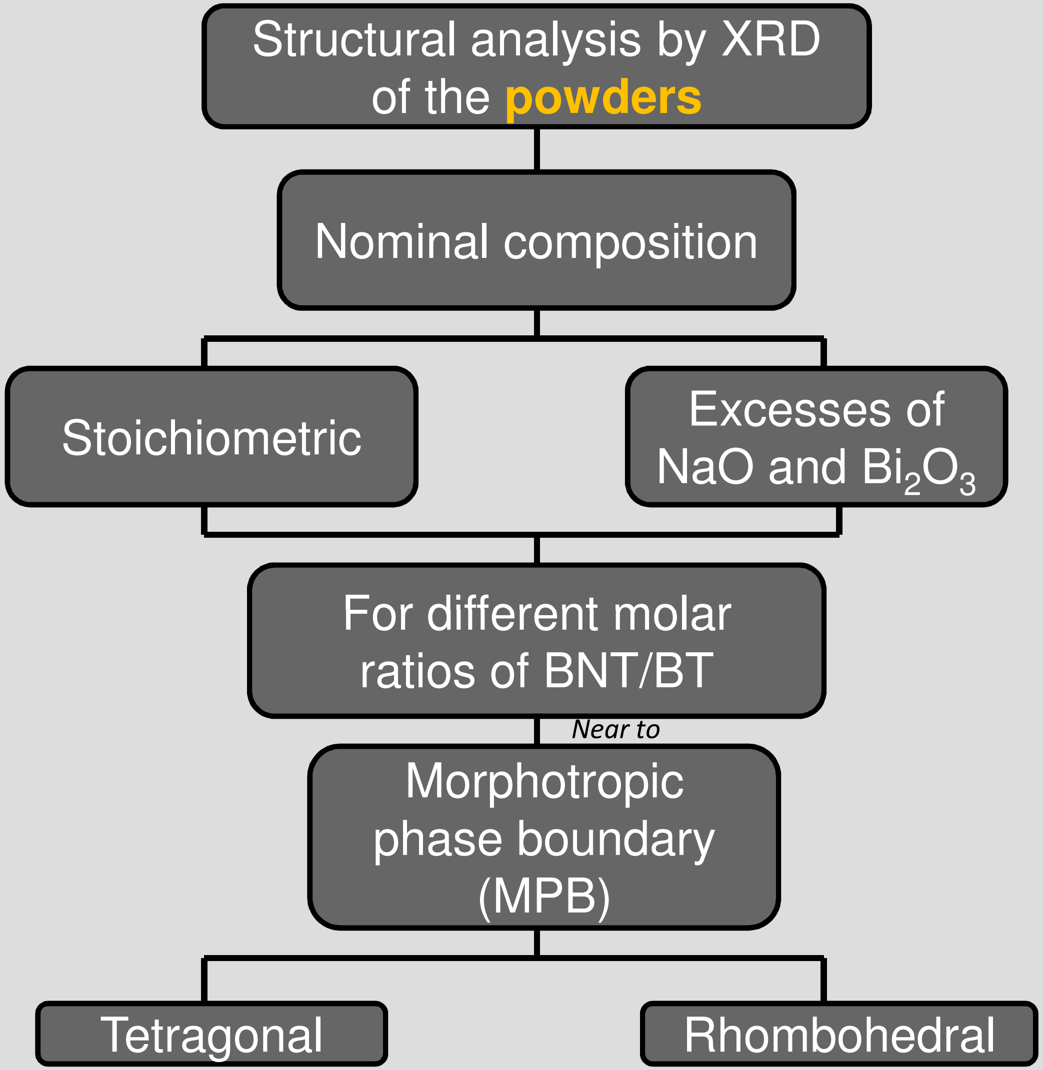
100ºC

Refrigeration

4. Results and discussion

4.1 Crystalline powders

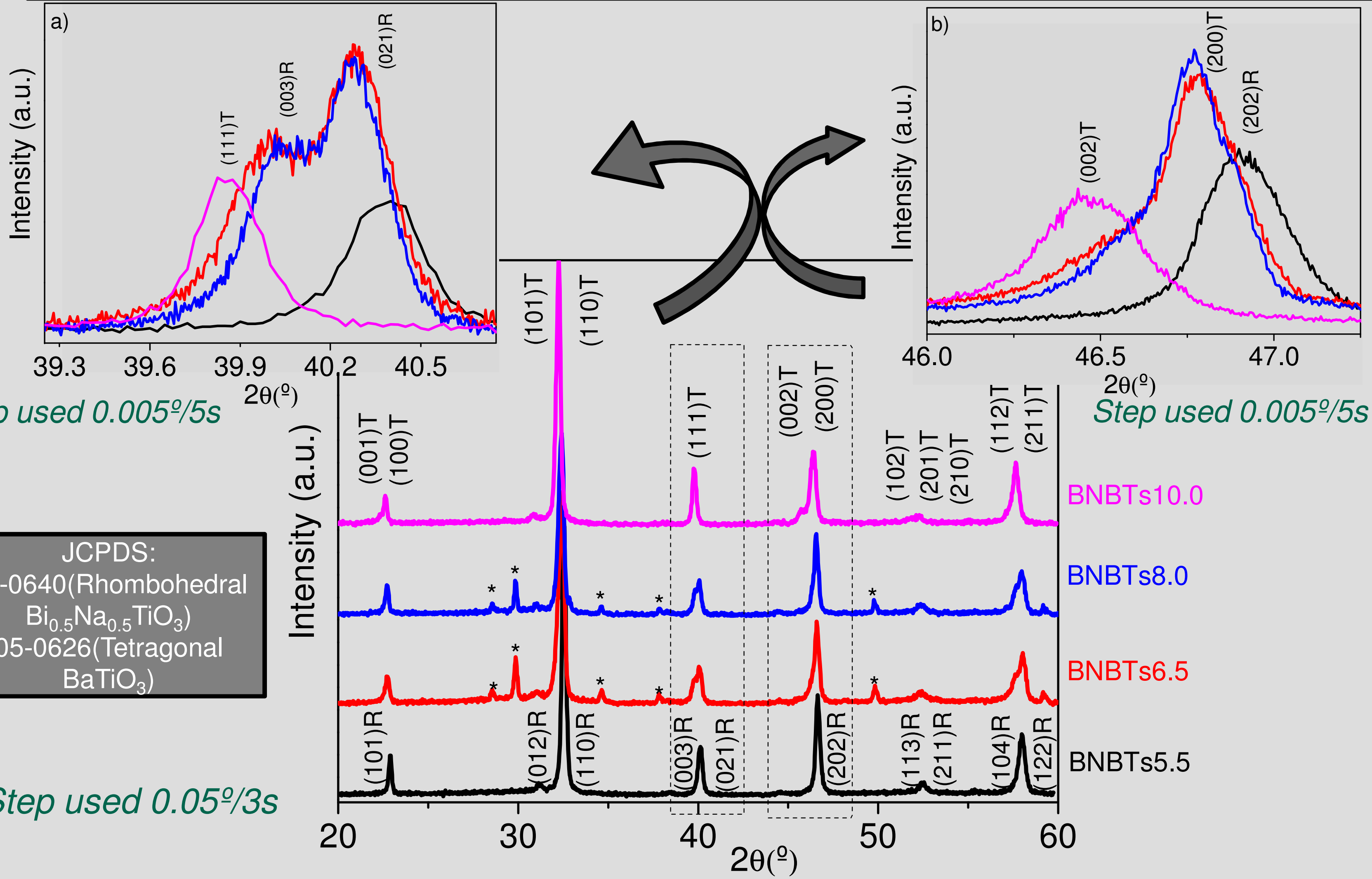
4. Results and discussion



Coexistence of these structures

*Takenaka et al. Jpn J Appl Phys **1991**; 30: 2236-39*

Structural analysis of the crystalline phase in the **stoichiometric powders** with different BNT/BT molar ratios



Step used 0.005º/5s

JCPDS:
36-0640(Rhombohedral $Bi_{0.5}Na_{0.5}TiO_3$)
