# Electroceramics VI

Edited by
Daniel Z. de Florio, Eliana N. S. Muccillo,
Fábio C. Fonseca and R. Muccillo

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*Edited by*

**Daniel Z. de Florio, Eliana N. S. Muccillo,
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# Table of Contents

## Chapter 5: Materials for Fuel Cells



## Chapter 6: Electroceramic Devices. Sensors and Actuators



## Chapter 7: Solar Photovoltaic and Photoelectrochemical Cells

## Chapter 8: Photonic and Electro-Optical Ceramics



## Chapter 9: Magneto-Electric Coupling and Multiferroics



## Chapter 10: Modeling and Simulation

# CHAPTER 1:

# Ferroelectrics, Piezoelectrics and Pyroelectrics

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# Ferroelectric Properties of $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ Ceramics

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**Keywords**: piezoelectric ceramics, lead-free compositions, ferroelectric properties.

**Abstract**. Different processing conditions and the effect of secondary phases on ferroelectric properties of $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ (BNKT) are studied. Ceramic powders are prepared by solid state reaction and different sintering temperatures (temperatures between 1075 and 1150 ºC) are analyzed. Finally, samples are characterized by X-ray diffraction, Raman micro-spectroscopy, scanning electron microscopy, impedance spectroscopy, and density measurements. Through XRD patterns, the perovskite structure is stabilized; together with small peaks corresponding to a secondary phase associated with $K_{2-x}Na_xTi_6O_{13}$ phase. Moreover, the content of the secondary phase, $d_{33}$ piezoelectric constant and dielectric properties increase with sintering temperature.

## Introduction

Lead titanate–zirconate piezoceramics are the most important and widely used materials for piezoelectric transducers, transformers and sensors. They have played a dominant role in the piezoelectric field for a long time owing their excellent piezoelectric properties [1]. However, the toxicity of lead is a serious threat to human health and environment [2]. Thus, considerable effort has been devoted towards the development of lead-free piezoelectric ceramics.

Numerous studies on lead-free piezoelectric ceramics, such as $(K,Na)NbO_3$, $BaTiO_3$-based, Bi-layered, bismuth sodium titanate and tungsten bronze-type materials, have been recently published. For this reason, $K_{0.5}Na_{0.5}NbO_3$ (KNN) system attracts much attention, due to its elevated Curie temperature (about 420°C) and high piezoelectric properties close to the morphotropic phase boundary (MPB) [3]. Nevertheless, it is difficult to obtain pure KNN ceramics with high density and great piezoelectric performance. Sodium bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (BNT) with a relatively large remnant polarization at room temperature and a relatively high Curie temperature, could be considered another promising candidate to lead-free piezoelectric ceramics. However, its high coercive field hinders the obtention of the desired piezoelectric properties. Therefore, a number of studies have been carried out to improve electrical properties of BNT by the formation of solid solutions with other $ABO_3$ perovskites [4-5]. It has been reported that BNT ceramics modified with $Bi_{0.5}K_{0.5}TiO_3$ (BKT) showed improved dielectric and piezoelectric properties, due to a rhombohedral–tetragonal morphotropic phase boundary (MPB) at the optimal composition of $Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}TiO_3$ [6].

In the current work, lead-free $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$-based ceramics are prepared by the solid state reaction method using a previous mecanochemical activation step of reagents. Results will be discussed considering the effect of secondary phases on structure, microstructure, dielectric and piezoelectric properties of these ceramics.

## Experimental Procedure

$Bi_{0.5}(K_{0.2}Na_{0.8})_{0.5}TiO_3$ was synthesized through solid state reaction, using $K_2CO_3$ and $Na_2CO_3$ (Cicarelli 99.99%; Argentina), $Bi_2O_3$ (Aldrich 99.8%; USA) and $TiO_2$ (Aldrich 99.9%; USA). Powders were mixed and milled using zirconia balls in an alcoholic medium for 5 h in a planetary mill (Fritsch, Pulverisette 7, 1450 rpm). Powders were dried and calcined at 700 ºC for 2 h. The resulting powders were milled again, pressed into disks and sintered at 1075 to 1150 °C for 2 h.

Crystalline phases were characterized by X-ray diffraction (XRD) (Philips PW1830), using $CuK_\alpha$ radiation. Raman spectra were acquired at room temperature with a Renishaw inVia microscope by means of the 514 nm Ar-ion laser line (50 mW nominal power) with a diffraction grating of 2400 lines/mm. Density values were determined using the Archimedes method. Microstructures were evaluated on polished and thermally etched samples using a Field Emission Scanning Electron Microscope, FE-SEM (Hitachi S-4700) equipped with energy dispersive spectroscopy, EDS. Previous to the electrical measurements, a fired silver paste was used for the electric contacts. Dielectric properties were determined at different frequencies using impedance analyzers Hioki 3532-3550 in the frequency range 100 mHz-10 MHz at room temperature. Samples were polled in a silicone oil bath at 25 ºC by applying a DC field of 30.0 kV/cm for 30 min. The piezoelectric constant $d_{33}$ was measured using a piezo $d_{33}$ meter (YE2730A $d_{33}$ Meter, APC International, Ltd., USA). Finally, the ferroelectric nature of these ceramics was determined using a hysteresis meter (RT 6000 HVS, Radiant Technologies).

