Dielectric and Raman spectroscopic studies of phase transitions in the (1-x)($Na_{0.5}Bi_{0.5}TiO_3$)-x($BaSnO_3$) Lead-free ferroelectric system

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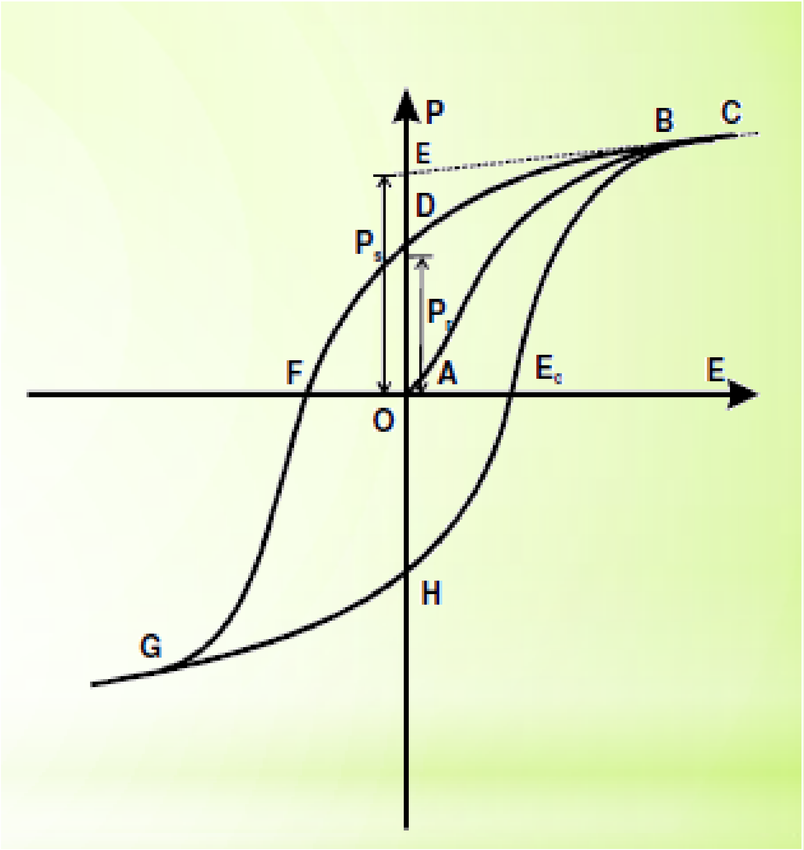
Plan of presentation

- ***Introduction.***
- ***Why $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)?***
- ***Problems to be addressed.***
- ***Objectives.***
- ***Results and Discussion***
- ***Summary and conclusions***

Introduction

- ***Ferroelectric materials have permanent dipoles and so there molecular structure lack center of symmetry.***
- ***All ferroelectric crystals must be piezoelectric though the converse is not true.***
- ***All ferroelectric materials have one or more phase transition temperatures.***
- ***Structural change take place at the curie temperature.***
- ***Immediately above the curie temperature, the dielectric constant of a ferroelectric material obeys Curie -Wiess law .***
- ***A ferroeletric is generally defined as one of which exhibits hysterisis loop.***



1)spontaneous Polarization (Ps)
2)Remnant Polarization (Pr)
3)Coercive Field (Ec)

Most studied material

- ***BT ($BaTiO_3$)***
- ***PZT ($Pb(Zr_xTi_{1-x})O_3$)***
- ***PLZT ($Pb_{1-x}La_x(Zr_yT_{1-y})_{1-x/4}O_3$)***
- ***PMN ($Pb(Mg_{1/3}Nb_{2/3}O_3$)- PT($PbTiO_3$)***

Why Lead free

- ***Lead (Pb) release into the environment at time of processing and remain for a long time in the environment and accumulates in living tissues which damages the brain and nervous system.***
- ***It could introduce to the ecosystem and cause "acid rain".***
- ***Restoring and recycling of lead-based materials is an extensive environmental issues.***

Why $(Na_{0.5}Bi_{0.5})TiO_3$?