05-0626(Tetragonal $BaTiO_3$)

Step used 0.05º/3s

*Jones et al. Acta Crystallogr B **2000**; B56:426-30*
*Jones et al. Acta Crystallogr B **2002**; B58:168-78*

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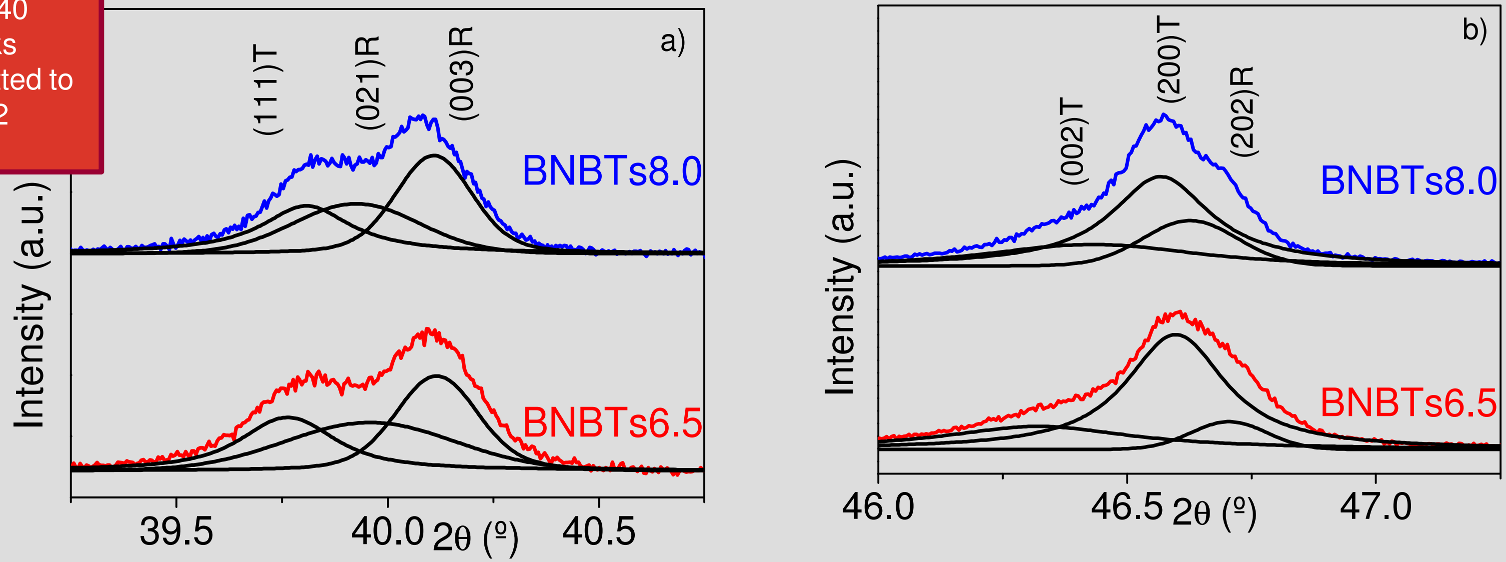
Structural analysis of crystalline **stoichiometric powders** for different BNT/BT molar ratios

Deconvolution has been made using program V1-40 and the peaks have been fitted to seudo-voigt 2 function