**Results and Discussion**

From XRD patterns (Fig. 1), the BNKT phase is stabilized in all sintered samples. However, samples sintered at temperatures higher than 1100 °C present secondary phases, which can be indexed to $K_{2-x}Na_xTi_6O_{13}$ phase (monoclinic structure, JCPDS Nos. 40-0403 and 74-0275).

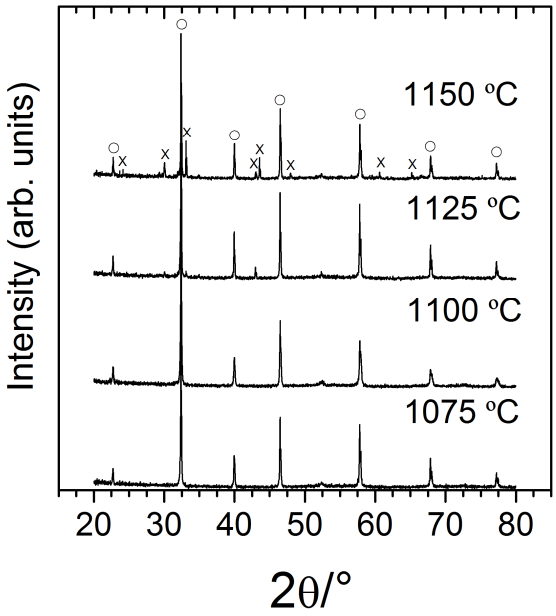


Figure 1 - XRD patterns of sintered samples. (o) Peaks corresponding to BNKT phase, (x) peaks associated with a secondary phase.

Raman analyses are performed on different regions of all sintered samples between 200 and 1000 $cm^{-1}$ (Fig. 2). From Raman spectra, six vibration bands corresponding to BNKT, in all sintered samples are observed. The amplitude and overlapping Raman bands reflect the strong anharmonicity and disorder inherent to A-sites. Moreover, new peaks related to a secondary phase assigned to $K_{2-x}Na_xTi_6O_{13}$ can be observed in Fig. 2. Peaks below 500 $cm^{-1}$ could be attributed to the K–O–Ti stretching vibration. Peaks at about 655 $cm^{-1}$ have been assigned to the Ti–O–Ti stretch in edge-shared $TiO_6$. Peaks near 870 $cm^{-1}$ are reported for a short Ti–O stretching vibration in distorted $TiO_6$. Weak peaks at around 240 and 400 $cm^{-1}$ characteristic of the K–O–Ti containing short Ti–O bonds are also observed. Although secondary phases are not detected through XRD patterns at the lowest sintering temperature, Raman spectra confirm the formation of a secondary phase with a composition close to $K_{2-x}Na_xTi_6O_{13}$ in all samples [7], see Fig. 2.

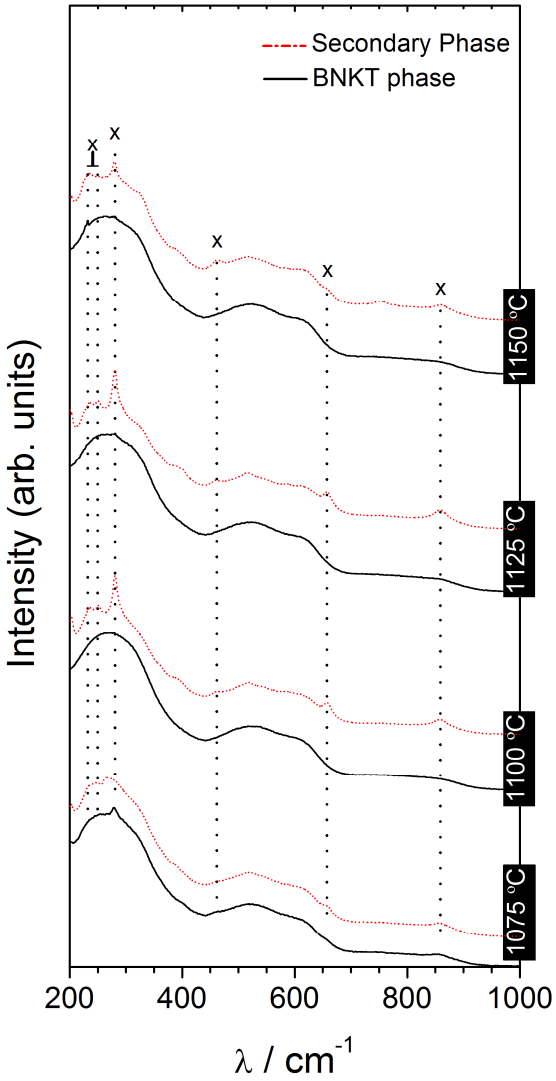


Figure 2 - Raman spectra of sintered samples. From the Raman spectra, the apparition of a secondary phase can be observed. The secondary phase associated with the BNKT phase is signaled with a red dash dot line, whereas the BNKT perovskite phase corresponds to the black solid line. In addition, the position of the main Raman modes associated to the secondary phase are marked with `x´ symbols