- *Lead free compound.*
- *Ferroelectric at room temperature.*
- *Complex phase transitions sequence & anomalies dielectric behaviors.*
- *High Curie temperature (T_c >320 ^{0}C) .*
- *Large Remnant polarization.*
- *Bi^{+3} ions are isoelectronic configuration with Pb^{+2}, both showing a lone pair effect.*

Sequence of Phase transitions NBT

Rhombohedral (R3c)

T_d ↓

(200-280 ^{o}C) Modulated Orthorhombic (R3c+ Pnma)

$T_{A\text{-}O}$ ↓

Orthorhombic (Pnma)

T_C ↓ ***Second order Phase transition (~320 ^{o}C)***

Tetragonal ($P4/mbm+P4_2/mnm$)

↓ ***First order phase transition***

Cubic (520-540 ^{o}C) (Pm-3m)

- **G. Trolliard and V. Dorcet, Chem. Mater. 20, 5074 (2008).**
- **V. Dorcet, G. Trolliard, and P. Boullay, Chem. Mater. 20, 5061 (2008).**

Problems Addressed

- ***High coercive field 73 KV/cm.***
- ***High conductivity cause problem during polling.***
- ***High Dielectric loss.***
- ***Low piezoelectric and electromechanical properties i.e. d_{33} of 92 pC/N and K_p coupling coefficients 18.6.***

To overcome the above mentioned problems, we have synthesized $(1\text{-}x)Na_{0.5}Bi_{0.5}TiO_3–xBaSnO_3$ ($0 \leq x \leq 0.15$)

Objective

Our main objective is to

(i) reduce the high dielectric loss and conductivity

(ii) improve the dielectric and ferroelectric properties.

(iii) study the fundamental physics related to phase transition of NBT-$BaSnO_3$ System.

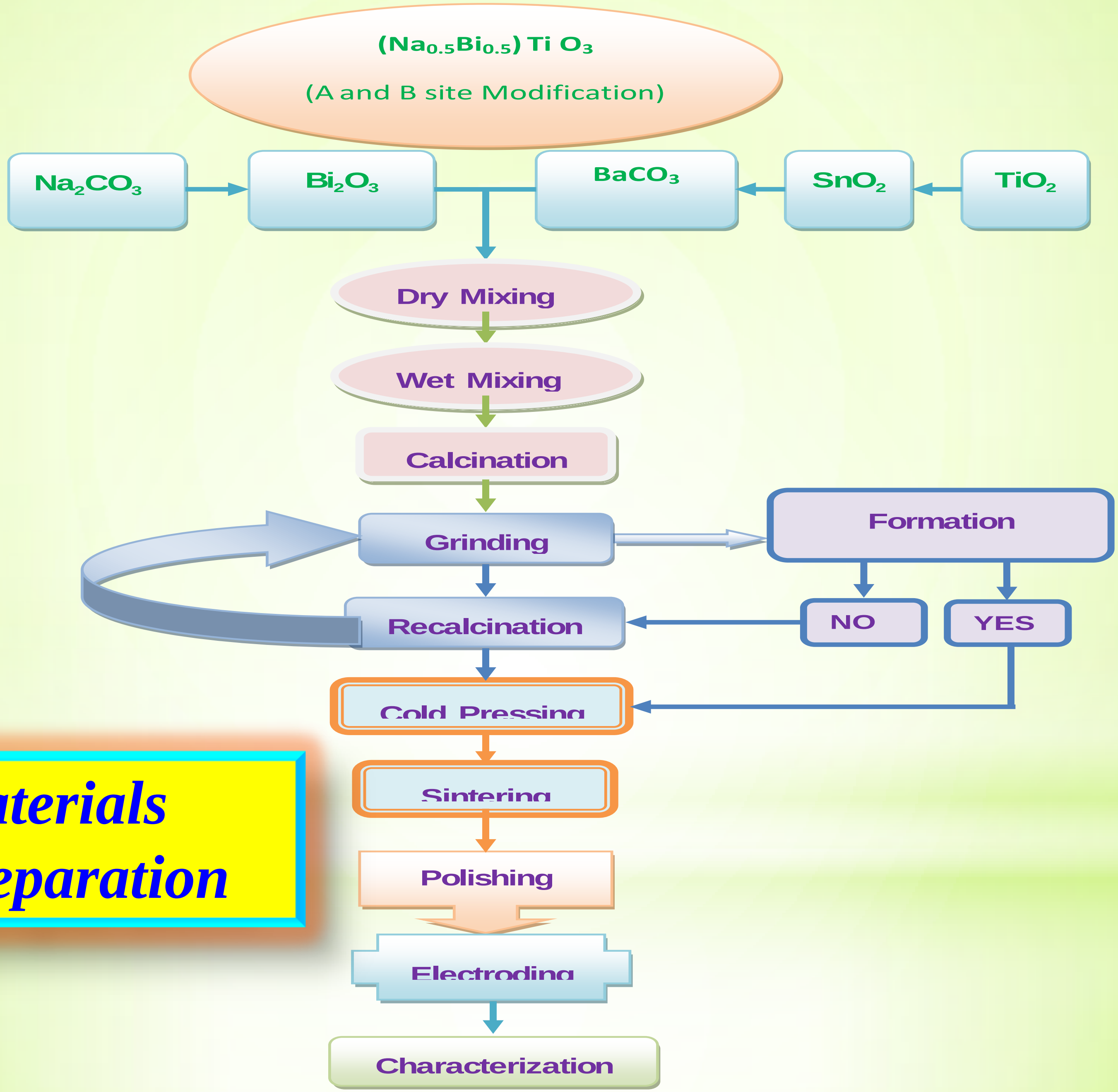
1.Ferroelectric to relaxor crossover(1-x)$BaTiO_3$-x$BaSnO_3$