SAMPLES	MOLAR RATIOS BNT/ BT	NOMINAL COMPOSITION (stoichiometric)	CRYSTALLINE STRUCTURES OBTAINED FROM XRD PATTERNS
BNBTs5.5	94.5/5.5	$(Bi_{0.5}Na_{0.5})_{0.945}Ba_{0.055}TiO_3$	Rhombohedral
BNBTs6.5	93.5/6.5	$(Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}TiO_3$	Rhombohedral + tetragonal (MPB)
BNBTs8.0	92.0/8.0	$(Bi_{0.5}Na_{0.5})_{0.920}Ba_{0.080}TiO_3$	Rombohedral + tetragonal (MPB)
BNBTs10.0	90.0/10.0	$(Bi_{0.5}Na_{0.5})_{0.900}Ba_{0.100}TiO_3$	Tetragonal

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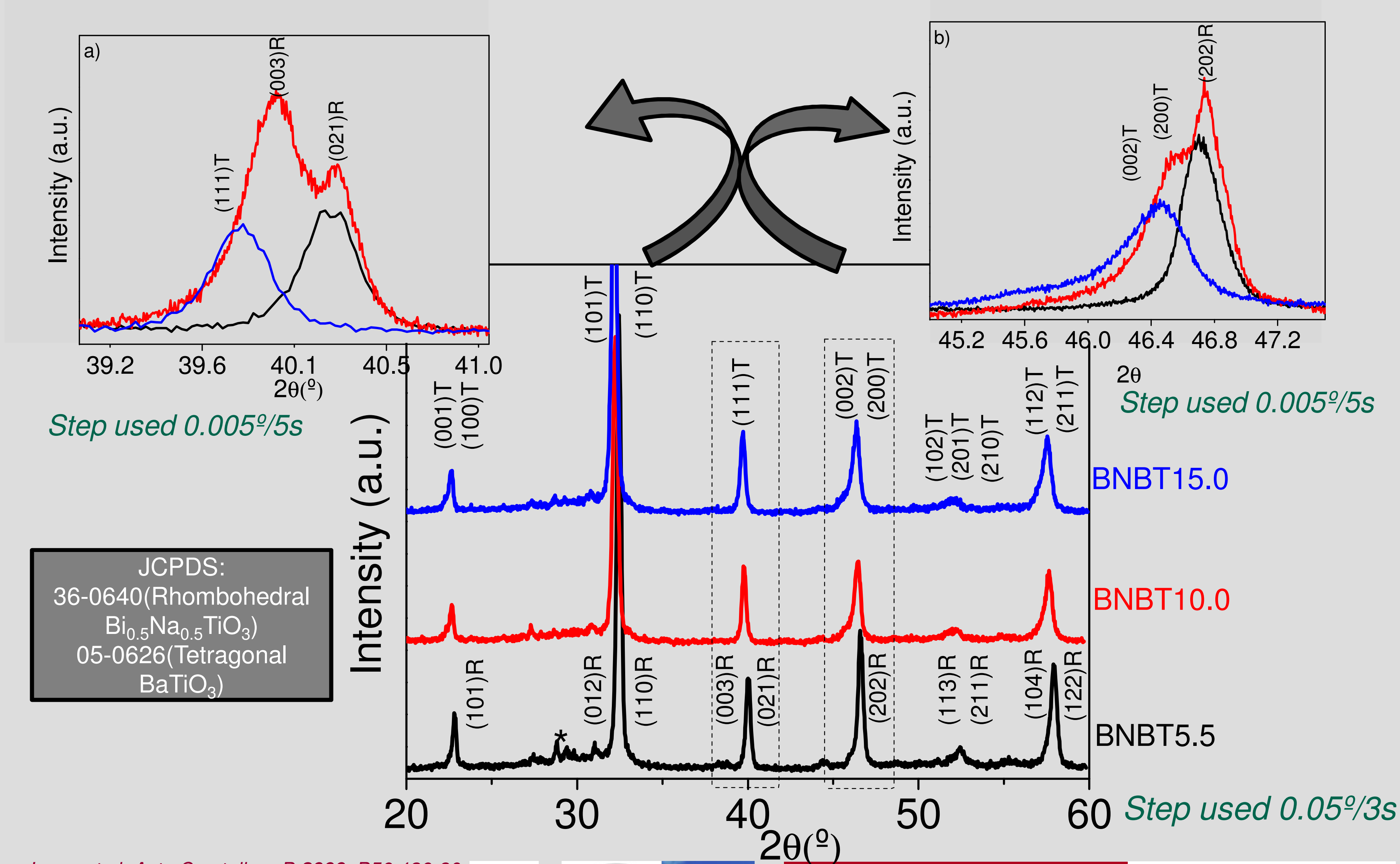
Structural analysis of the **crystalline powders** containing **excesses of Na(I) and Bi(III)**



Jones et al. Acta Crystallogr B ***2000****; B56:426-30*
Jones et al. Acta Crystallogr B ***2002****; B58:168-78*