Microstructural characteristics of sintered samples are observed through Field Emission Scanning Electron Microscopy (FE-SEM) (Fig. 3). The FE-SEM micrographs show the typical BNKT morphology consisting of very small faceted grains. Furthermore, it was determined that sintering temperature affects the grain size and the amount of the secondary phase. This phase, which is present in the form of rods, has a composition close to $K_{2-x}Na_xTi_6O_{13}$ as detected by EDS, XRD and Raman microspectroscopy. All systems show small grains ($\leq 1$ μm) that become finer at low sintering temperatures.

Relative permittivity and dielectric loss values as a function of frequency for samples sintered at different temperatures are measured at room temperature (Fig. 4). In all cases, it is determined that at low frequencies, permittivity decreases drastically due to a space charge relaxation process characteristic of the polycrystalline material. Additionally, from the Fig. 4 a relaxation process at high frequency (8~MHz), which is associated with a dipolar relaxation phenomena can be observed. In these samples, the improvement in the real permittivity value with the sintering temperature could be related to the secondary phase formation, the grain size increase and the densification degree.

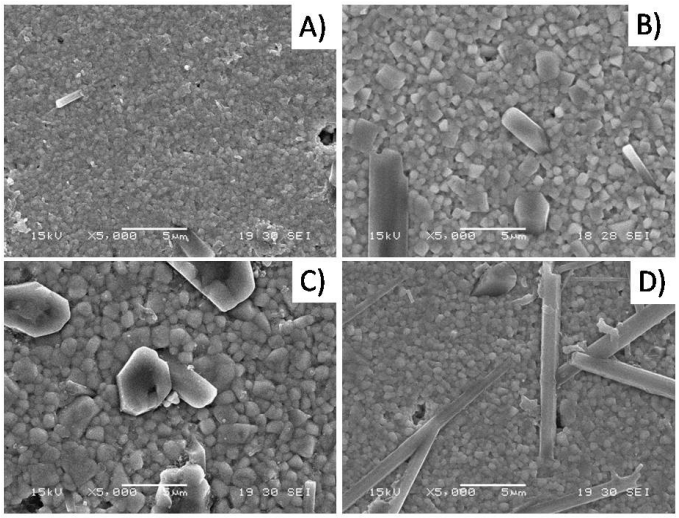


Figure 3 - FE-SEM images of pure BNKT sintered at (A) 1075 ºC, (B) 1100 ºC, (C) 1125 ºC and (D) 1150 ºC.

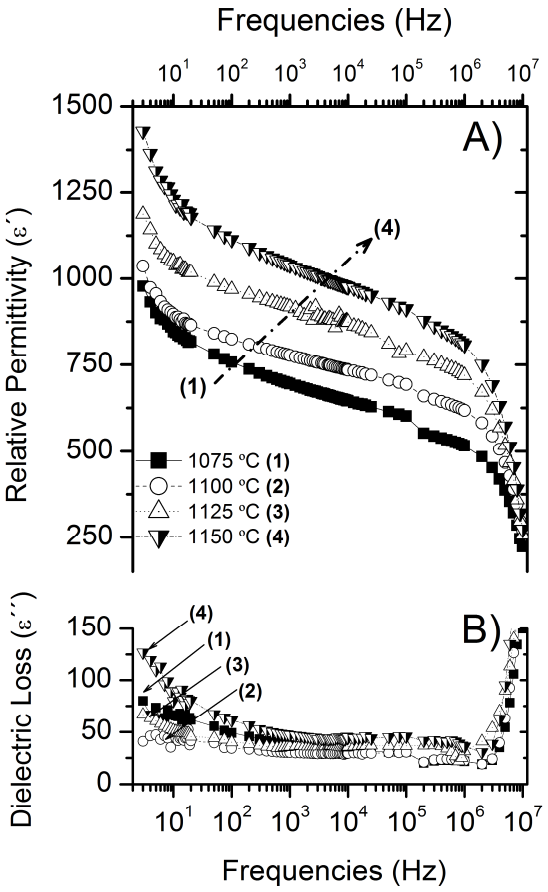


Figure 4 - Curves of relative permittivity (A) and dielectric loss (B) as a function of frequency at room temperature. The sintering temperatures of BNKT ceramics represented in Fig. (A-B) are the following: **(1)** 1075 ºC; **(2)** 1100 ºC; **(3)** 1125 ºC; **(4)** 1150 ºC. The dotted arrow marked in (A) corresponds to the evolution of the relative permittivity depending on sintering temperatures of the BNKT system.

From density measurements, samples sintered at 1100 °C present the maximum value of the complete set of samples (Table 1). Interestingly, the higher the sintering temperature of the system, the higher the piezoelectric coefficient ($d_{33}$) and real permittivity values (see Table 1). Although this