2.Relaxor ferroelectric behavior of $BaSnO_3$-$PbTiO_3$ solid solution with MPB

1. C. Lei, A. A. Bokov, and Z. G. Ye, J. Appl. Phys. 101, 084105 (2007).

2. X. Han, X. Li, X. Long, H. He, and Y. Cao, J. Mater Chem. 19, 6132 (2009).

Materials Preparation



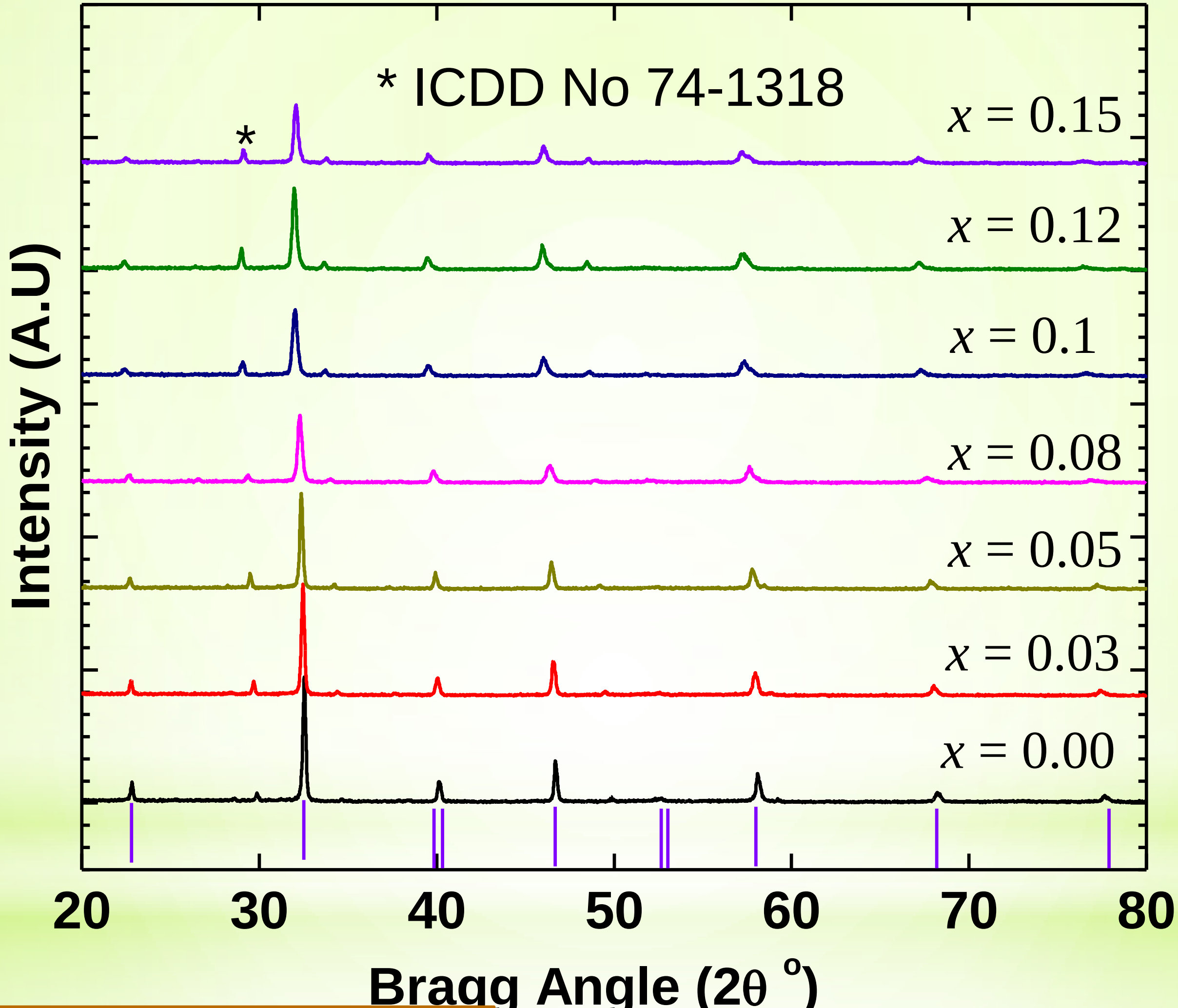
Materials Characterization

Structure Determination → XRD analysis (PANalytical's X'Pert PRO)

Raman Spectroscopy → Ranishaw *micro*-Raman spectrometer (Model-INVIA)