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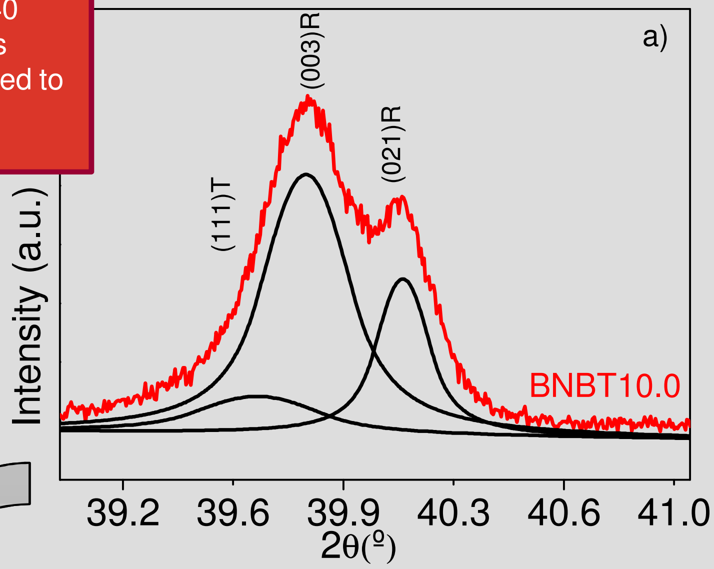
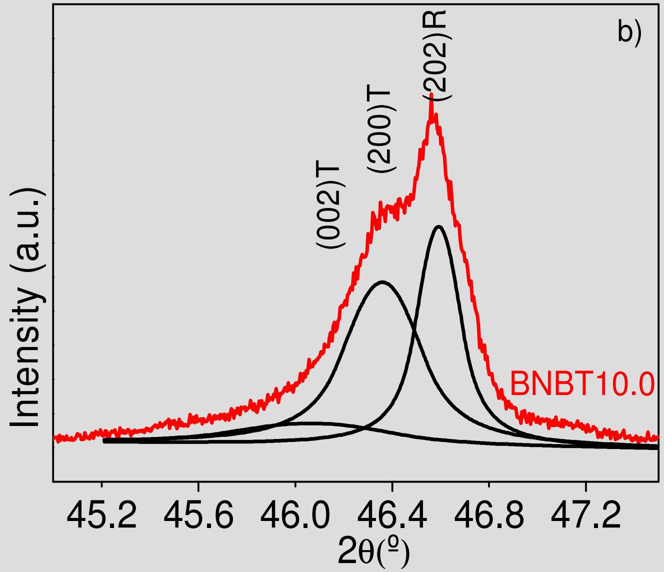
Structural analysis of **crystalline powders with excesses of Na(I) and Bi(III)** for different BNT/BT molar ratios

Deconvolution has been made using program V1-40 and the peaks have been fitted to seudo-voigt 2 function





SAMPLE	MOLAR RATIOS BNBT/BT	NOMINAL COMPOSITION (10%molar exceso Bi_2O_3+ 10%molar exceso NaO)	CRYSTALLINE STRUCTURE OBTAINED FROM XRD PATTERNS
BNBT5.5	94.5/5.5	$(Bi_{0.5}Na_{0.5})_{0.945}Ba_{0.055}TiO_3$	Rhombohedral
BNBT10.0	90.0/10.0	$(Bi_{0.5}Na_{0.5})_{0.900}Ba_{0.100}TiO_3$	Rhombohedral+ tetragonal (MPB)
BNBT15.0	85.0/15.0	$(Bi_{0.5}Na_{0.5})_{0.850}Ba_{0.150}TiO_3$	Tetragonal

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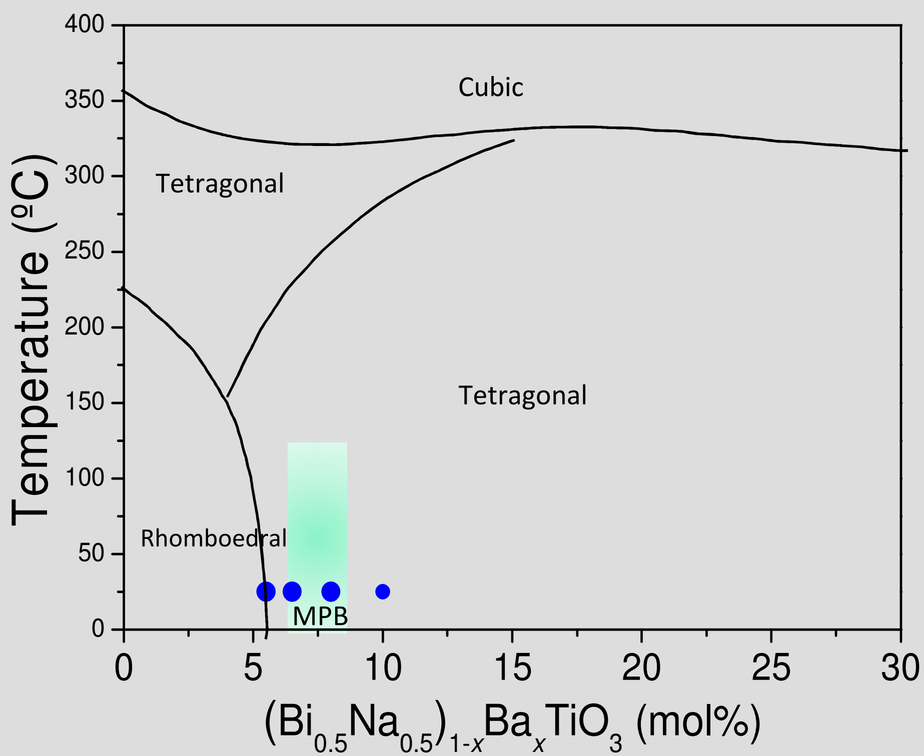
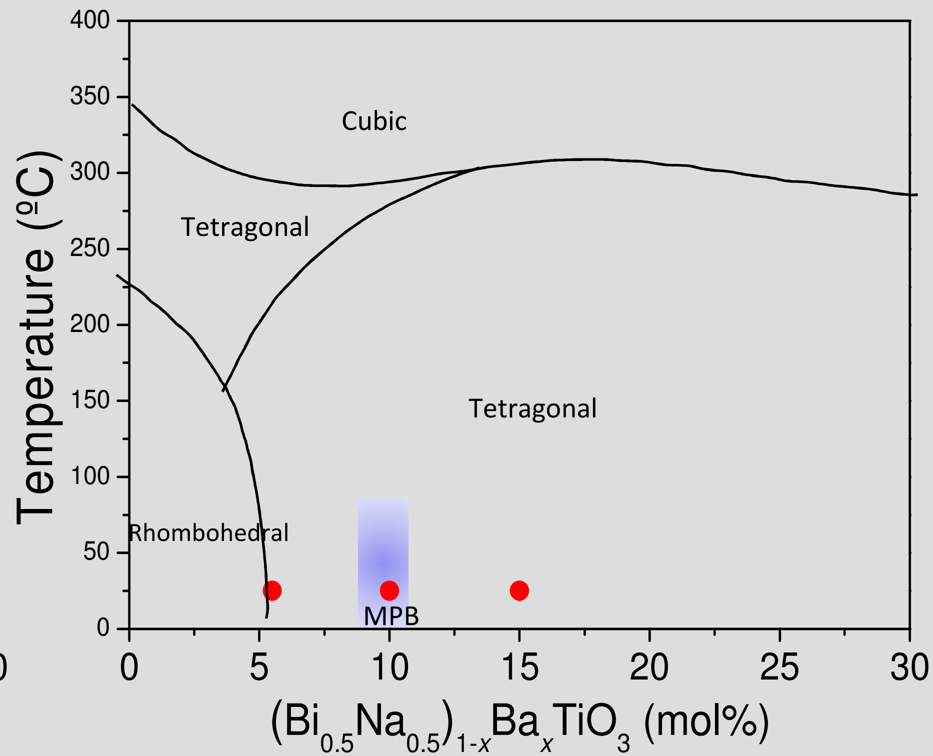
Determination of the morphotropic phase boundary (MPB) for the **crystalline powders**

Stoichiometric nominal composition

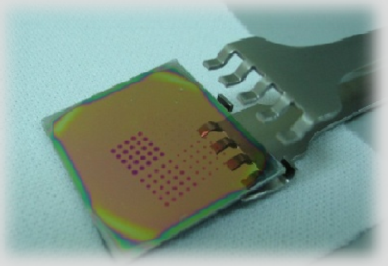


Nominal composition containing excesses of Na(I) +Bi(III)



*Rout et al. J Ceram Soc Jpn **2009**; 117 [7]: 797-800*

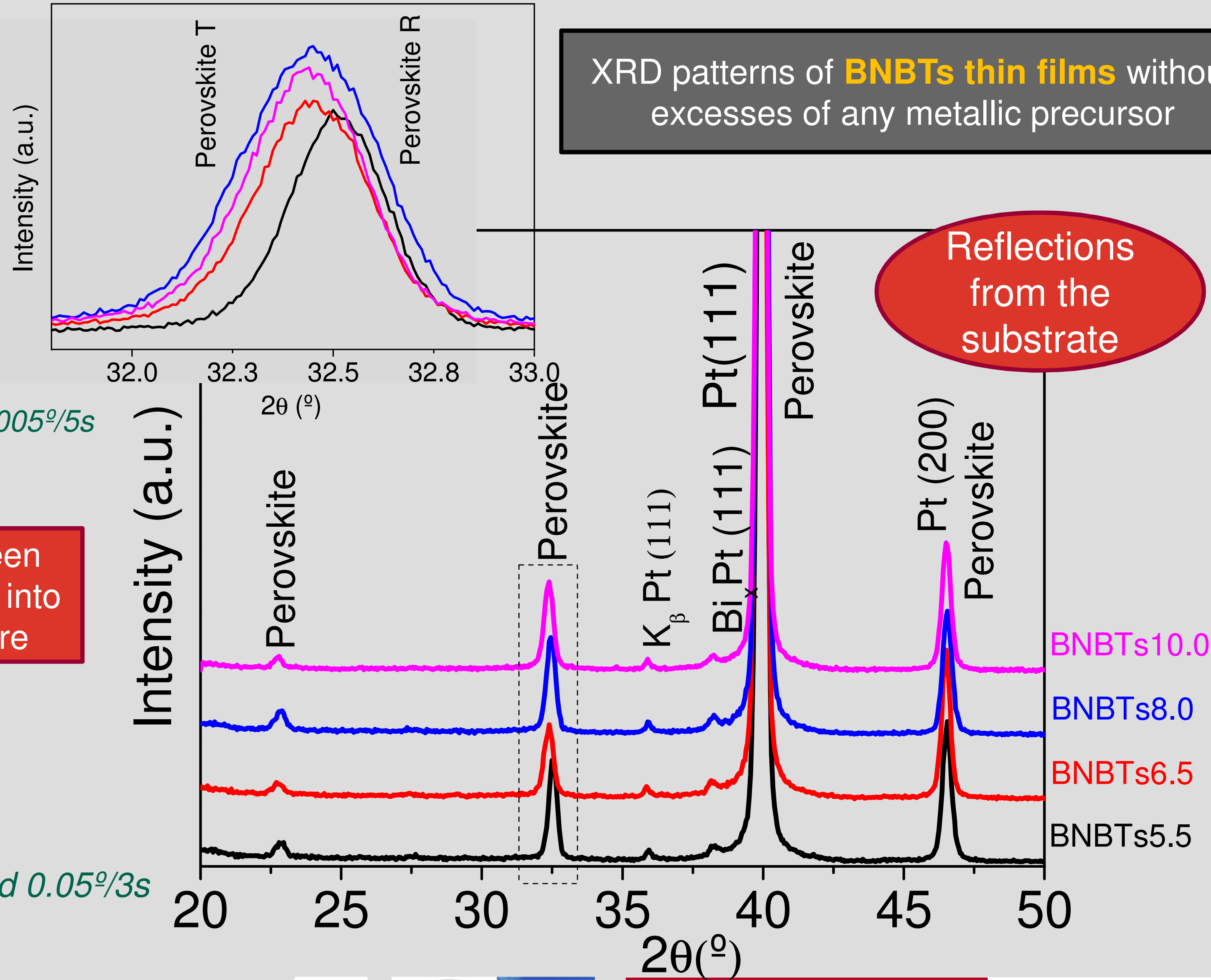
4.2 Thin films



Ferroelectric system in thin film form:

- Lost by volatilization of Na(I)+Bi(III)
- Change of the phase because of structural effects induced by the substrate