Dielectric, Impedance Measurement → **PSM LCR 4NL, Model: 1735, UK**

Structural Studies



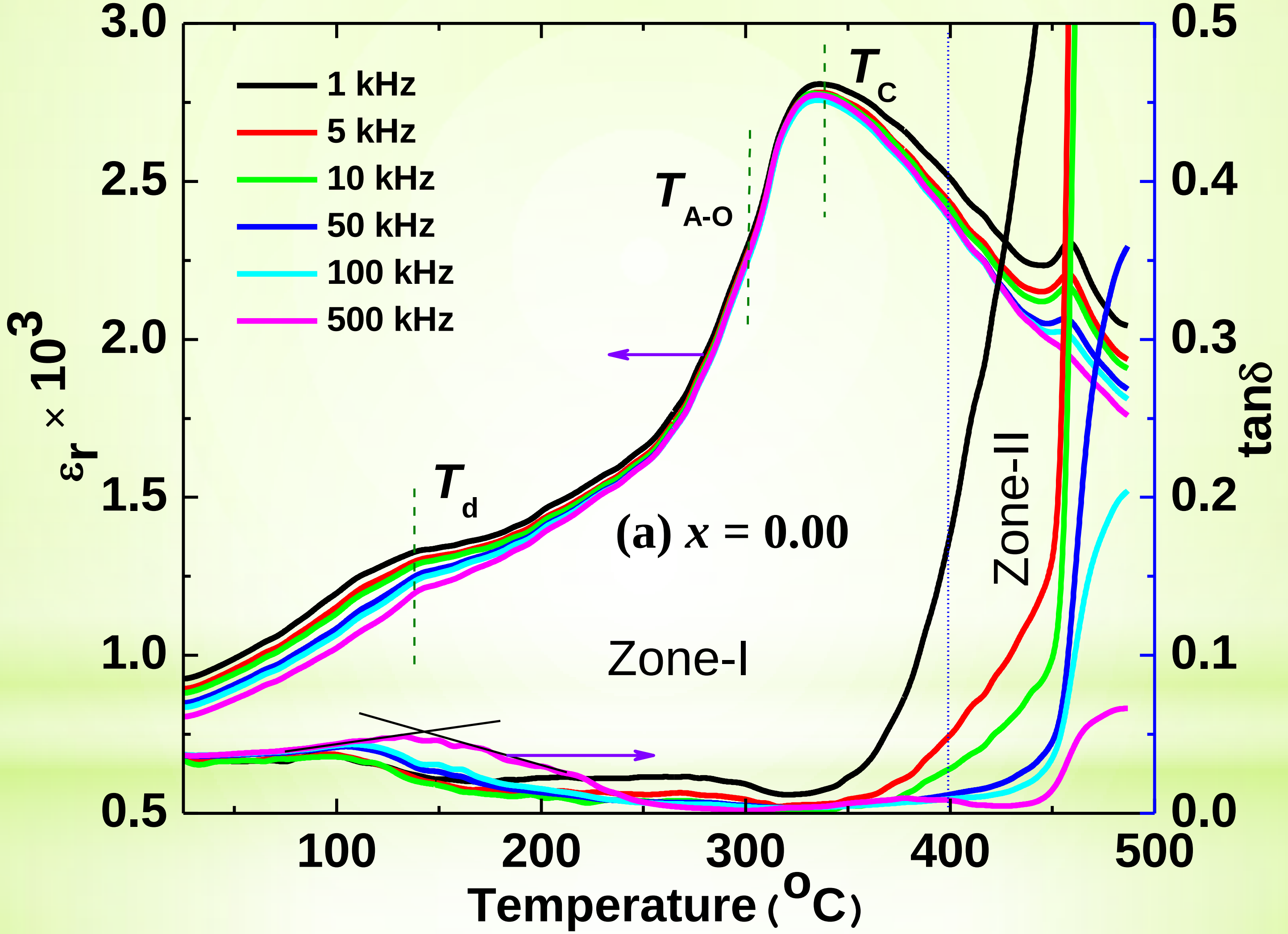
*$Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (ICDD No 74-1318).