XRD patterns of **BNBTs thin films** without excesses of any metallic precursor



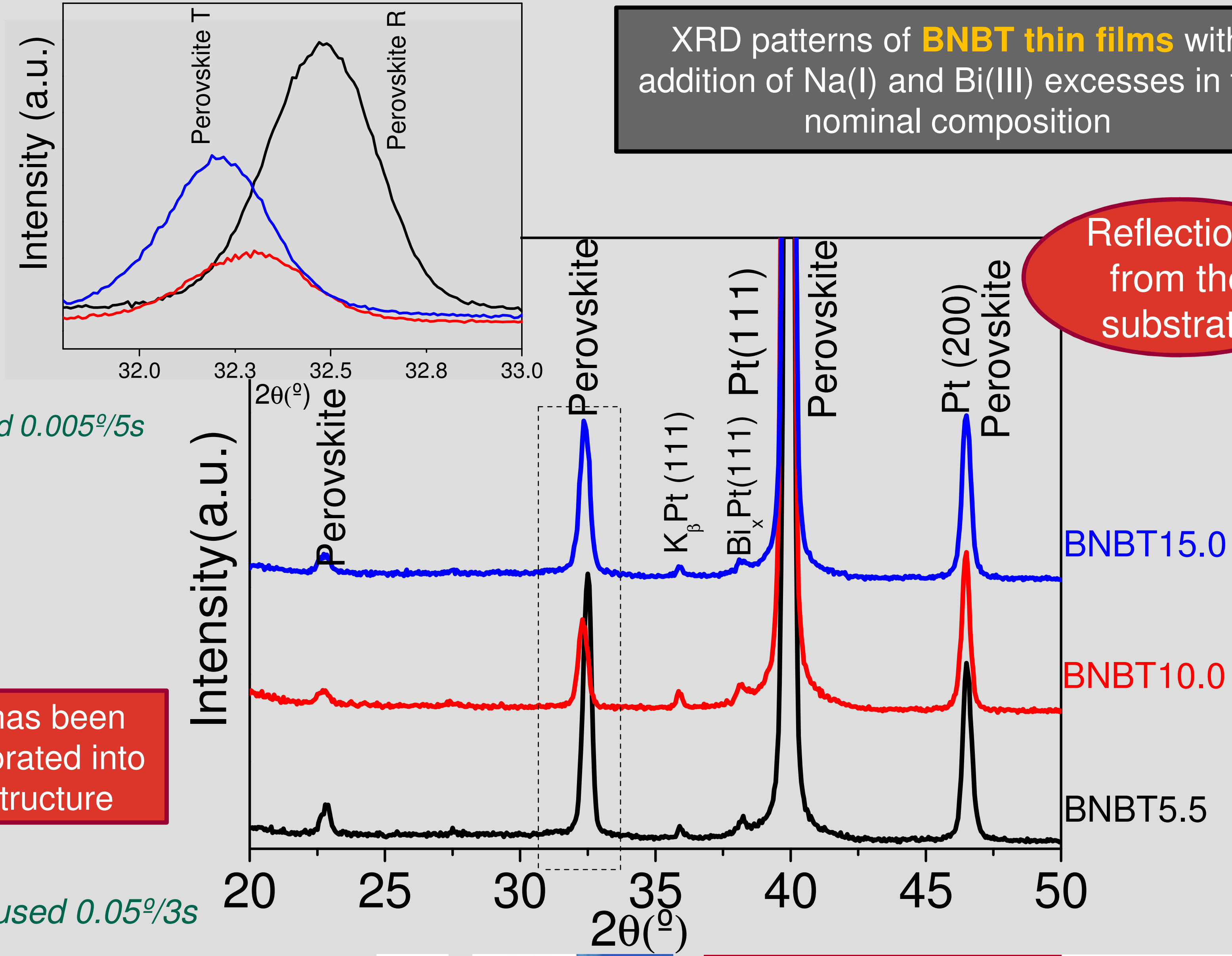
Reflections from the substrate

Step used 0.005º/5s

Step used 0.05º/3s

Ba^{2+} has been incorporated into the structure

XRD patterns of **BNBT thin films** with addition of Na(I) and Bi(III) excesses in the nominal composition