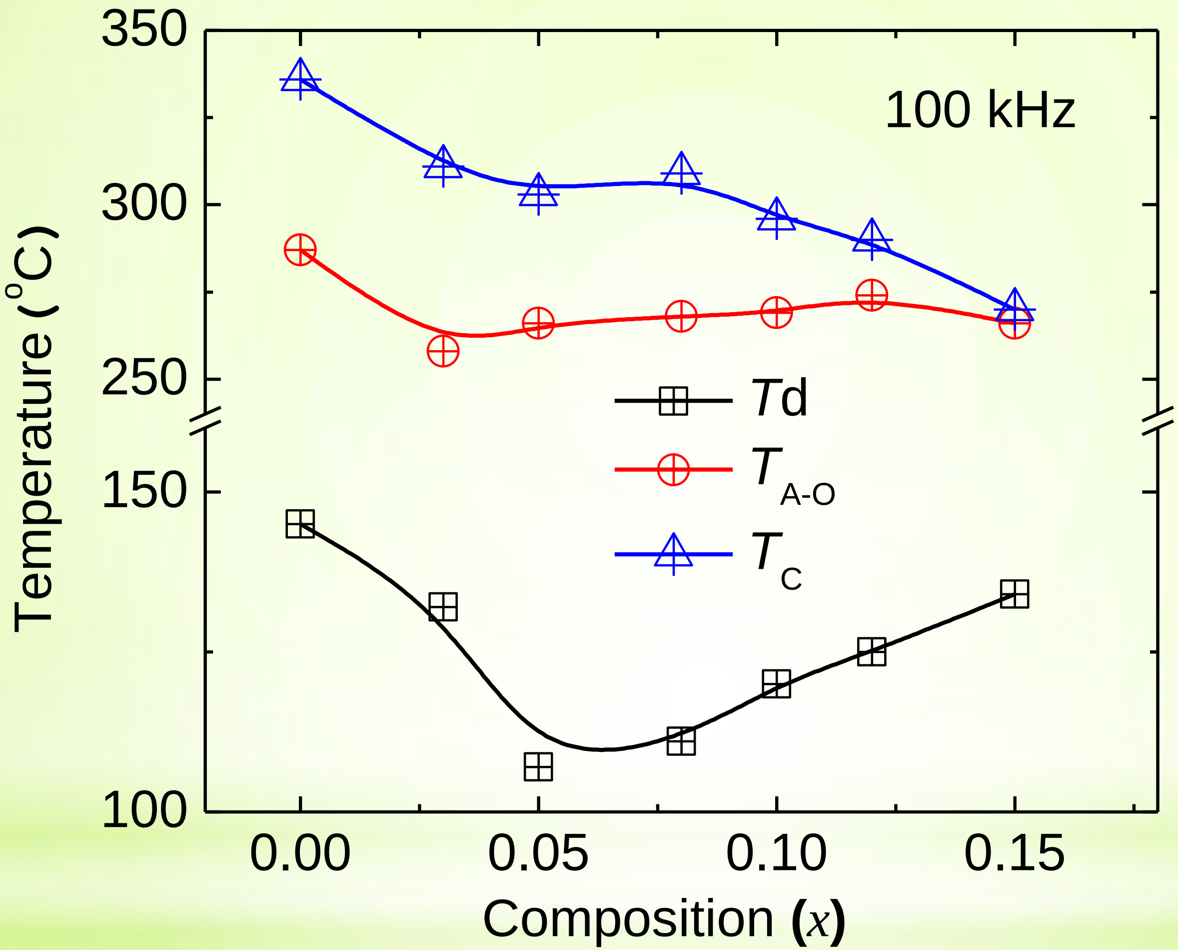
For, NBT a = b = 5.4972(17) Å and c = 13.4551(21) Å