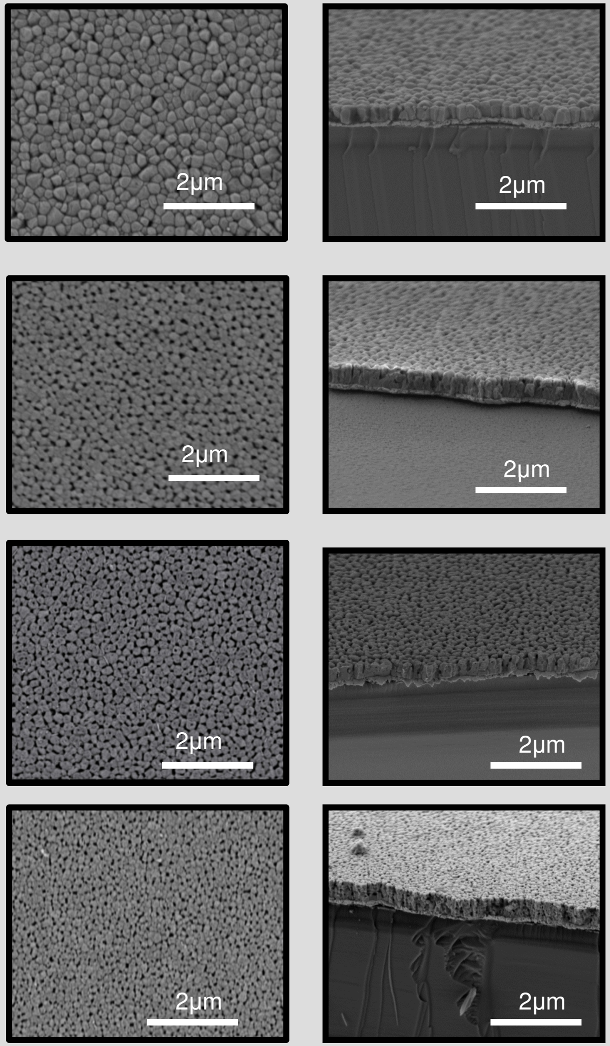
Reflections from the substrate

Step used 0.005º/5s

Step used 0.05º/3s

Ba^{2+} has been incorporated into the structure

Cross-section and plan-view images of **BNBTs** nominal **stoichiometric films**



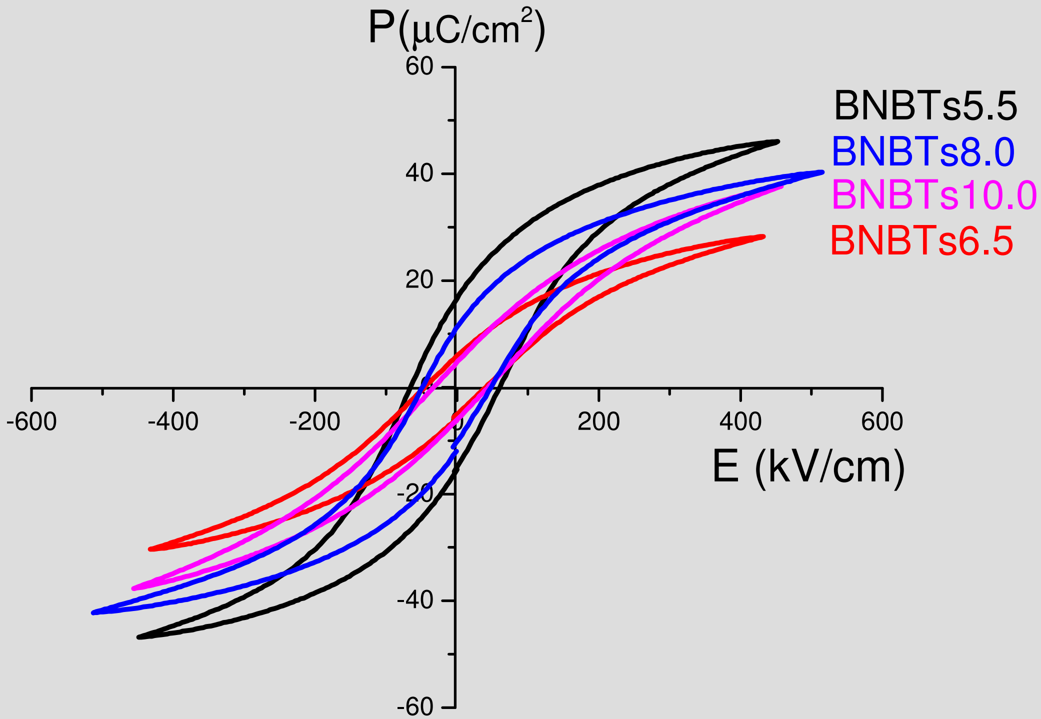
BNBTs5.5

BNBTs6.5

BNBTs8.0

BNBTs10.0

Electrical measurement of **BNBTs** nominal **stoichiometric thin films**



Sample	BNBTs5.5	BNBTs6.5	BNBTs8.0	BNBTs10.0
Grain size	≈288 nm	≈194 nm	≈179 nm	≈119 nm
Thickness	≈341 nm	≈459 nm	≈329 nm	≈435 nm

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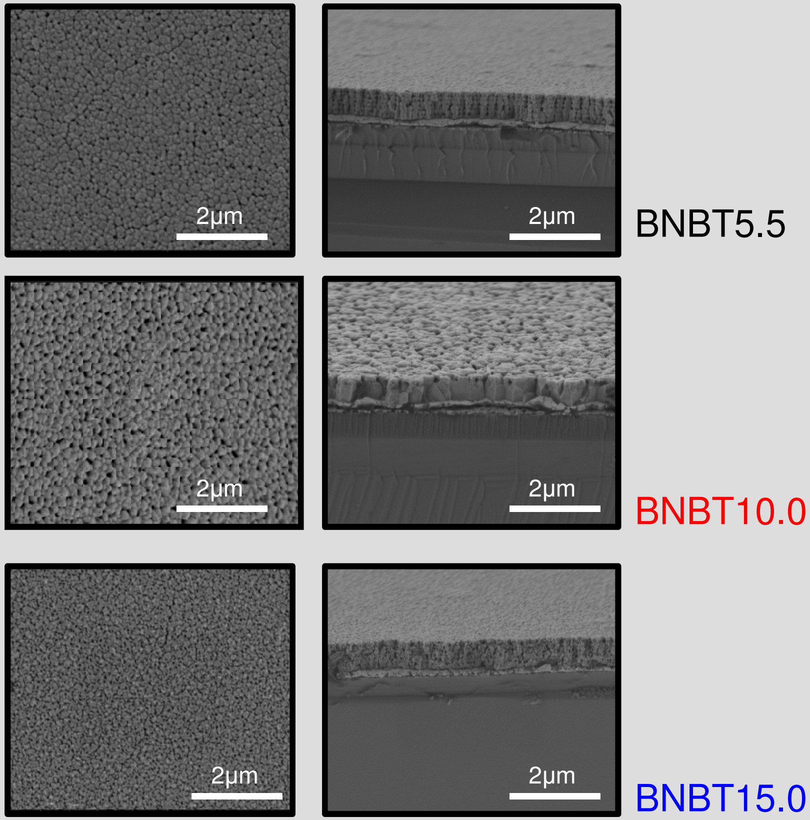
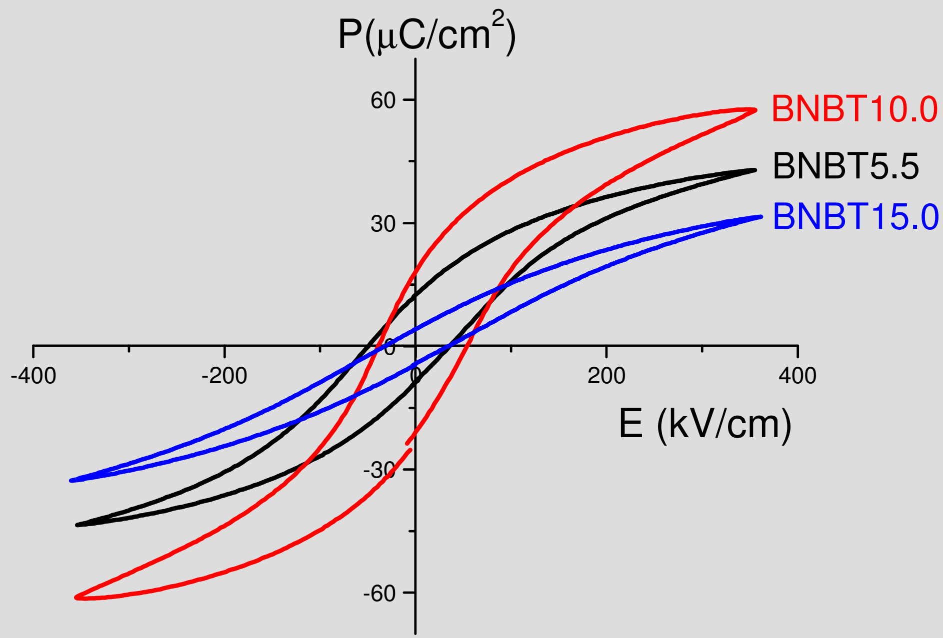
4. Results and discussion