For, 0≤ x ≤ 0.08; Rhombohedral

For, 0.1≤ x ≤ 0.15; Orthorhombic

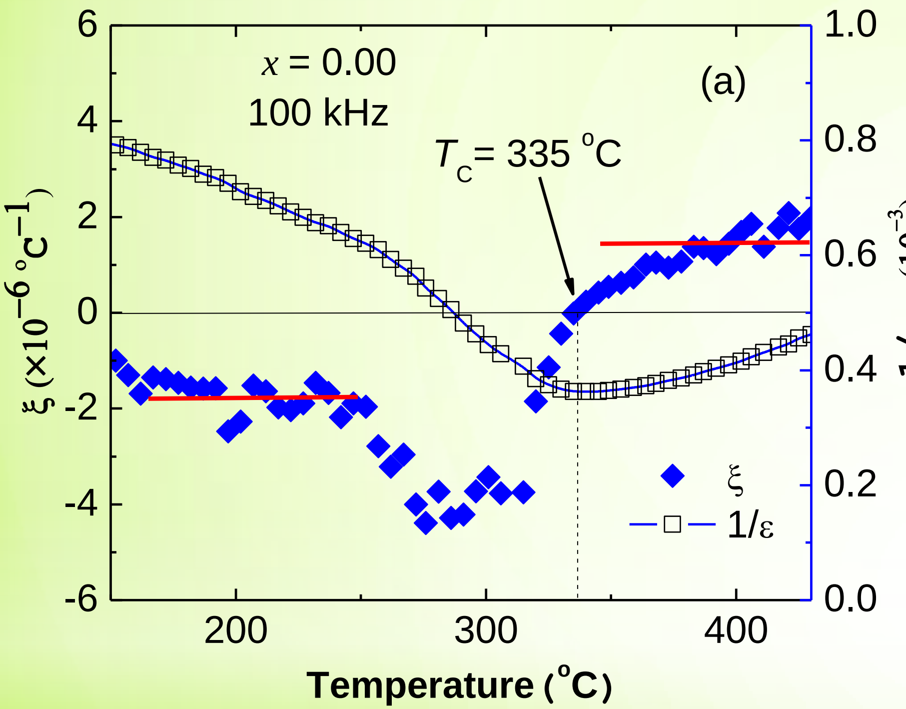
Dielectric Studies

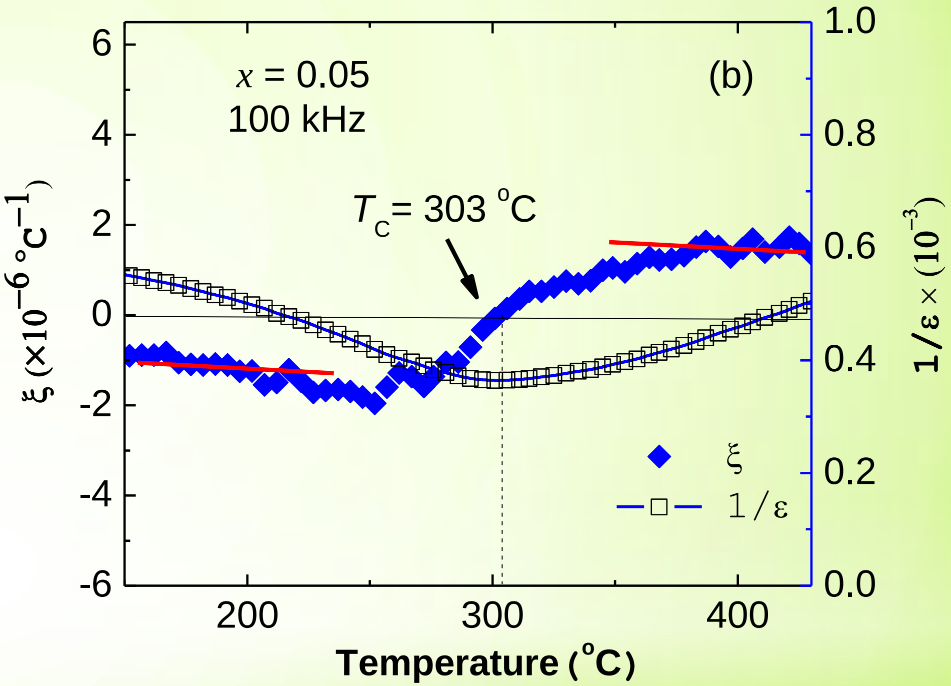




a) *Appearance and enhancement of modulated orthorhombic phase*
b) *Decrease in ferroelectric transition temperature*