Cross-section and plan-view images of **BNBT films containing excesses** of Na(I)+Bi(III) in the nominal composition



Electrical measurement of **BNBT thin films with Na(I)+Bi(III) excesses** in the nominal composition



Sample	BNBT5.5	BNBT10.0	BNBT15.0
Grain size	≈153 nm	≈170 nm	≈97 nm
Thickness	≈559 nm	≈553 nm	≈550 nm

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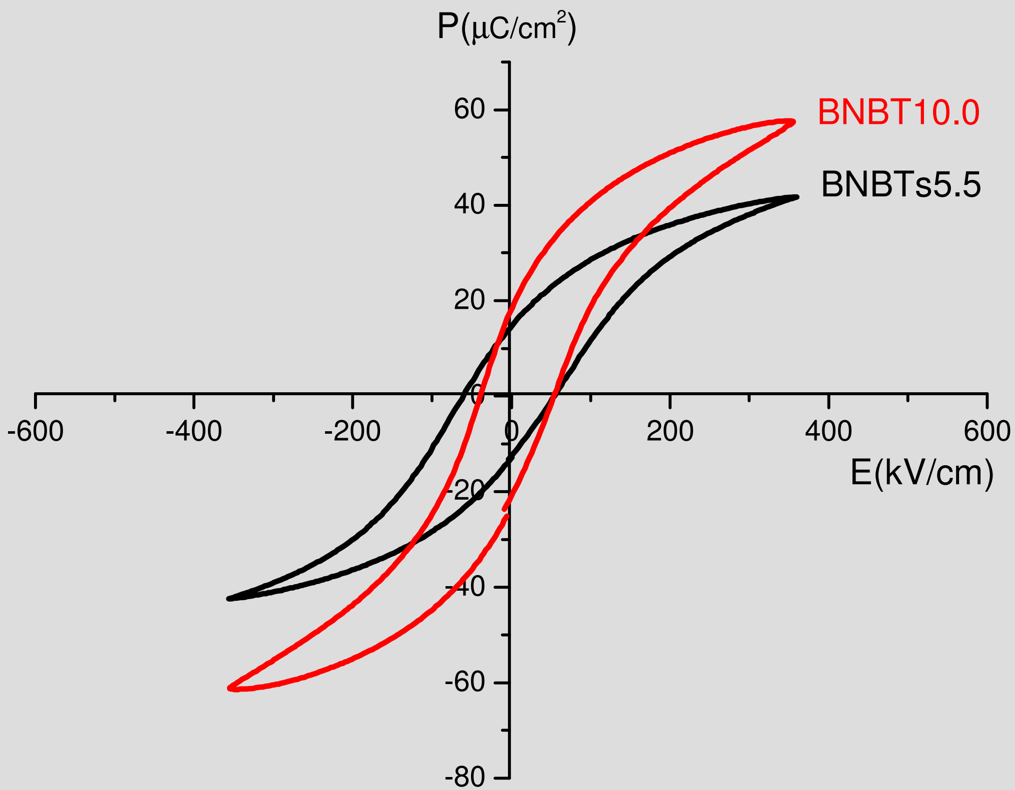
Electrical measurements comparison between the best stoichiometric and the best not stoichiometric **films**



5. Conclusions

5. Conclusions

•The morphotropic phase boundary (MPB) of **BNBT powders** has been situated for 93.5/6.5 and 92.0/8.0 'stoichiometric' nominal composition. Addition of Na(I) and Bi(III) excesses to the system leads to a shift of the MPB for these powders to the 90.0/10.0 nominal composition.

•The best ferroelectric response for **BNBT films** has been obtained for the 90.0/10.0 composition with addition of Na(I) and Bi(III) excesses to the respective precursor solution (P_r 23 $\mu C/cm^2$ and Ps≈60 $\mu C/cm^2$), the composition for which has identified the MPB in the crystalline powders.

•Studies are in progress to elucidate the either **intrinsic** (e.g. compositional effects) or **extrinsic** (e.g. scaling effects) driving nature of the boundary displacement observed in these BNBT films with respect to bulk counterparts.

SOLUTION DERIVED LEAD- FREE $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$ (BNBT) THIN FILMS IN THE PROXIMITY OF THE MORPHOTROPIC PHASE BOUNDARY (MPB)

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