2^{nd} Order Phase transition



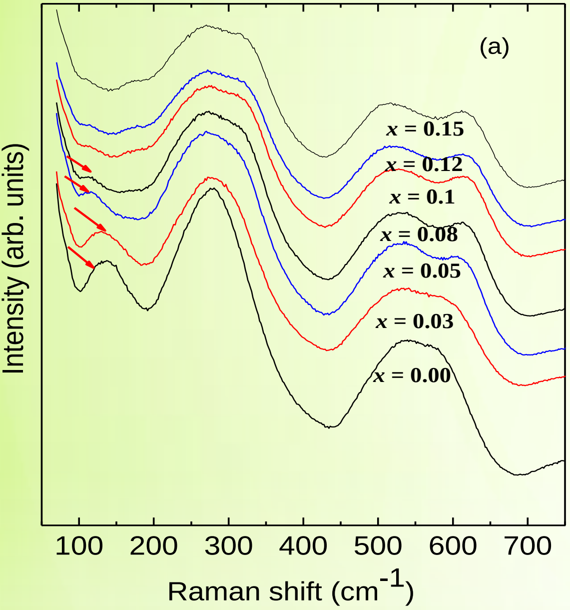


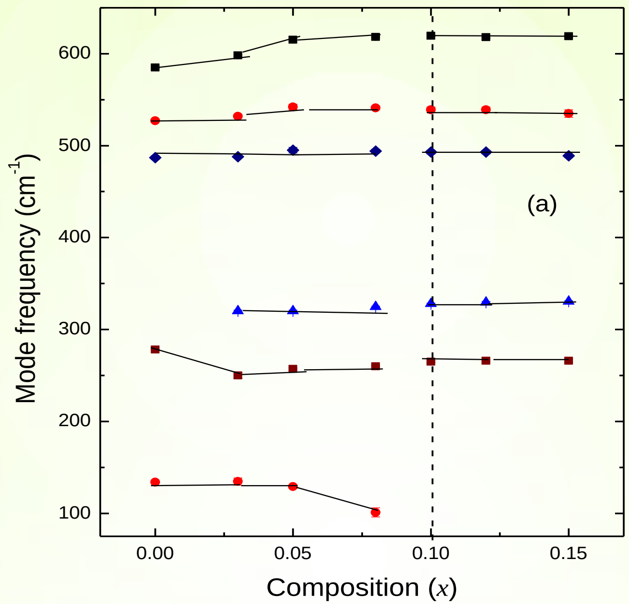
The derivative ξ (T) $\xi = \frac{\partial}{\partial T}\left(\frac{1}{\varepsilon(T)}\right)$ ***plays a qualitative role in determining the order of phase transition.***

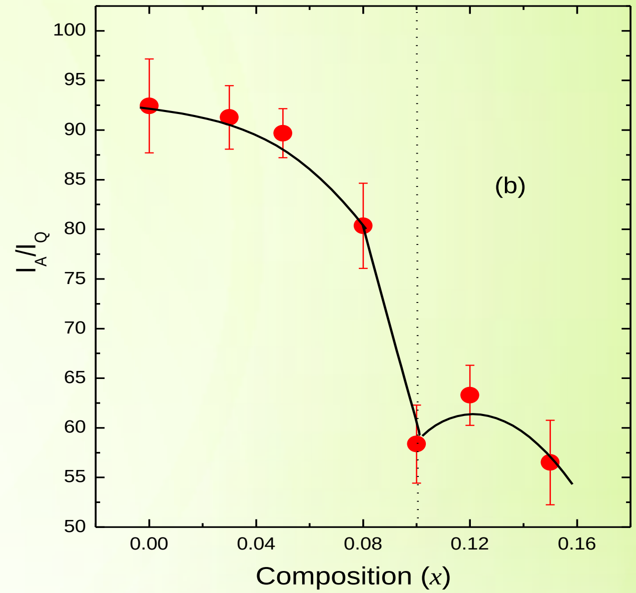
For, x=0.00 $\xi_{320^o C} / \xi_{350^o C} \approx 2.6$

Raman Spectroscopy

A. Compositional Dependence







- ***Mode (~278 - ~585 cm^{-1}) are associated with the TiO_6 octahedral vibration.***
- ***Disappearance of A_1-mode at ~134 cm^{-1} as the sample undergoes a structural phase transition from rhombohedral to orthorhombic at x = 0.1 composition.***

Conclusion

- ***To conclude, lead free solid solutions of (1-x)NBT-xBSN ($0 \leq x \leq 0.15$) were synthesized by solid-state reaction method.***
- ***Phase transition temperatures T_d, $T_{A\text{-}O}$ and T_C were obtained from the detailed dielectric data analysis.***
- ***A decrease in ferroelectric phase transition temperature as a function of x is obtained and finally T_C merges with $T_{A\text{-}O}$ at composition $x = 0.15$.***
- ***In-situ temperature dependent Raman spectroscopy shows disappearance and discontinuous changes in the phonon mode frequencies across the orthorhombic-tetragonal phase transition.***

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